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ON THE NEUTRON RESONANCE CROSS-SECTION

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THE INFLUENCE OF ATOMIC, MOLECULAR AND SOLID STATE EFFECTS ON THE NEUTRON RESONANCE CROSS-SECTION *

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ABSTRACT

This paper gives a review of recent research into the influence of atomic, molecular and solid-state effects in a target on the cross-section for the interaction of neutrons with nuclei at lowenergy neutron resonances. The influence of these effects on Doppler broadening is examined, and calculated and experimental results are compared. The results are also given of an investigation of temperature and chemical shifts in neutron resonances analogous to the second-order Doppler effect and isomer shift familiar from Mössbauer gamma-ray spectroscopy.

Introduction

The cross-section for nuclear reactions is usually examined independently of the atomic, molecular or solid-state characteristics of the sample under investigation. The reason for this is that the energy of nuclear processes, as a rule, exceeds by many orders of magnitude the typical energies for chemical bonds or thermal motion of atoms in crystal lattices or molecules. However, there are some exceptions where the influence of crystal and molecular effects must be taken into account. One of these exceptions is the interaction of slow neutrons with nuclei.

The present paper reviews recent research into the influence of atomic, molecular and solid-state effects on the cross-section for the interaction of neutrons with nuclei at low-energy neutron resonances. Neutron resonances are clearly defined narrow maxima in the cross-section for nuclear reactions involving neutrons which lead to the formation of isolated excited states of a compound nucleus with an energy somewhat greater than the neutron bonding energy. Resolved neutron resonances exist within a neutron energy range of one electronvolt to one kiloelectronvolt, depending on the nuclides in

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question. The precise energy position and shape of the neutron resonances depend not only on the nuclear characteristics of the nuclides, but also on the surrounding medium. Research into this area has been going on since nuclear physics began. Thus, Doppler broadening of resonances was discussed as early as 1937 in a paper by Bethe [1], and the fundamental theoretical work on Doppler broadening for crystalline solid bodies was done by Lamb [2] in 1939. Neutron spectroscopy of nuclei with resonance neutrons using powerful pulsed sources has undergone such enormous development in recent years that new and more fine effects have been found in the experiments. These effects are related both to the structure of the nuclei and to their surrounding medium. It has, for instance, become possible to investigate the area of hyperfine interaction.

In section 1, a short description is given of the experimental methodology used to investigate such effects as Doppler broadening and temperature and chemical shift in neutron resonances [3-10].

To investigate these fine effects one must have a more precise understanding of the influence of atomic, molecular, and in particular solid state characteristics on the behaviour of the neutron resonance crosssection. This is relevant, primarily, of course, to the most significant effect - Doppler broadening. A comparison of the position and shape of measured neutron resonances for target nuclei bonded in different chemical compounds clearly shows the influence of the various vibration spectra of solid bodies and molecules on Doppler broadening [3, 5-8]. Section 2 presents methods for describing Doppler broadening of neutron resonances. By comparing the results obtained using these methods with experimental data, the accuracy of the theoretical methods can be evaluated.

Thermal motion of target nuclei not only causes broadening of the neutron resonances, but also temperature-related displacements in the resonance positions. There is a well-known analogue to these displacements the temperature shifts of Mössbauer gamma lines [11, 12]. Temperature shift

of neutron resonances was first recorded experimentally, and substantiated theoretically, in Ref. [10]. This effect is dealt with in section 3.

Section 4 examines the influence of hyperfine interaction between the nucleus and the atomic shell on neutron resonances. The first experimental investigation of this type of phenomenon - a shift in the position of the neutron resonances when performing measurements with polarized neutrons or with oriented nuclei and a change in polarization - is described in Refs [13, 14]. This shift is caused by the interaction of the atomic nucleus with the atom's internal magnetic field. By measuring the shift one may determine the magnetic moments of the atomic nucleus in the highly excited states occurring during resonance capture of neutrons. When measuring the passage of neutrons through targets containing various chemical compounds of the nucleus under investigation [3], chemical shifts in the neutron resonances caused by electrical hyperfine interaction of the nuclear charge with the electron shell were observed. Using this effect, one can determine the mean square charge radii of nuclei in highly excited compound states [3, 4, 9, 15]. Both effects have analogues in Mössbauer spectroscopy - in hyperfine splitting and isomer shift [16, 17]. In the present paper, we will limit ourselves to investigations using unpolarized neutrons and nuclei, while Ref. [18] deals in detail with the investigation of the interaction of polarized neutrons with nuclei.

1. Measurement of fine effects in the total resonance cross_section

These atomic, molecular and solid-state effects in the resonance cross-section are, as a rule, small $(\Delta\sigma/\sigma \approx 10^{-3}-10^{-1})$. Therefore, it is essential that a high level of statistical accuracy in the measurement of the resonance spectra and a suitably high resolution of the neutron resonances be achieved. These spectrometer power and resolution requirements can be met in measurements of neutron transmission through samples using the time-of-flight method and powerful pulsed neutron sources.

The dependence of neutron transmission on the total interaction cross-section $\sigma(E_n)$ for neutrons of energy E_n with nuclei is determined using the expression

$$T(E_n) = \exp[-N\sigma(E_n)], \qquad (1)$$

where N is the number of nuclei per unit area of the sample; the neutron energy E_n , measured in eV, is determined from the time-of-flight t, measured in μ s,

$$E_n = (72.3L/t)^2$$
,

L being the length of the flight path in m.

Owing to the negligible scale of the effects under consideration, the main aim of the experiments consists in measuring differences in the resonance cross-sections of various samples. Hence, the following requirements which must be met by those experiments:

(a) Owing to the limited resolving power of the spectrometer, the energy spread ΔE_n should, as a rule, be less than the width Γ of the resonance under investigation:

$$\Delta E_{n} \leq \Gamma$$
 (2)

In time-of-flight experiments with a neutron pulse length of Δt_r

$$\Delta E_n = \frac{\Delta t_r}{36,2L} E_n^{3/2},\tag{3}$$

where ΔE_n and E_n are measured in eV, L in m, and Δt_r in μs . Expressions (2) and (3) set the upper limit on the energy of neutron resonances for which these investigations are possible;

(b) To achieve statistical accuracy of measured spectra when studying effects in the range $\Delta\sigma/\sigma \approx 10^{-3} - 10^{-2}$, more than 10^{6} counts are required in each time channel. At the same time, the channel

width should be less than the time resolution. This places additional restrictions on the scope for investigating effects from the point of view of intensity;

- (c) The relative difference in the number of nuclei of a given nuclide per unit area for two samples being compared must be less than 10^{-3} . Remaining experimental conditions should be as identical as possible. All these requirements for the experiment are very stringent;
- (d) An important condition for reliable measurement of the cross-section in the resonance region is optimum thickness of the sample

$$N \approx (2-3) \frac{1}{\sigma(E_0)} ,$$

where $\sigma(E_0)$ is the cross-section at the resonance maximum. If sample thickness (owing to a large resonance cross-section) is very small (0.1-0.01 mm) and samples in powder form are being used, the uneven thickness due to the graininess of the powder must be taken into account in expression (1).

From these requirements it is clear that the investigation of these fine effects is an extremely difficult experimental task.

Let us examine the actual equipment set-up used for such experiments of the OIYaI (Joint Nuclear Research Institute) [3-10]. The experimental layout is shown in Fig. 1. The spectra of neutrons passing through the samples under investigation are measured using the beam of an IBR-30 pulsed reactor working in booster mode with an LUEH-40 linear electron accelerator [19]. The flight path L = 50-60 m and the neutron pulse duration $\Delta t_r \approx 4.5 \ \mu s$. This means that the condition $\Delta E_n < \Gamma$ [cf. (2)] is met the energy region $E_n \leq 13 \ eV$ where $\Gamma \sim 0.1 \ eV$. In order to achieve identical experimental measuring conditions for different samples, measurements are performed on two (or three) samples which are introduced into the beam one after another for a short time, e.g. for five minutes. Each five-minute spectrum is checked against the



Fig. 1. Experimental layout in Refs [3-10]: IBR-30 - pulsed reactor operating in booster mode with the LUEh-40 accelerator; 1, II - samples under investigation; D - neutron detector; R - sample with reference resonances; M - neutron beam monitor.



Fig. 2. Experimental time-of-flight spectrum for a natural uranium sample with a Tb control sample in the beam (t - number of the time channel of width 2 µs, N - number of readings).

readings of the beam monitor and the reactor starting pulse counter. When the conditions for spectrum consistency laid down by the experimenter are fulfilled, the spectrum is recorded in the computer memory.

Then the next sample is introduced into the beam. The total time required to measure two samples where loads in the detector channel can momentarily reach 3 x 10^5 pulses/s is at least several days. A scintillation detector with a lithium window is used to register neutrons. In addition to the sample under investigation, a reference sample is constantly held in the beam, and the resonances from this sample provide an objective control for the time spectra. In Fig. 2, one of the spectra for a uranium sample is shown; it was obtained over ten hours of measurement during which time three spectra were obtained from different samples. Some experimental examples of differences in neutron transmission are given in Fig. 7.

The IBR-30 reactor operating in booster mode with an LUEh-40 linear accelerator is, at present, one of the most powerful pulsed neutron sources available for studying effects of this type. With this device, measurements of this kind are limited by the above-mentioned requirements to low-energy resonances covering the energy region E_0 up to 25 eV. This means that at present, a maximum of approximately 200 resonances for 100 nuclides can be investigated.

The development of pulsed neutron sources using high current proton accelerators and pulsed boosters [20] will open up the possibility of investigating fine effects in neutron resonances at energies up to one kiloelectronvolt and will help reduce measurement times and sample mass correspondingly.

2. <u>Doppler broadening of neutron resonances</u>

<u>The cross-section in the region of isolated resonances for a stationary</u> <u>target nucleus</u>. The energy dependence of the total cross-section for neutron interaction with nuclei for a stationary nucleus $\sigma_0(E_x)$ can be represented by the following summation:

$$\sigma_{0}(E_{\mathbf{x}}) = \sigma_{p} + \sum_{j} [\sigma_{BW}(E_{\mathbf{x}}) + \sigma_{int}^{p}(E_{\mathbf{x}}) + \sigma_{int}^{r}(E_{\mathbf{x}})]_{j}.$$
(4)

The potential scattering cross-section σ is determined using the p expression:

$$\sigma_{\rm p}=4\pi R_{\rm p}^2,$$

where R_n is the potential scattering radius.

The summation in expression (4) is carried out for all resonances j contributing to the total cross-section at the energy under consideration.

The first term in the summation is given by the well-known Breit-Wigner formula [21]:

$$\sigma_{BW}(E_x) = \frac{\pi}{k^2} g \frac{\kappa k \Gamma_n(E_0) \Gamma}{(E_x - E_0)^2 + (\Gamma/2)^2},$$

$$g = \frac{2J - 1}{2(2I - 1)} \& \kappa = \frac{\hbar}{\sqrt{2m_n |E_0|}}.$$
(5)

where

Here E_0 is the resonance energy; Γ is the total width; $\Gamma_n(E_0)$ is the neutron width for E_0 ; J is the resonance spin; I is the target nucleus spin; k is the neutron wave number and m is the neutron mass. The quantity $\sigma_{int}^{p}(Ex_{x})$ takes into account interference between potential and resonance scattering:

$$\sigma_{\text{int}}^{p}(E_{x}) = 4\pi \varkappa g R_{p} \frac{\Gamma_{n}(E_{0})(E_{x}-E_{0})}{(E_{x}-E_{0})^{2} + (\Gamma/2)^{2}}.$$

The last term in the summation contained in expression (4) describes the interference of resonance j with neighbouring resonances [22]:

$$\sigma_{\rm int}^{r}(E_{x}) = \frac{\pi}{k^{2}} g \frac{\sqrt{E_{x}} (u\Gamma + v (E_{x} - E_{0}))}{(E_{x} - E_{0})^{2} + (\Gamma/2)^{2}}.$$
 (6)

The parameters u and v, like the other resonance parameters, can be determined experimentally. Formula (6) gives only one possible, simple description of the interference (for other methods of describing this see Refs [22-26]). The interference contributes σ_{int}^{r} to the cross-section if resonances with identical spin overlap and if the condition $\Gamma_{f} + \Gamma_{n} \ge \Gamma_{\gamma}$ holds for the fission width Γ_{f} , the gamma-decay width Γ_{γ} , and the neutron width Γ_{n} [27]. Where this is not the case, its contribution is negligibly small. The influence on the cross-section of a nuclear state with an energy somewhat lower than the neutron binding energy can be accounted for in terms of a resonance with a negative energy E_{0} .

The influence of target nucleus motion on the cross-section. A real atom is not attached to anything; it is surrounded by a medium which allows its external degrees of freedom to be excited, i.e. the atom is brought into a state of motion in the gas, liquid or crystal. Since momentum is conserved in

neutron absorption by a nucleus, some part of the neutron's kinetic energy E_t is transferred to these external degrees of freedom. Therefore, the nucleus excitation energy E* after capture of the neutron is:

$$\mathbf{E}^{\star} = \mathbf{B}_{\mathbf{n}} + (\mathbf{E}_{\mathbf{n}} - \mathbf{E}_{\mathbf{t}}) \approx \mathbf{B}_{\mathbf{n}} + \mathbf{E}_{\mathbf{x}}$$

where B_n is the neutron binding energy in the nucleus.

The cross-section $\sigma_0(\mathbf{E}_x)$, which is dependent on the energy \mathbf{E}_x imparted to the nucleus, is determined exclusively by the properties of the nucleus. In experiments, however, the cross-section $\sigma(\mathbf{E}_n)$ is measured as a function of the neutron energy \mathbf{E}_n in the laboratory system of co-ordinates. The connection between the cross-sections $\sigma(\mathbf{E}_n)$ and $\sigma_0(\mathbf{E}_x)$ can be given as follows:

$$\sigma(E_n) = \int_{-\infty}^{E_n} \sigma_0(E_n - E_t) S(E_n, E_t) dE_t, \qquad (7)$$

where the transfer function $S(E_n, E_t)$ determines the probability of transfer of energy E_t to the external degrees of freedom of the atom.

Motion of the atom absorbing the neutron before and after capture of the neutron produces so-called Doppler broadening of neutron resonances. It is determined by the characteristics of the transfer function $S(E_n, E_t)$. Doppler broadening significantly complicates the exact measurement of all nuclear parameters of neutron resonances. Therefore, an exact description of Doppler broadening, is in many cases, a precondition for the accurate determination of the nuclear characteristics of neutron resonances.

Finer effects such as, for instance, temperature shift of neutron resonances (see section 3) require detailed examination. The neutron wave number k, which is dependent on the relative motion of the neutron and the target nucleus prior to capture, forms part of the resonance cross-section $\sigma_{RW}(E_x)$ [see expression (5)]:

$$\mathbf{k}=\frac{1}{\hbar}\mid\mathbf{p}_{n}-\mathbf{p}_{A}\mid.$$

where p_n is the momentum of the neutron, and p_A is the momentum of the

absorbing nucleus. For an ideal gas, the law of conservation of momentum operates in the "neutron + atom" system, and we therefore obtain the following relationship for the wave number:

$$k_{G} = \frac{1}{\hbar} \sqrt{2m_{n} \left(E_{n} - E_{t}\right)} \tag{8}$$

However, if the target nucleus is bonded in a crystal lattice, the law of conservation of momentum must be applied to the "neutron + crystal" system. The quantum mechanical mean of the momentum of a single atom in a crystal lattice is zero, and hence

$$k_{\rm g} = \frac{1}{\hbar} \sqrt{2m_{\rm n}E_{\rm n}}.$$
 (9)

In the case of a molecular gas, where absorption of a neutron may cause excitation of intramolecular degrees of freedom, we have:

$$k_{\rm M} = \frac{1}{\hbar} \sqrt{2m_n \left(E_n - E_t - \Delta E_{\rm M}\right)},$$

where $\Delta E_{\underline{M}}$ is the change in excitation energy of the internal degrees of freedom of the molecule.

Ideal gas of target nuclei. Doppler broadening for a monoatomic ideal gas can be described using classical mechanics. When a neutron of energy E_n (in the laboratory system of co-ordinates) is captured by an atom of mass M at a velocity w, the kinetic energy of the atom increases by E_+ :

$$E_{\sharp} = \frac{m_n}{M + m_n} E_n + \frac{M}{M + m_n} \sqrt{2m_n E_n} w_{\sharp} - \frac{m_n M}{2(M + m_n)} (w_{\sharp}^{*} + w_{\star}^{*}), \qquad (10)$$

where w_{\parallel} and w_{\perp} are the components of the velocity w parallel and perpendicular to the direction of motion of the neutron.

Using the Boltzmann distribution for the velocity components w_{\parallel} and w_{\perp} , and taking into account the kinematics of the motion of the neutron and the atom, we obtain the transfer function

$$S_{G}(E_{n}, E_{t}) = \frac{1}{\pi^{1/2}\Delta_{D}} \left(\frac{M+m_{n}}{M}\right)^{3/2} \left(\frac{E_{n}-E_{t}}{E_{n}}\right)^{1/2} \times \left\{ \exp\left[-\left(\frac{2E_{n}\left(1-\sqrt{(1-E_{t}/E_{n})\frac{M+m_{n}}{M}}\right)}{\Delta_{D}}\right)^{2}\right] - \left(11\right) - \exp\left[-\left(\frac{2E_{n}\left(1+\sqrt{(1-E_{t}/E_{n})\frac{M+m_{n}}{M}}\right)}{\Delta_{D}}\right)^{2}\right]\right\},$$

where Δ_D is the Doppler width, which is a measure of the broadening of neutron resonances and is determined using the expression

$$\Delta_{\rm D} = 2 \, \sqrt{k_{\rm B} T E_n \, \frac{m_n}{M}} \,, \tag{12}$$

where $k_{_{R}}$ is the Boltzmann constant and T is the gas temperature.

In addition to broadening, there is a small displacement of the resonance towards the lower energy region. It is determined in a first approximation by the recoil energy

$$R=\frac{m_n}{M+m_n}E_n.$$

This displacement of the resonance is discussed in greater detail in section 3.

In the rest of this investigation of neutron cross-sections we shall depart somewhat from the traditional approach [1, 28]. In the latter, the cross-section at temperature T = 0 is taken as σ_0 and, consequently, the neutron resonance parameters E_0 , Γ , Γ_n ... are in the laboratory system. In our approach, we use resonance parameters in the centre-of-mass system (CMS), i.e. the same parameters as for crystalline and molecular gaseous samples.

Working from the approximation $M \gg m_n$ and $E_n \gg \frac{1}{2} Mw^2$, we obtain from expression (11) the following expression for the transfer function which is already familiar to us from the paper by Bethe [1]:

$$S'_{G}(E_{n}, E_{t}) = \frac{1}{\pi^{1/2} \Delta_{D}} \exp\left[-\frac{(E_{t} - E_{n}/A)^{2}}{\Delta_{D}^{2}}\right],$$
 (13)

 $(A = M/m_n)$. By introducing a few additional approximations, the integral in

expression (7) can be expressed using the functions ψ and χ familiar from optics [29].

It should be noted that, although the ideal gas model is correct only for inert gases, it is widely used in other cases too (see below).

<u>Crystalline solid-state target</u>. It is customary to use the concept of "Doppler broadening" of neutron resonances for solid bodies as well, even though the physical picture is significantly different from the classical Doppler effect. When neutrons are captured by atoms in a crystal lattice, they are absorbed and phonons are emitted. These processes have a noticeable influence on the energy behaviour of the resonance cross-section. Displacement of atoms from lattice points through neutron capture can be disregarded, since the recoil energy for the low-energy neutron resonances under investigation is significantly smaller than the bonding energy of atoms in the lattice.

Assuming that the crystal lattice during neutron capture passes from the $|\alpha\rangle$ state to the $|n\rangle$ state, then

$$E_t = E_n - E_{\alpha}$$

The main type of excitation in the crystal lattice during capture of resonance neutrons is vibrational modes. Vibrations of atoms in a crystal lattice can be described using the system of normal co-ordinates. At low excitation energy levels, vibrations in the lattice can be represented by 3N independent harmonic oscillators, where N is the number of atoms in the crystal. Here, the transfer function takes the following form [2]:

$$S_{\mathbf{x}}(E_{n}, E_{t}) = \sum_{\{\alpha_{s}\}} w_{\{\alpha_{s}\}}(I') \sum_{\{n_{s}\}} |\langle \{n_{s}\} | \exp(i\mathbf{p}_{n}(E_{n})\mathbf{r}\cdot\hbar^{2}) | \{\alpha_{s}\}\rangle|^{2} \times \delta(E_{t} - \sum_{s} (n_{s} - \alpha_{s})h\mathbf{v}_{s}), \qquad (14)$$

where $\{\alpha_s\}$ and $\{n_s\}$ are the sets of quantum numbers characterizing the vibrational state of the lattice before and after neutron capture; $w_{\{\alpha_s\}}$ (T) is the probability of the state $\{\alpha_s\}$ being populated before neutron

capture at temperature T; hv_s is the phonon energy in relation to the normal co-ordinate s; p_n is the neutron momentum and r the displacement of the atom from its position of equilibrium. The matrix element is the probability of transition from state $\{\alpha_s\}$ to state $\{n_s\}$ during neutron capture. If we are only looking at neutron absorption, then the matrix element is used in the same form for any nuclear reactions taking place by way of a compound nucleus as well. The δ -function in expression (14) takes into account the conservation of energy. Note that, in formula (14), the increase in mass of the atom due to neutron capture is disregarded, i.e. the approximation $M + m_n \approx M$ is used.

We do not intend to describe in detail the methods for transforming expression (14) into a convenient form for calculations. The relevant details of the expansion of the function $S_{L}(E_{n},E_{+})$ are contained in Refs [2, 30-33].

For a monoatomic ideal isotropic crystal, the transfer function S k can take the following form [31]:

$$S_{R}(E_{n}, E_{t}) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \exp[-iE_{t}t] \exp\{R[\gamma(t) - \gamma(0)]\},$$
 (15)

where

$$\gamma(t) = \int_{0}^{\infty} d(h\nu) \frac{\rho(h\nu)}{h\nu} \left[\operatorname{cth} \left(\frac{h\nu}{2k_{\mathrm{E}}T} \right) \cos(h\nu t) + \mathrm{i} \sin(h\nu t) \right];$$
$$R = \frac{m_{n}}{M} E_{n}.$$

Assuming isotropy of the crystal enables us to express the transfer function in terms of the spectrum of normal crystal frequencies (phonon spectrum) $\rho(h\nu)$ only.

A relationship like the one in expression (15) can be established also for multicomponent lattices, such as exist, for example, in chemical compounds, if the elements of the transition matrix in expression (14) are not dependent on the direction of the incident neutron. Isotropy of this kind occurs for certain types of lattice with cubic symmetry, e.g. lattices of the NaCl and CaF₂ type. Where a neutron is absorbed by a nucleus of X bonded in a chemical compound XY, the transfer function $S_k(E_n, E_t)$ takes the following form [34, 35]:

$$S_{\kappa}(E_n, E_t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \exp\left[-iE_t t\right] \exp\left\{R\left[\gamma_{\rm X}\left(t\right) - \gamma_{\rm X}\left(0\right)\right]\right\}.$$
 (16)

where

$$\gamma_{\rm X}(t) = \int_{0}^{\infty} d(h, v) \frac{\rho_{\rm X}(hv)}{hv} \left[\operatorname{cth} \left(\frac{hv}{2k_{\rm E}T} \right) \cos(hvt) + i \sin(hvt) \right];$$
$$R = \frac{m_n}{M_{\rm X}} E_n.$$

In place of the phonon spectrum $\rho(h\nu)$, a weighted phonon spectrum $\rho X(h\nu)$ is introduced into expression (16); it contains only those vibrational states of the lattice which are possible when a neutron is absorbed by a nucleus of X. The recoil energy R is determined by the mass M_{ν} of the nucleus of X.

Computation of the transition matrix for a non-isotropic crystal must be performed separately for all directions of vibration of the atoms. Then the matrix elements are averaged over the orientations of the crystallites in the sample under investigation. Since neutron resonance shape does not depend on fine structures in the phonon spectrum (see below), and since few data are available on the phonon spectra of polycrystalline samples, the method given in this section for calculating the function $S_k(E_n, E_t)$ meets current requirements entirely.

The lattice phonon spectrum during neutron capture. If the target consists only of atoms of one element, the target nucleus vibrations are described by the full phonon spectrum $\rho(h\nu)$. If, however, the target nucleus of X is bonded in a lattice with other nuclides of Y, the target nucleus of X is not displaced from its position of equilibrium for every vibrational state of the lattice. In other words, when neutrons are absorbed by a nucleus of X, not all states of the spectrum $\rho(h\nu)$ are excited. Therefore, when calculating the transfer function, the weighted spectrum is used, which is determined in the following manner [34]:

$$\rho_{\mathbf{X}}(h\mathbf{v}) = \lim_{\Delta h\mathbf{v} \to 0} \frac{\left[\sum_{g} \sum_{j} \left| u^{j} \left(\begin{array}{c} q \\ \mathbf{X} \end{array} \right) \right|^{2} \right]_{\Delta h\mathbf{v}}}{\Delta h\mathbf{v}},$$

where $u^{j}\begin{pmatrix}q\\\chi\end{pmatrix}$ is the normalized displacement of the atom of X from the position of equilibrium, j is the dispersion relation branch number, and q the phonon wave vector. For the present paper low-energy neutron resonances, occurring mainly in heavy nuclides, are of special interest. If chemical compounds of these elements include light elements such as H, O, C, N, etc. where $M_{\chi} >> M_{\gamma}$ the weighted phonon spectrum will differ substantially from the full spectrum.



Fig. 3. Normal frequency spectra $\rho(h\nu)$ for vibration in UO₂ and UC lattices, and the contributions of U-weighted spectra (shaded)[3].

Let us consider, for example, UO₂ and UC, for which full and weighted spectra were calculated in Refs [34, 36]; these spectra are presented in Fig. 3. Debye spectra with upper frequency limits corresponding to the Debye temperatures Θ_D are often used for the quantitative description of phonon spectra. Clearly, the Debye temperature of the total spectrum Θ_D , for $M_X \gg M_Y$ will differ substantially from the corresponding effective Debye temperature Θ_X for the weighted spectrum $\rho_X(hv)$. For UO₂, $\Theta_D = 520$ K, but for the U in UO₂ the effective temperature $\Theta_U = 250$ K and for the O in UO₂ the effective temperature $\Theta_0 = 749$ K (where T = 293K)[37].

Approximation of the phonon spectrum using delta functions.

Computation of the transfer function using expressions (15) or (16) for continuous phonon spectra is a fairly complex task. It is therefore useful to introduce an approximation for the phonon spectra in the form of a summation of Dirac δ -functions, as follows:

$$\rho_{\mathbf{X}}(h\mathbf{v}) = \sum_{j=1}^{m} a_j \delta(h\mathbf{v} - h\mathbf{v}_j)$$
(17)

with the normalization

$$\sum_{j=1}^m a_j = 1.$$

By choosing an appropriate set of values for v_j and a_j , expression (17) can be used to give an approximate description of any phonon spectrum. The larger the number m, the better that approximation is. By inserting expression (17) into the function $\gamma(t)$ in expression (15) [or $\gamma_{\chi}(t)$ in expression (16)], we obtain

$$\gamma(t) = \frac{1}{RE_n} \sum_{j=1}^m (b_j^* e^{ih\nu_j t} + b_j^- e^{ih\nu_j t});$$

$$b_j^* = \frac{Ra_j}{h\nu_j (1 - \exp(-h\nu_j/k_B T))};$$

$$b_j^- = b_j^* \exp(-h\nu_j/k_B T).$$

By expanding the exponential functions

$$\exp\left(b_{j}^{\pm}\mathrm{e}^{\pm\mathrm{i}h\mathbf{v}_{j}t}\right) = \sum_{k=0}^{\infty} \frac{b_{j}^{\pm}\mathrm{e}^{\pm k\mathbf{v}_{j}t}}{k!}$$

we obtain from expression (15) for the transfer function:

$$S_{\kappa}(E_{n}, E_{t}) = D(E_{n}) \sum_{\rho_{1}=-\infty}^{\infty} \sum_{\rho_{2}=-\infty}^{\infty} \dots \sum_{\rho_{m}=-\infty}^{\infty} S_{\rho_{1}} S_{\rho_{2}} S_{\rho_{m}} \times \delta\left(E_{t} + \sum_{j=1}^{n} \rho_{j} h \nu_{j}\right), \qquad (18)$$

where D(E_n) is the Debye-Waller factor:

$$D(E_n) = \exp\left(-R\sum_{j=1}^m \frac{a_j}{hv_j} \operatorname{cth}\left(\frac{hv_j}{2k_{\mathrm{B}}T}\right)\right)$$
$$S_{\rho_j} = \sum_{n=l}^\infty \frac{(b_j^\star)^{\rho_j+n} (b_j^\star)^n}{(\rho_j+n)! n!};$$

$$l = \begin{cases} -\rho_j, \text{ if } \rho_j < 0 & (\text{photon absorption}); \\ 0, \text{ if } \rho_j > 0 & (\text{photon emission}). \end{cases}$$

The values of S are the probabilities of ρ_j phonons with an energy of hv_j being absorbed or emitted during reaction of the neutron with the nucleus. Since expression (18) for $S_k(E_n, E_t)$ contains δ -functions, it can be used for easy computation of the cross-section $\sigma(E_n)$. The summations in expression (18) proved to converge fairly quickly.

In Refs [3-9, 32], the Nernst-Lindemann approximation was used for the weighted phonon spectrum:

$$p_{\mathbf{X}}(h\mathbf{v}) = a_1 \delta (h\mathbf{v} - h\mathbf{v}_1) + a_2 \delta (h\mathbf{v} - h\mathbf{v}_2),$$

$$a_1 + a_2 = 1,$$
 (19)

i.e. a spectrum of the type given in expression (17) was used for m = 2. For metallic samples, the Einstein model proved appropriate, i.e.

$$\rho(h\nu) = \delta(h\nu - h\nu_1).$$
⁽²⁰⁾

Let us attempt a qualitative discussion of this approach and examine briefly the basic features of the weighted phonon spectrum for compounds where $M_X >> M_Y$. There exist normal vibrations of low frequency ($\approx v_1$), associated with movements of heavy atoms of X, which make a basic contribution to the weighted phonon spectrum $\rho_X(hv)$. Interaction of atoms of X with atoms of Y leads to a small contribution at higher frequencies ($\approx v_2$), described by the second term in expression (19). The energy hv_1 can also be evaluated from data on the specific heat capacity in the temperature region T ≤ 100 K, where the hv_2 mode remains practically unexcited. For the frequencies v_1 and v_2 we obtain, in the first approximation,

$$v_{1,2} \sim (M_{X,Y})^{1/2}$$

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and

The weighted phonon spectrum parameters obtained when using expression (19) to analyse the behaviour of the neutron resonance cross section are given in Table 1 for several uranium compounds.

Parameters of U-weighted phonon spectra $ho_U(hv)$ for several uranium compounds, obtained from an analysis of neutron resonances.

Table 1

Sample	aı	_{hν1} , meV	hv₂, meV	Reference
U UO2 U308 α-UO3 γ-UO8 UF4-H20 UO2(NO8)2-6H20	$\begin{array}{c} 1,0\\ 0,92\pm 0,02\\ 0,90\pm 0,05\\ 0,84\pm 0,03\\ 0,90\pm 0,02\\ 0,82\pm 0,04\\ 0,53\pm 0,06\\ 0,82\pm 0,04\\ \end{array}$	$ \begin{array}{c} 11 \pm 2 \\ 12 \pm 3 \\ 13 \pm 3 \\ 10 \pm 3 \\ 10 \pm 3 \\ 10 \pm 3 \\ 14 \pm 1 \\ 8 \pm 1 \\ 14 \pm 1 \end{array} $	$ \begin{array}{c}$	[32] [9] [32] [9] [9] [3] [3] [3]



cross-sections. In Fig. 4, the resonance shapes calculated using expressions (19) and (20) are shown. At top left is the 6.67 eV resonance for metallic 238 U at room temperature. The parameters for $\rho_{\rm U}$ (hv) correspond to the data given in Table 1. As may be seen, the cross-section is made up of a

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Fig. 4.

recoil-free component and of components associated with the excitation (right) and absorption (left) of phonons. The top right of Fig. 4 depicts calculated cross-sections for the compound $U_3 O_8$. The contribution of the recoil-free component and the sum of the contributions associated with excitation and absorption of hv_1 and hv_2 phonons are highlighted, as is the joint action of both vibration types hv_1 and hv_2 . The lower part of Fig. 4 shows the difference between the cross-sections for metallic uranium and $U_3 O_8$.

<u>Ideal gas approximation for solid-state samples</u>. Lamb, in Ref. [2], noted two simple extreme cases for the determination of the transfer function $S_k(E_n, E_t)$. The first is characterized by weak bonding of the atoms in the lattice. Here, the following relation holds:

$$\Gamma + \Delta_{\rm D} \gg 2k_{\rm B}\Theta_{\rm D},\tag{21}$$

where Γ is the total resonance width, Δ_{D} is the Doppler width defined in expression (12), and Θ_{D} is the Debye temperature of the sample. The shape and position of the neutron resonance coincide with the corresponding values for an ideal gas of target nuclei with, however, an effective temperature of T_{ef} instead of the crystal temperature T. The effective temperature is determined by the mean energy of the atoms of the crystal per vibrational degree of freedom:

$$T_{ef} = \langle \varepsilon \rangle / k_{B}$$

where

$$(\varepsilon) = \frac{1}{2} \int hv\rho(hv) \operatorname{cth}\left(\frac{hv}{2k_{\mathrm{B}}T}\right) d(hv).$$

In Fig. 5, the relationship between T_{ef} and T is shown for monocomponent crystals and various Debye temperatures. The formula for determining T_{ef} from Debye temperature data and specific heat capacity data is given in Ref. [38].



Fig. 5. Dependence of the effective temperature T_{ef} on the crystal temperature T measured in units of the Debye temperature Θ_n of the crystal [2].

The relationship in expression (21) holds in the first instance for monocomponent lattices. For polycomponent lattices it is modified in line with the above considerations to

$$T_{ef} = \langle \varepsilon \rangle_{\chi} / k_{B}, \qquad (22)$$

where

$$\langle \varepsilon \rangle_{\rm X} = \frac{1}{2} \int h v \rho_{\rm X} (h v) \operatorname{cth} \left(\frac{h v}{2 k_{\rm B} T} \right) d(h v)$$

is the mean energy per degree of freedom of the atom of X absorbing the neutron, and $\rho_{\rm y}({\rm hv})$ is the relevant weighted phonon spectrum.

Figure 6 gives, in addition to the behaviour of the 6.67 eV crosssection of the ²³⁸U resonance according to the Breit-Wigner formula (4), the cross-sections for a crystalline sample of UO₃ calculated at a temperature T = 300 K using $\rho_{\chi}(h\nu)$ from expression (19), in a gas approximation with a corresponding temperature $T_{ef} = 324$ K, and for an ideal gas at a temperature T = 300 K. Both models give generally similar resonance shapes. However, in the gas model the resonance curve is more symmetrical than for the crystal sample. The difference in the curves is up to 4×10^{-22} cm², i.e. 5% of the cross-section at the resonance maximum. The use of T_{ef} instead of T does not improve the reproduction of the resonance curve for a solid-state target; on the contrary, there remain qualitative differences. Condition (21) is here fulfilled at the level $(\Gamma + A_{p})/(2k_{p}\Theta_{H}) \approx 2$.



The second extreme case mentioned in Ref. [2] is a strong bond in the lattice, when the following conditions are fulfilled:

$$\Gamma$$
, < ε >, R << k_B Θ

In this case, the curve $\sigma_0(E_n)$ obtained using the relationship in expression (4) is recoil-free and not broadened (see Fig. 6). This case can be viewed as being analogous to the Mössbauer effect [39].

Comparison of model and experimental results for solid-state targets. The influence of crystal bonding on Doppler broadening can be clearly shown by investigating the difference in Doppler broadening for the same resonance in different samples as illustrated in Fig. 4. In Refs [3-9] the transmission spectra for various chemical compounds of uranium are measured for low-energy resonances. Some examples are given in Fig. 7. The differences in the experimentally obtained curves are described using the simple expression (19) for phonon spectra with the accuracy achieved experimentally.

In Refs [3-10], target nuclei with mass numbers A = 109, 161, 234, 235 and 238 were investigated over an energy range of 1-15 eV. The total widths Γ of the resonances studied ranged from 25 to 120 MeV. Apart from measurements at room temperature, samples were heated to temperatures of 373 and 670 K in a number of experiments; in addition, resonance curves for a solid-state sample of UO₃ and gaseous UF₆ were compared. In all cases,



Fig. 7. Transmission spectra (top) and spectrum differences (bottom) in the 6.67 eV resonance range for 238 U. Sample temperatures (left to right): room temperature, 373 K, room temperature, 370 K; sample thicknesses: 12×10^{20} , 4×10^{20} , 12×10^{20} , 5.5×10^{20} nuclei/cm² [8].

expression (19) for phonon spectra proved applicable. Firstly, the natural neutron resonance width Γ evens out the influence of phonon spectrum fine structures. Structures with a width of less than Γ are unresolvable in principle. Secondly, in the extreme case of a weak crystal bond, the sole parameter determining the energy behaviour of the resonance cross-section is the mean energy of atoms per vibrational degree of freedom $\langle \varepsilon \rangle_{\chi}$ [see expression (22)]. This parameter is virtually independent of phonon spectrum details.



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Fig. 8. Differences in the 6.67 eV resonance cross-sections for 238 U in UO₂ and U for atom vibrations in the lattice (continuous line), using the gas model with appropriate values of T_{ef} (broken line), and the gas model with values for T_{ef} and Γ_{γ} adjusted by $\sigma\Gamma_{\gamma} = 1$ meV (dotted line) [8].

In addition, it proved impossible to describe the measured differences in the cross-sections of various samples satisfactorily using the gas model. In Fig. 8, by way of example, a comparison is drawn between the difference in the cross-sections $\Delta\sigma$ for samples of UO₂ and U in the 6.67 eV resonance region for ²³⁸U calculated using a model with a phonon spectrum, and the difference obtained when using the gas model. Asymmetric behaviour with regard to the resonance maximum is due to the quantum nature of vibrations in a crystal lattice. The gas model result is different in both value and shape from the lattice model result. For the sake of comparison, results of a calculation using the gas model with a different value for Γ_{γ} changed by 1 meV are given in the same figure. This level of accuracy is required for nuclear power engineering calculations [40]. As may be seen, calculations using different models give a very noticeable difference in cross-sections.

Usually, Doppler broadening is described within the framework of the gas model. In this respect, the question arises under what conditions and to what extent solid-state effects influence the resonance cross-section. Let us consider first of all the dependence of solid-state effects on sample temperature. Figure 9 shows the difference and the ratio between the 6.67 eV



Fig. 9. Difference Δ_{σ} and ratio σ/σ_{G} for 6.67 eV resonance cross-sections for ²³⁸U calculated for vibrations in the lattice and using the gas model for values of T = 300 and 600 K [8].

resonance cross-sections for 238 U at T = 300 and 600 K, obtained either by taking into account crystal lattice vibrations, or using the gas model (for identical resonance parameters). As may be seen, when the temperature is doubled the differences are reduced by approximately half. (The use of T_{ef} instead of T in the gas model does not fundamentally alter the picture.)

In Fig. 10, results are given for various resonances: 6.67, 20.9 and 36.7 eV for 238 U, and 1.06 eV for 240 Pu in a UO₂ sample at T = 300 K. As a measure of the difference in the cross-section we will use the quantity

$$P = \frac{\left\{\int dE_n \left[\sigma(E_n) - \sigma_{gas}(E_n)\right]^2\right\}^{1/2}}{\int dE_n \sigma(E_n)}.$$

In Fig. 10, P is shown as a function of the value $\frac{1}{2}(\Gamma + \Delta_{D}) = \frac{1}{2}\Gamma + (E_{0} < c >_{U} M/m_{n})^{1/2}, \text{ which according to expression (21)}$



Fig. 10. Convergence of the cross-section difference in UO_{γ} [8].

should, if the gas model is correct, be much larger than $k_B \Theta_D$. For the UO_2 sample under investigation here, $K_B \Theta_D \approx 22$ meV. As may be seen, P falls fairly quickly as the energy E_0 and the resonance width Γ increase. This means that solid-state effects have a strong impact on the resonance cross-section for the lowest-energy neutron resonances in heavy nuclides. The higher the Debye temperature and the lower the sample temperature, the stronger the effect. The data in Table 2 for the 6.67 eV resonance of ^{238}U show the error in determining the resonance parameters from experimentally obtained spectra in a gas model approximation rather than an exact description of Doppler broadening [41]. The value found for the width Γ_n was up by 1%, and that for Γ_{γ} by several per cent. In conclusion, one might add that systematically taking into account lattice vibrations for low-energy resonances in uranium could be of interest to experimenters.

Table 2

Change in the widths $\Delta\Gamma_n$ and $\Delta\Gamma_\gamma$ due to the use of the gas model for Doppler broadening of the 667 eV resonance for 238 U for the samples and temperatures indicated [41].

Sample	т, к	$\Delta \Gamma_n / \Gamma_n$	$\Delta \Gamma_{\gamma}/\Gamma_{\gamma}$
UO2	300	-0,009	-0,08
UO2	600	-0,006	-0,07
U	300	-0,005	-0,04

<u>Molecular gas</u>. The neutron resonance cross-section for a molecular gas is determined not only by the overall thermal motion of the molecules, but also to a significant extent by internal excitations. Vibration and rotation spectra and other essential parameters, chiefly the force constants of many molecules, are already known to a fair degree of accuracy. Therefore, resonance cross-section calculations for molecular gases are more unambiguous than for solid bodies. The transfer function for neutron absorption in a molecular gas can be given in the form

$$S_{M}(E_{n}, E_{t}) = \sum_{\{n_{i}\}} W_{\{n_{i}\}} \sum_{\{n_{i}\}} \overline{P_{\{n_{i}\}}^{(n_{i})}} S_{G}(E_{n}, E_{t} - (E_{b} - E_{a})).$$
(23)

where $\{n_i^a\}$, $\{n_i^b\}$ are the sets of quantum numbers defining the states of the molecule before and after capture of a neutron having the corresponding energies E and E. Only those excitations which may change as a result of resonance capture of a neutron by a nucleus of X must be taken into account here. (This is analogous to the introduction of the weighted phonon spectrum in the case of solid bodies.) $W_{\{n_{i}^{a}\}}$ is the probability of the molecular state $\{n_i^a\}$ being populated before neutron capture at a specific gas temperature; $P_{\binom{n_i^b}{n_i^a}}^{\binom{n_i^b}{i}}$ is the probability of a molecule passing from the $\{n_i^a\}$ state to the $\{n_i^b\}$ state on neutron capture. The line denotes averaging over the molecule's orientations relative to the neutron's direction of motion; S_c is the transfer function for a monoatomic ideal gas as given in expression (11), but E_t must be replaced by the energy E_t - (E_b - E_a), and M by the mass of the whole molecule. When a resonance cross-section is calculated using formula (23), many states $\{n_i^a\}$ must be taken into account, and in the case of asymmetrical molecules the cross-sections must be averaged over the molecules' orientations.

At low-energy neutron resonances, the energy of the neutrons is too low to break up the molecule. Consequently, the vibrational states of the molecules and rotations, and also the connection between them must generally

be taken into account. This problem was examined in Ref. [42] for the capture of gamma quanta by biatomic molecules. The situation is simpler for symmetrical molecules of the type $XY_{Q}(l = 2, 3, 4, 5, 6)$, where the X nuclei absorb neutrons and are situated at the mass centre of the molecules. For molecules of this type only the vibrational transitions need to be considered, whereas the rotational ones can be ignored [43].

In Refs [43, 44] a general theory was developed for the emission and absorption of gamma quanta by nuclei of X in symmetrical molecules of the type XY_{g} . This theory served in Ref. [5, 45] as a basis for the calculation of neutron resonance cross-sections for gaseous UF₆. Symmetrical molecules of the type XY_{g} have several normal vibrations which, in the vast majority of cases, are degenerate. There are some too where the nucleus remains at rest. These normal vibrations are not excited when a neutron is captured by a nucleus of X, and therefore they are not of interest when calculating the neutron resonance absorption cross-section.

The molecular vibrations which are of interest to us are described by the set of quantum numbers $\{n_{S\alpha}\}$. The index s denotes the various normal vibrations, while α stands for the various components of a single degenerate normal vibration. The probability of a molecule passing from the $\{n_{S\alpha}^{a}\}$ state to the $K\{n_{S\alpha}^{b}\}$ state when a neutron is captured by a nucleus of X may be calculated, according to Ref. [43], using the formula

$$P_{\{n_{s\alpha}^{b}\}}^{\{n_{s\alpha}^{b}\}} = \prod_{s,\alpha} |\langle \Phi_{n_{s\alpha}^{b}}(Q_{s\alpha})| \exp\{ik_{\alpha}b_{s\alpha}Q_{s\alpha}M_{X}^{-1/2}\}| \Phi_{n_{s\alpha}^{a}}(Q_{s\alpha})\rangle|^{2},$$
(24)

where $Q_{S\alpha}$ is the normal co-ordinate of the α -component of the s-th normal vibration; $\Phi_{n_{S\alpha}^a}$ and $\Phi_{n_{S\alpha}^b}$ are the linear harmonic oscillator wave functions; $b_{S\alpha}$ is the normalized displacement of the nucleus of X from its equilibrium position; k_{α} is the neutron wave vector; and M_X is the mass of the nucleus of X. The value of $b_{S\alpha}$ may be determined from the elements of the matrix \hat{k} , which performs the inverse transformation of the matrix of mass-weighted Cartesian co-ordinates \hat{q} into the matrix of normal co-ordinates

 \hat{Q} [43, 46], or it may be determined from the molecular force constants. The matrix elements in expression (24) were calculated in Ref. [43]. In the event of energy absorption by a molecule $(n_{s\alpha}^b \ge n_{s\alpha}^a)$ we get the following

$$\begin{split} |\langle \Phi_{n_{s\alpha}^{b}}(Q_{s\alpha})| \exp \{ik_{\alpha}b_{s\alpha}Q_{s\alpha}M_{X}^{-1/2}\} |\Phi_{n_{s\alpha}^{a}}(Q_{s\alpha})\rangle|^{2} = \\ &= \left(\frac{n_{s\alpha}^{a}!}{n_{s\alpha}^{b}!}\right) Z_{s\alpha}^{n_{s\alpha}^{b}-n_{s\alpha}^{a}} \exp \{-Z_{s\alpha}\cos^{2}(\beta_{s\alpha})\} \times \\ &\times \cos^{2\left(n_{s\alpha}^{b}-n_{s\alpha}^{a}\right)}(\beta_{s\alpha}) \left[L_{n_{s\alpha}^{a}}^{\left(n_{s\alpha}^{b}-n_{s\alpha}^{a}\right)}(Z_{s\alpha}\cos^{2}(\beta_{s\alpha}))\right]^{2}, \end{split}$$
(25)

where L are associated Laguerre polynomials; $\beta_{S\alpha}$ is the angle between the direction of the incident neutron and the displacement direction of the nucleus of X due to the α -component of the s-th normal vibration. Where $(n_{S\alpha}^{b} < n_{S\alpha}^{a})$ we get an analogous formula because the matrix element does not change if we switch round the initial and final states. The parameters $Z_{S\alpha}$ essentially determine the transition probability.

$$Z_{s\alpha} = \frac{R}{hv_s} \frac{M + m_n}{M_X + m_n} b_{s\alpha}^2, \qquad (26)$$

where R is the recoil energy of the molecule, and hv_s is the energy of a quantum of the s-th normal vibration.

<u>Comparison of model and experimental results for UF_6 </u>. Resonance cross-sections for an energy of 6.67 eV in gaseous $^{238}UF_6$ were calculated in Refs [5, 45] for various temperatures using expressions (23)-(26).

Molecules of gaseous UF₆ belong to point group 0; they have an octahedral structure. The uranium atom is at the mass centre of the molecule. The distances between the uranium atom and the fluorine atoms are identical. The angles between the U-F bond lines are 90° or 180° only. UF₆ has six normal vibrations. However, only the triply degenerate normal vibrations v_3 and v_4 of symmetry type $F_{1\mu}$ contribute to the displacement of the uranium nucleus. The necessary frequencies of v_3 and v_4 are given in Ref. [47]: $hv_3 = 0.0776 \text{ eV}$, $hv_4 = 0.0231 \text{ eV}$. The b_{sa} parameters were calculated from force constants [47, 48].



Fig. 11. Cross-section for the 6.67 eV resonance in UF_6 at T = 373 K both taking into account (continuous line), and not taking into account (broken line), internal molecule excitations [5].



Fig. 12.

Ratio of the 6.67 eV resonance cross-sections for ²³⁸U₃O₈ and ²³⁸UF₆ at room temperature: dots - experimental result from Ref. [45]; broken line - calculated result from Ref. [45]; continuous line - calculated result from Ref. [5].

In Fig. 11, the neutron resonance absorption cross-sections obtained in Ref. [5] for the 6.67 eV resonance are shown both taking into account, and not taking into account, internal excitation of the molecules. In Ref. [45], the ratio of the neutron resonance absorption cross-sections for polycrystalline $U_3^0{}_8$ and for gaseous UF₆ at room temperature was measured. The experimental result is presented in Fig. 12 together with the results of theoretical calculations from Refs [5, 45]. The resonance cross-section for polycrystalline $U_3^0{}_8$ was described in both papers using the above methods and the phonon spectrum from Ref. [32]. Some approximations were made when calculating the cross-section for UF₆ in Ref. [45]: in particular, the number of states $n_{S\alpha}$ was significantly cut down, and transitions involving the transmission of more than 1 phonon of the same energy were disregarded, as was the dependence of the $Z_{S\alpha}$ parameter on energy. In Ref. [5] there are no approximations of this kind, and the calculated result agrees fairly well with the experimental data. Fig. 7 shows the differences in the transmission spectra for UF₆ and UO₃ which were measured in Ref. [5] in the 6.67 eV resonance range for 238 U, and the corresponding calculated result.

3. <u>Temperature shift of neutron resonances</u>

Temperature shift of Mössbauer lines and neutron resonances.

Temperature shift of Mössbauer resonance γ -lines was discovered in 1960 [11, 12, 49]. A change in source or absorber temperature leads to energy shift of the resonance γ -line but no significant change in its shape. This shift is equal to:

$$\delta E_{\gamma} = -\frac{E_{\gamma}}{Mc^2} \Delta \langle \varepsilon_k \rangle, \qquad (27)$$

where $\Delta < \epsilon_k >$ is the difference in the mean kinetic energies of the atoms which corresponds to the temperature difference $\Delta T = T_2 - T_1$, and

$$\langle \varepsilon_h \rangle = \frac{3}{4} \int_0^\infty h \nu \rho (h \nu) \operatorname{cth} \left(\frac{h \nu}{2k_{\mathrm{B}} T} \right) d(h \nu);$$

M being the mass of the atoms, and $\rho(h\nu)$ the crystal phonon spectrum. At high temperatures expression (27) takes the form:

$$\delta E_{\gamma} pprox - rac{3}{2} rac{E_{\gamma}}{Mc^2} k_{\mathrm{B}} \Delta T.$$

A similar effect should also exist during neutron capture [15]. In contrast to Mössbauer γ -lines, the shape of the neutron resonance in crystalline samples is determined to a considerable extent by phonon emission and absorption. A temperature rise leads to broadening of the resonance. Let

us define the concept of resonance "shift": in this paper, the position of the centre of mass of a resonance will be taken to be the position of that resonance:

$$\overline{E}_{n} = \frac{\int_{E_{1}}^{E_{2}} \sigma_{R}(E_{n}) E_{n} dE_{n}}{\int_{E_{1}}^{E_{2}} \sigma_{R}(E_{n}) dE_{n}}, \qquad (28)$$

where $\sigma_{R}(E_{n})$ is the resonance portion of the total cross-section, and the integration limits E_{1} , E_{2} are set at the points where the cross-section $\sigma_{R}(E_{n})$ may, with the experimental accuracy achieved, be assumed to equal zero:

$$\sigma_{\rm R}({\rm E}_1) \approx \sigma_{\rm R}({\rm E}_2) \approx 0. \tag{29}$$

Of course, one must be dealing here only with isolated resonances. The following quantity is called the temperature shift:

$$\Delta \overline{E}_{n} = \overline{E}_{n}(T_{2}) - \overline{E}_{n}(T_{1}). \qquad (30)$$

<u>Description in the monoatomic ideal gas model</u>. Let us consider the simplest case of an ideal gas. If we insert into expression (7) the transfer function contained in expression (11), and use the δ -function (an infinitely narrow resonance) for the stationary nucleus cross-section σ_0 :

$$\sigma_0(E_x) \sim \delta(E_x - E_0),$$

formula (28) generates the integrals:

$$\int_{0}^{\infty} dx x^{n} \exp\left(-ax^{2}\right) \operatorname{sh}\left(bx\right);$$
$$a = \frac{A}{k_{\mathrm{B}}T}, \quad b = \frac{2}{k_{\mathrm{B}}T} \sqrt{A(A+1)E_{0}}$$

where A is the mass number of the target nucleus and n = 2 or n = 0 [the numerator or denominator of expression (28)]. Integration [50] yields the centre of mass:

$$\overline{E}_{nG} = E_0 + \frac{1}{A} \left[E_0 + \frac{1}{3} \langle \varepsilon_k \rangle_G \right] + \frac{\widetilde{x} \exp\left(-\widetilde{x^2}\right)}{A \sqrt{\pi} \operatorname{erf}\left(\widetilde{x}\right)} \frac{2}{3} \langle \varepsilon_k \rangle_G.$$

where

$$\operatorname{erf} \left(\widetilde{x} \right) = \frac{2}{\sqrt{\pi}} \int_{0}^{\widetilde{x}} dt \exp\left(-t^{2}\right);$$
$$\widetilde{x} = \left\{ (A+1) \frac{3E_{0}}{2 \langle \varepsilon_{k} \rangle_{G}} \right\}^{1/2};$$

 $\langle \epsilon_k \rangle_G$ is the mean kinetic energy of an atom in an ideal gas at temperature T:

$$\langle \varepsilon_k \rangle_G = \frac{3}{2} k_{\mathbf{B}} T.$$

Any cross-section $\sigma_0(\mathbf{E}_x)$ which is dependent on the neutron wave number k can be given in the form:

$$\sigma_0(E_x) = \sum_i c_i \delta(E_x - E_{0i}).$$

From this it is not difficult to obtain:

$$\overline{E}_{nG} = \overline{E}_0 + \frac{1}{A} \left[\overline{E}_0 + \frac{1}{3} \langle \varepsilon_k \rangle_G \right], \qquad (31)$$

where \overline{E}_0 is the centre of mass of a cross-section $\sigma_0(E_x)$ of arbitrary shape.

If, instead of expression (11), we use the Bethe transfer function (13), we obtain as the centre of mass:

$$\overline{E}'_{nG} = \overline{E}_0 + \frac{1}{A} \left[\overline{E}_0 + \frac{4}{3} \langle \varepsilon_k \rangle_G \right].$$
(32)

The difference between expression (31) and (32) may be understood if we look at the energy E_T as in expression (10). Averaging (10) over a Maxwellian distribution, we obtain:

$$\bar{E}_{i} = \frac{1}{A+1} E_{n} - \frac{1}{A+1} \langle \varepsilon_{k} \rangle_{G}.$$

In the Bethe approximation, the last term of expression (10) is ignored, and therefore:

$$\overline{E}_t' = \frac{1}{A+1} E_n \approx \frac{1}{A} E_n.$$

As may be seen, the Bethe approximation overestimates \overline{E}_t by $\sim \frac{1}{A} < \epsilon_k >_G$ and this is precisely the difference between expressions (31) and (32), i.e. the Bethe approximation, in which the increase in the atom's mass as a result of neutron capture is disregarded, is inadequate for an accurate description of temperature shift in a neutron resonance.

<u>Description for the case of a solid-state target</u>. To calculate the centre of mass of a resonance as a transfer function we use Lamb's

expression (14). However, as is shown above, the increase in the atom's mass by the mass of the neutron on its absorption must not be neglected. Expression (14) contains the same approximation as the Bethe formula: $M + m_n \approx M$ or $A + 1 \approx A$. Let us account for the mass increase in terms of the change in the energy associated with the nucleus's motion in the crystal after neutron capture

$$\sum_{s} h \widetilde{v}_{s} \left(n_{s} + \frac{1}{2} \right) = \widetilde{E}_{f} \quad (|\{n_{s}\}\rangle = |f\rangle)$$

and before neutron capture

$$\sum_{s} h v_{s} \left(\alpha_{s} + \frac{1}{2} \right) = E_{j} \quad (|\{\alpha_{s}\}\rangle = |j\rangle).$$

The energies E_j and \tilde{E}_f relate to the different Hamiltonian functions H and \tilde{H} :

$$H|j\rangle = E_j|j\rangle;$$

$$H(\hat{\mathbf{p}}_A) = \frac{\hat{\mathbf{p}}_A^2}{2m_n A} + V(\mathbf{r});$$

$$\widetilde{H}|f\rangle = \widetilde{E}_f|f\rangle;$$

$$\hat{H}(\hat{\mathbf{p}}_A) = \frac{\hat{\mathbf{p}}_A^2}{2m_n (A+1)} + V(\mathbf{r}).$$

The first term in the Hamiltonians gives the kinetic energy and the second the potential energy. Note that the Hamiltonians H and \tilde{H} relate to different sets of eigenfunctions. As to the description of the cross-section $\sigma_0(E_x)$ for the stationary nucleus, we shall use the Breit-Wigner formula (5) with the condition $\Gamma_n \ll \Gamma$. Using also the transformation

$$\delta(E) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \exp\left(\frac{\mathrm{i}}{\hbar} Et\right) \,,$$

the relationship

$$\exp\left(-\frac{\mathrm{i}}{\hbar}\mathbf{p}_{n}\mathbf{r}\right)\hat{H}\left(\mathbf{p}_{A}\right)\exp\left(\frac{\mathrm{i}}{\hbar}\mathbf{p}_{n}\mathbf{r}\right)=\tilde{H}\left(\mathbf{p}_{A}+\mathbf{p}_{n}\right)=\frac{(\mathbf{p}_{A}+\mathbf{p}_{n})^{2}}{2m_{n}\left(A+1\right)}+V\left(\mathbf{r}\right)$$

and expressions (5), (9) and (14), the cross-section (7) can be presented in the form

$$\sigma(E_n) \sim \int_{-\infty}^{\infty} \frac{dE_t \Gamma_n(E_0) \Gamma/p_n}{(E_t - E_0)^2 + \Gamma^2/4} \int_{-\infty}^{\infty} \frac{dt}{2\pi} S(t) \exp\left[\frac{i}{\hbar} (E_n - E_t) t\right], \quad (33)$$

where

$$S(t) = \sum_{j} W_{j} \left\langle j \left| \exp \left[-\frac{i}{\hbar} \hat{H} \left(\hat{\mathbf{p}}_{A} + \mathbf{p}_{n} \right) \right] \right| j \right\rangle \exp \left(\frac{i}{\hbar} E_{j} t \right).$$
(34)

As only small values of $E_t(|E_t| \ll E_n)$ contribute to the integral in (7), infinity has been substituted for the upper limit E_n in the integral. In the harmonic approximation, using the method of second quantization, we have the operators

$$\hat{\mathbf{p}}_{A} = \sum_{s} i \sqrt{h v_{s} m_{n} (A+1)/2N} (\hat{a}_{s}^{*} - \hat{a}_{s}) \mathbf{e}_{s},$$

where N is the number of atoms in the crystal;

$$\hat{H}(\hat{\mathbf{p}}_{A}+\mathbf{p}_{n}) = \sum_{s} h \tilde{\mathbf{v}}_{s} \left[(\hat{a}_{s}^{*}-i\alpha_{s}) (\hat{a}_{s}^{*}+i\alpha_{s}) + \frac{1}{2} \right];$$
$$\alpha_{s} = (\mathbf{p}_{n}\mathbf{e}_{s}) / \sqrt{2m_{n} (A+1) Nh \mathbf{v}_{s}}.$$

Since the various s mode vibrations are independent of one another, expression (34) can be presented in the form of a product

$$S(t) = \prod_{\bullet} S_{\bullet}(t) = \prod_{\bullet} \sum_{l} \langle l | \hat{Q}_{\bullet} | l \rangle (X_{\bullet}^{l}/Z_{\bullet}) \exp [2\pi i \delta v_{\bullet} t].$$

Here we introduce the designations

$$\begin{aligned} |l\rangle_{(s)} &= \frac{(a_s^*)^l}{\sqrt{l!}} |0\rangle_{(s)}, \quad \hat{Q}_s = \exp\left[-2\pi i \tilde{v}_s t\right] (a_s^* - i\alpha_s) (a_s^* + i\alpha_s); \\ X_s &= \exp\left(-\frac{hv_s}{k_{\rm B}T} + 2\pi i v_s t\right); \quad Z_s = \sum_l \exp\left(-l \frac{hv_s}{k_{\rm B}T}\right) = \\ &= \frac{1}{1 - \exp\left(-\frac{hv_s}{k_{\rm B}T}\right)}; \\ \delta v_s &= v_s - \tilde{v}_s. \end{aligned}$$

To calculate the function S(t) we shall use the Berezin method [51]. The quantity δv_s in the first approximation can be given by the expression

$$\delta v_s = \frac{v_s}{2AN}$$
.

After integrating expression (33) with respect to E_t and t the cross-section $\sigma(E_r)$ takes the form

$$\sigma(E_n) \sim \frac{1}{\sqrt{E_n}} \left[1 + 3 \frac{\langle e_{h1} \rangle}{A} \frac{d}{dE_n} + 2 \frac{\langle e_{h1} \rangle}{A} \frac{d^2}{dE_n^2} \right] \frac{\Gamma_n(E_0) \Gamma}{(E_n - \widetilde{E}_0)^2 + \Gamma^2/4} ;$$
$$\widetilde{E}_0 = E_0 A / (A+1),$$

where $\langle \epsilon_{k1} \rangle$ is the mean kinetic energy per degree of freedom:

$$\langle \varepsilon_{k1} \rangle = \frac{1}{3} \langle \varepsilon_k \rangle.$$

and $\langle \epsilon_{k1} || \rangle$ is the kinetic energy corresponding only to the co-ordinate x_1 , which is related to the direction of motion of the neutron $p_n = p_n \cdot e_{x_1}$. From the foregoing it is not difficult to find the position of the centre of mass of the resonance using formula (28):

$$\overline{E}_{n} = \sqrt{\overline{E}_{0}^{2} + (\Gamma/2)^{2}} - \frac{3}{2A} \left(\langle \varepsilon_{k1} \rangle - \langle \varepsilon_{k1} \rangle \right) - \frac{1}{2A} \left(3 \langle \varepsilon_{k1} \rangle - \langle \varepsilon_{k1} \rangle \right) \cos \left(\frac{3\phi}{2} \right) \cos \left(\frac{\phi}{2} \right);$$

$$\phi = \arctan \left(\Gamma/\widetilde{E}_{0} \right).$$

For a cubic crystal we may assume $<\epsilon_{k1} \parallel > = <\epsilon_k >$, and so, where $\phi \ll 1$, we get

$$\overline{E}_n = \sqrt{\overline{\tilde{E}_{\nu}^2 + (\Gamma/2)^2}} - \langle \varepsilon_k \rangle / 3A,$$

and, consequently, the temperature shift in crystals

$$\Delta \overline{E}_{n\kappa} = -\frac{1}{3A} \Delta \langle \varepsilon_k \rangle_{\kappa}.$$
(35)

At high temperatures we have $\langle \epsilon_k \rangle_K \approx \langle \epsilon_k \rangle_G = \frac{3}{2} k_B T$. The result in (35) can also be used as an approximation for any polycrystalline solid body.

If we disregard the increase in the atom's mass due to neutron absorption, i.e. H = H, we obtain a result which differs by the term $(1/A)\Delta < \epsilon_k >_K$ from expression (35) in exact analogy to the results for a gas. If we use k_G (8) instead of k_K (9) for the neutron wave number, then we get for the temperature shift the expression $\Delta \overline{E}'_n = \frac{1}{3A}\Delta < \epsilon_k >_K$, i.e. the sign changes. Thus these fine points, which are practically unnoticeable in Doppler broadening of resonances, play a major role in temperature shift.

Experimental observation of shifts in the centre of mass of neutron resonances. Temperature shifts in the centre of mass of neutron resonances were observed for the first time in Ref. [10]. In this paper, transmissions through Dy, Rh and Ag samples were measured at various temperatures in the low-energy resonance region. The experimental layout is described in

section 1. To measure the neutron transmission, two identical samples at different temperatures T_1 and T_2 were introduced successively into the beam for ten minutes. Every twelve hours the temperature of the samples was changed to T_2 and T_1 respectively. The energy behaviour of the spectrum for the incident beam and background was measured in additional experiments.

The temperature shifts $\Delta \tilde{E}_n$ were determined using two methods. In the first method, the difference between the measured resonance cross-sections is determined: $\Delta \sigma_R(E_n) = \sigma_R(T_2,E_n) - \sigma_R(T_1,E_n)$. When this difference is determined correctly, the following condition must hold:

$$\int_{E_1}^{E_2} \Delta \sigma_R(E_n) \, dE_n = 0,$$

if \mathbf{E}_1 and \mathbf{E}_2 are selected in accordance with condition (29). In practice, however, condition (29) is not strictly satisfied, and minor corrections must therefore be introduced. The error for the shift obtained is determined from the error in the determination of the background, the resolution function and the incident beam spectrum. The second method consists, in essence, of a comparison of experimental spectra with theoretical calculations. The cross-sections $\sigma_{\mathbf{R}}(\mathbf{T}_2,\mathbf{E}_n)$ and $\sigma_{\mathbf{R}}(\mathbf{T}_1,\mathbf{E}_n)$ were calculated on the basis of the methods described in section 2. The Einstein model (20) was used for the phonon spectrum, hv being chosen such that the thermal capacity's temperature behaviour was correctly described. In addition, at one of the temperatures an additional energy shift Δ is introduced and serves as a fitting parameter:

$$\sigma'_{R}(T_{2}, E_{n}) = \sigma_{R} (T_{2}, E_{n} - \Delta).$$

The theoretical transmission spectra $N_{th}(T,t)$ are then calculated, and the parameter Δ is found by fitting the differential theoretical spectrum $\Delta N_{th}(t) = N_{th}(T_2,t) - N_{th}(T_1,t)$ to the differential experimental spectrum $\Delta N_{exp}(t)$, after which the temperature shift is obtained from formulae (28) and (30). The second method is good in that the results obtained thereby are less affected by errors in the measurement of the incident beam and background spectrum than in the case with the first method. The main errors here are related to the choice of resonance parameters and the phonon spectrum. In this respect both methods are independent.



Fig. 13. Dependence of temperature-related resonance shifts on ∆<ε >k/A [10]: □, ■ - ¹⁰⁹Rh (1.26 eV); ▼ - ¹⁰⁹Ag (5.19 eV); o, • - Dy (¹⁶³Dy 1.71 eV, ¹⁶¹Dy 2.72, 3.68, 4.34 eV); the black symbols represent shifts obtained using the first method, and the white those obtained using in the second method; the broken line is formula (35).

The results of the experiment are shown in Fig. 13. For 109 Ag and 161 Dy, the first method did not yield results owing to the difficulties of determining the cross-section at a distance from the resonance maximum, or owing to resonance overlap. In the remaining cases, the results obtained by the various methods show a high level of agreement one with another. The shifts measured for polycrystalline samples are negative, i.e. when the temperature rises the centre of mass moves in the direction of lower energies. The experimental results agree satisfactorily with the theoretical evaluation given in expression (35). Within the limits of error of the experiment, there were no additional effects related to recoil energy, phonon spectrum, or resonance parameters which might have imitated a temperature shift.

4. <u>The influence of hyperfine interaction on neutron resonances</u>

<u>Chemical shift of neutron resonances</u>. Interaction of an atomic nucleus with electrons produces a dependence of the observed energy levels of the nucleus and electron shell both on the electric and magnetic moments of the nucleus, and on the electron shell configuration. This hyperfine interaction manifests itself during any quantum transitions in the nucleus and the shell in the form of such familiar phenomena as isotope and isomer shifts, multipole splitting, etc. These phenomena are observed in shell spectroscopy in the optical and X-ray ranges, in Mössbauer spectroscopy, and in muonic atom spectroscopy. In principle, they also occur when compound states of the nucleus are excited by neutrons, and they cause displacements and broadenings of neutron resonances.

F.L. Shapiro was the first to point out the possibility of measuring such effects (with a view to determining the electromagnetic moments of compound nuclei) in 1967 [52]. In Ref. [15] by V.K. Ignatovich et al., the existence of chemical shift of neutron resonances as an analogue to Mössbauer isomer shift is pointed out, as is the possibility of using it to determine mean square radii of the nucleus in isolated compound states.

In order to calculate the effects of hyperfine interaction effects in neutron resonances, we will consider its electric and magnetic components separately:

$$E_{\rm nf} = E_{\rm ef} + E_{\rm mg}$$

Let us consider first of all the electric contribution. We will begin with the Coulomb interaction

$$E_{\rm C} = \sum_{r_e, r_p} \left\langle \psi_k \varphi_e \left| \frac{-e^2/4\pi\epsilon_0}{|r_e - r_p|} \right| \psi_k \varphi_e \right\rangle, \tag{36}$$

where ψ_k and ϕ_e are the wave functions of the nucleus and electrons, and the summation is carried out for all electron co-ordinates r_e and proton co-ordinates r_p . Expanding $\frac{1}{|r_e - r_p|}$ from expression (36) using spherical harmonics, we obtain E_c in the form of a summation with ascending orders of multipoles. Only the monopole term is written out below:

$$E_{\mathbf{C}} = \sum_{r_e, r_p} \left\langle \psi_k \varphi_e \left| \frac{-e^2 / 4\pi e_0}{r_e} \right| \psi_k \varphi_e \right\rangle + \sum_{r_e, r_p} \psi_k \left| -\frac{e^2}{4\pi e_0} \int_{r_e \leqslant r_p} \left(\frac{1}{r_p} - \frac{1}{r_e} \right) \varphi_e \varphi_e^* d\tau_e \left| \psi_k \right\rangle + \dots$$
(37)

The first sum in expression (37) represents the Coulomb energy (not contributing to the hyperfine interaction) between the point nucleus and the shell electrons, and the second sum represents the deviation from that energy due to the finite dimensions of the atomic nucleus. The next non-zero term of expansion (37) describes the quadrupole interaction which is discussed below. The remaining terms with higher orders of multipoles are negligibly small or equal to zero.

With a view to simplifying expression (37) still further, let us consider the electron density within the boundaries of the nucleus. In the non-relativistic case, i.e. for lighter atoms, it is made up only of s-electrons. For heavy atoms, where electron motion is relativistic, $p_{1/2}$ -electrons also make a small contribution. Their density in a first approximation is constant within the boundaries of the nucleus. Under those circumstances, the second sum in expression (37) can be rewritten as

$$E_{\rm el, 0} = \frac{e^2 Z}{6\epsilon_0} \rho_e(0) \langle r_{\rm ch}^2 \rangle, \qquad (38)$$

where $\rho_e(0)$ is the electron density at the nucleus's position; Z is the charge number of the nucleus, and $\langle r_{ch}^2 \rangle$ is the mean square charge radius of the atomic nucleus. Figure 14 illustrates schematically the shifts $E_{el,0}$ caused by the finite dimensions of the nucleus for the ground and excited levels. These shifts amount to approximately 350 eV for a heavy nucleus, for example of uranium. For two samples consisting of different chemical compounds (I and II) with different electron densities $\rho_I(0)$ and $\rho_{II}(0)$ the positions E_0 of the neutron resonance differ by

$$\Delta E_0 = [E_{el,0} (I, c) - E_{el,0} (I, g) - E_{el,0} (II, c) - E_{el,0} (II, g)].$$



Fig. 14. Influence of electric interaction of the nucleus with the electron shell at the energies of the ground and excited states.

By substituting $E_{el.0}$ from expression (38) into this formula we obtain

$$\Delta E_0 = \frac{e^2 Z}{6\varepsilon_0} \left(\rho_{\rm I} \left(0 \right) - \rho_{\rm II} \left(0 \right) \right) \left(\langle r_{\rm ch}^2 \rangle_{\rm c} - \langle r_{\rm ch}^2 \rangle_{g} \right). \tag{39}$$

In deriving expression (39) it was assumed that the changes in $\rho_{I}(0)$ and $\rho_{II}(0)$ due to excitation of the nucleus were mutually compensatory. This assumption was confirmed by the evaluations performed.

The order of magnitude of chemical shifts. Let us now look at the magnitude of chemical shifts. Figure 15 shows evaluations of the differences in the electron densities $\Delta \rho_e(0)$ for various pairs of chemical compounds as a function of Z. The data were calculated using the Hartree-Fock-Slater method from Ref. [53] for free ions. The difference $\Delta \rho_e(0)$ is caused by delocalization of s- and $p_{1/2}$ -electrons, as far as they take part in the chemical bond, and, indirectly, by the remaining p- and d-electrons etc. through screening of external s- and $p_{1/2}$ -electrons. A sharp rise in $\Delta \rho_e(0)$ may be seen as the atomic number Z of the element increases. Using the above-mentioned calculations [53], we obtain

$$\Delta \rho_e (0) \approx 6.7 \cdot 10^{24} \cdot e^{0.07Z} \text{ cm}^{-3}.$$
 (40)



Fig. 15. Maximum differences in the electron densities $\Delta \rho_e(0)$ between different chemical compounds as a function of the atomic number Z, based on data from Ref. [53].



<u>Fig. 16</u>. Dependence of the chemical shift ΔE_0 on the atomic number Z when $\Delta < r_{ch}^2 > varies$.

The change in the mean square radius of the nucleus is due, primarily, to the isotope effect between the target nucleus and the ground state of the compound nucleus, and secondly, to the change in $\langle r_{ch}^2 \rangle$ resulting from excitation of the nucleus. If we assume the variation in r_{ch}^2 to range from a fraction of a per cent to several per cent [54, 55], and using expression (40), we obtain the evaluation of chemical shifts given in Fig. 16. For heavy nuclei the shifts may be greater than $10^2 \mu eV$, whereas for lighter nuclei they are substantially smaller.

<u>Determination of chemical shifts</u>. Despite the small scale of chemical shifts by comparison with the width of neutron resonances ($\Gamma \approx 100 \text{ meV}$) and additional difficulties connected with the influence of Doppler broadening of neutron resonances, measurements have been performed in recent years for

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• •,

several resonances of uranium isotopes [3, 4, 9]. The experiments were carried out using a pulsed IBR-30 reactor working on the principle described in section 1. Neutron transmission through targets of different chemical compounds of uranium was measured for identical sample temperature. By contrast, the temperature shifts were investigated using samples of the same substance, but at different temperatures. Both in the first and the second case, the difference in the kinetic energies of the atoms

$$\Delta \langle \varepsilon \rangle = \langle \varepsilon (T) \rangle_{I} - \langle \varepsilon (T) \rangle_{II}$$

in both samples being compared (I and II) causes a resonance shift [see (35)]

$$\Delta \bar{E}_{n} = -\frac{1}{3A} \left[\langle e(T) \rangle_{I} - \langle e(T) \rangle_{II} \right].$$

This shift, which occurs in addition to the chemical shift, is so small as to be negligible in the first instance. For all the samples investigated it is less than 4 µeV. The chemical shifts were determined directly from the experimental transmission spectra $N_I(t)$ and $N_{II}(t)$ using the method described in section 3; the spectra were compared in the resonance range using the method of least squares, and varying $N_{II}(t)$ in relation to $N_I(t)$ by the parameter $\Delta t(N_{II}(t) \rightarrow N'_{II}(t + \Delta t))$. Doppler broadening and several other factors affecting transmission were determined by calculating spectra having the same shapes as $N_I(t)$ and $N_{II}(t)$ but no chemical shift.

Figure 17 shows chemical shifts for the 6.67 eV resonance in 238 U as a function of $\Delta \rho_{e}(0)$. Table 3 gives values for $\Delta < r_{ch}^{2} >$ for all the resonances investigated, obtained while measuring chemical shifts in neutron resonances. The values of $\Delta \rho_{e}(0)$ were obtained within the framework of the "effective configurations of valence electrons" model, using experimental data on chemical shifts of X-ray lines in uranium and isomer shift of the Mössbauer line in the neighbouring nuclide 237 Np.

<u>The influence of dipole and quadrupole interaction</u>. If the atomic nucleus has a spin I > 0, then in addition to electric monopole interaction there will be contributions from hyperfine interaction of a higher order up



Fig. 17. Dependence of the chemical shift ΔE_0 on the difference in electron densities $\Delta \rho_e(0)$ for the pairs of chemical compounds indicated, measured for the 6.67 eV resonance in $^{238}_{U}$ [3].

Table 3

Changes in mean square radii of nuclei, determined from the chemical shifts in resonances measured in Refs [3, 9].

Target nucleus	Resonance E0, eV	$\Delta (r_{\rm ch}^2), {\rm fm}^2$	Target nucleus	Resonance ^{E0,} eV	$\Delta \langle r_{cb}^{3} \rangle \cdot fm^{2}$
234U 235U 235U 235U 235U 235U	5,16 1,14 2,03 3,15 3,61	$\begin{array}{r} -0,41\pm0,25\\ +0,01\pm0,22\\ -0,13\pm0,21\\ +0,20\pm0,48\\ +0,02\pm0,25\end{array}$	235U 255U 255U 255U 235U 238U	4,85 8,77 11,67 12,39 6,67	$\begin{vmatrix} -0,52\pm0,25\\ +0,09\pm0,26\\ -0,24\pm0,29\\ +0,25\pm0,31\\ -1,7\pm0,5 \end{vmatrix}$

to l = 2I. Of course, other contributions apart from magnetic dipole and electric quadrupole interaction are too small to be significant. Dipole and quadrupole interaction causes splitting of nuclear levels. The influence of this splitting on the neutron resonance cross-section is discussed separately in this section for purely dipole and purely quadrupole interaction.

Magnetic dipole interaction of an atomic nucleus having spin I and dipole moment μ with a magnetic field of strength H existing at the nucleus position causes Zeeman splitting of each energy level into 2I + 1 equidistant sub-levels. For splitting, we have

$$E_{\rm mg}=-\frac{\mu}{I}mH,$$

where m is the projection of the spin onto the direction of the magnetic field, m = I, I - 1, ..., - I. The intra-atomic magnetic field is produced by uncompensated electrons in the atomic shell and their interaction. In the transition elements (iron group, lanthanides and actinides) the field strength is as high as 10^5-10^7 Oe [56]. For H = 10^6 Oe and $\mu = 1$, the distance between the highest and lowest sub-level is approximately 5 µeV.

Since both the ground state of the target nucleus and the compound state are subject to Zeeman splitting, the resonance cross-section is made up correspondingly of the cross-sections for the transitions between the individual sub-levels m_I and m_J of the ground and compound states with energies differing by ΔE_{mg} (m_I, m_J). For the total cross-section we obtain

$$\sigma_{0}(E_{x}) = \sum_{m_{I}, m_{J}} \sigma_{0}(E_{x}, E_{0} + \Delta E_{mg}(m_{I}, m_{J}))W(m_{I}, m_{J}), \qquad (41)$$

where W (m_I, m_J) is the probability of transition between the states m_I and m_J . If the sample temperature is not very low (over a millikelvin), then population of the individual Zeeman states is equally probable and, consequently, $(m_I) = 0$. In addition, for unpolarized neutrons we have $(m_J) = 0$. Hence for unpolarized nuclei and neutrons, displacement of the centre of the neutron resonance can not, on principle, occur. There is, however, broadening of the neutron resonance. Its order can be evaluated using the expression μ H/I, which varies from several microelectronvolts to several tens of microelectronvolts. Experimental research into the broadening of the neutron resonance working with values of this order is unlikely to be successful with currently available experimental facilities. Nevertheless, it has proved possible to measure the small energy shift in neutron resonances caused by dipole interaction in the case of polarized nuclei or neutrons [18]. The energy of interaction of the automatic nucleus's spectroscopic quadrupole moment Q_{I} with an electric field gradient, for the simplest case of an axially symmetrical gradient V_{z} , may be written in the form

$$E_{\rm el, 2} = \frac{3eV_z Q_I}{4I(2I-1)} \left(m_I^2 - \frac{I(I+1)}{3} \right) , \qquad (42)$$

where I is the spin of the nucleus and m_I its projection onto the gradient's direction, and $m_I = I, I - 1, ..., - I$. In the general case, expression (42) is of course more complicated, but it suffices for a discussion of the main effects.

The resonance cross-section $\sigma_0(E_x)$ is made up of the cross-sections for the individual transitions as in the case of dipole interaction. We must simply replace $\Delta E_{mg}(m_1,m_j)$ in expression (41) with the energy differences $\Delta E_{e1,2}(m_1,m_j)$ which correspond to the quadrupole sub-levels. From expression (42), it may be seen that level splitting yields non-equidistant sub-levels. Hence, it follows that, even for unoriented and unpolarized neutrons, a small shift in the centre of mass of the resonance in the order of 1 µeV or less may occur. In addition, the resonance is broadened, by an order which may be evaluated using the expression eV_2Q_1/I . This broadening amounts at most to some tens of microelectronvolts. If such small shifts in neutron resonances with values of approximately 1 µeV could be measured, as mentioned in Ref. [52], it would be possible to determine also the quadrupole moments of nuclei in excited compound states. This would certainly be interesting, especially for fissile nuclei.

Conclusion

Research into neutron resonances has been going on since nuclear physics begun, and for that reason it is numbered amongst the traditional, classical areas of nuclear physics. Nevertheless, thanks to the constant improvement of neutron spectroscopy methods, new phenomena are being discovered in this area even today. On the basis of research using neutrons,

it has proved possible in recent years to penetrate deeper into the area of physics concerned with the characteristics of atomic nuclei themselves and their interaction with the environment.

The observation of hyperfine interaction effects in neutron resonances has opened up a new branch in the study of nuclear compound states formed during resonance neutron capture. In addition to those characteristics of these nuclear states which have been studied in depth already, such as energy, spin, parity and width, it became feasible about ten years ago to study the magnetic moments of nuclei. In recent years it has proved possible for the first time to measure the mean square radii of nuclei in compound states. On the basis of these data, our knowledge of the structure of highly-excited nuclear states has been significantly extended. For the heaviest nuclei, these states are fissile, with fairly large fluctuations in the fission probability from resonance to resonance. Naturally, the search for correlations between the mean square radii of resonance states and their fission probabilities is an interesting subject for research.

Detailed study of neutron resonance structure has uncovered connections between target nuclei and their surrounding medium. The influence of the vibrations of different lattices on Doppler broadening of neutron resonances and on temperature shift in neutron resonances, for example, has been observed experimentally. Effects of this type have proved significant for applications as well. Thus, for example, taking into account the influence of bonds in a solid body is essential for an accurate determination of nuclear constants for nuclear reactor calculations.

Research indicates that there are still a lot of new effects in the border region of nuclear physical and solid-state phenomena. Increasing the power of neutron sources will facilitate further research in this area.

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- BETHE, H.A., BACHER, R.F., Rev. Mod. Phys. <u>8</u> (1936) 82-230;
 BETHE, H.A., PLACZEK G., Phys. Rev. <u>51</u> (1937) 450-484;
 BETHE, H.A., Rev. Mod. Phys. <u>9</u> (1937) 69-244.
- [2] LAMB, W.E., Phys. Rev. <u>55</u> (1939) 190-197.
- [3] AKOPYAN, G.G., VAGOV, V.A., SEIDEL, K., et al., OIYaI report R3-11740, Dubna (1978); SEIDEL, K., MEISTER, A., PABST, D., PIKELNER, L.B., OIYaI report R3-11741, Dubna (1978); R3-11742, Dubna (1978); R3-80-135, Dubna (1980); MEISTER, A.J., PABST, D., PIKELNER, L.B., SEIDEL, K., Nucl. Phys. A362 (1981) 18-44.
- [4] SEIDEL, K., MEISTER, A., PABST, D., PIKELNER, L.B., Dokl. Akad. Nauk SSSR <u>256</u> (1981) 360-363.
- [5] SEIDEL, K., MEISTER, A., PABST, D., et al., Yad. Fiz. <u>34</u> (181) 1173-1180; OIYaI preprint R3-81-89, Dubna (1981).
- [6] MEISTER, A., PABST, D., PIKELNER, L.B., et al., Proc. IAEA Consultants Meeting on Uranium and Plutonium Isotope Resonance Parameters, Vienna (1981) INDC(NDS)-129/GS, 265; Preprint TU Dresden 05-17-81 (1981).
- [7] MEISTER, A., MITTAG, S., PABST, D., et al., Proc. Intern. Conf. Nuclear Data for Science and Technology, Antwerp (1982) 968, 970; Preprint TU Dresden 05-27-82 (1982).
- [8] SEIDEL, K., SEIFERT, A., SEELIGER, D., et al., Proc. 6th Conf. on Neutron Physics, <u>2</u> Kiev (1983) 379-383.
- [9] MITTAG, S., PABST, D., PIKELNER, L.B., et al., Nucl. Phys. <u>A435</u> (1985) 97, 109; OIYaI preprint R3-83-820, Dubna (1983).
- [10] SEIDEL, K., SEELIGER, D., IGNATOVICH, V.K., et al., Yad. Fiz. <u>42</u> (1985) 1040, 1049; OIYal preprint R3-85-17, Dubna (1985).
- [11] POUND, R.V., REBKA, G.A., Phys. Rev. Lett. 4 (1960) 337-341.
- [12] JOSEPHSON, B.D., Phys. Rev. Lett. 4 (1960) 341-344.
- [13] ALFIMENKOV, V.P., LASON, L., MAREEV, Yu.D., et al., Nucl. Phys. <u>A267</u> (1976) 172-180.
- [14] BECKURTS, K.H., BRUNHART, G., Phys. Rev. <u>C1</u> (1970) 726-734.
- [15] IGNATOVICH, V.K., OSTANEVICH, Yu.M., CHER, L., OIYal report R4-7296, Dubna (1973).
- [16] WERTHEIM, G.K., Mössbauer Effekt: Principles and Applications, N.Y., Acad. Press (1964).
- [17] SHENOY, G.K., WAGNER, F.E. (Eds), Mössbauer Isomer Shifts, Amsterdam, North Holland (1978).
- [18] ALFIMENKOV, B.P., PIKELNER, L.B., SHARAPOV, Eh.I., EhChAYa <u>11</u> (1980) 411-453.
- [19] FRANK, I.M., EhChAYa <u>2</u> (1972) 805-860; GOLIKOV, V.V., KOZLOV, Zh.A., KUL'KIN, L.K., et al., OIYaI report 3-5736 (1971).

- [20] SHABALIN, E.P., At. Ehnerg. <u>52</u> (1982) 92-100.
- [21] BREIT, G., WIGNER, E., Phys. Rev. <u>49</u> (1936) 519-531; HARVEY, J.A., HUGHES, D.J., et al., Phys. Rev. <u>99</u> (1955) 10-33.
- [22] TAKANO, H., ISHIGURO, Y., J. Nucl. Sci. and Technology 14 (1977) 627.
- [23] SHORE, F.J., SAILOR, V.L., Phys. Rev. <u>112</u> (1958) 191-202.
- [24] REICH, C.W., MOORE, M.S., Phys. Rev. <u>111</u> (1958) 929-933.
- [25] VOGT, E., Phys. Rev. <u>112</u> (1958) 929-933.
- [26] ADLER, D.B., ADLER, F.T., Trans. Amer. Nucl. Soc. <u>5</u> (1962) 53.
- [27] HARVEY, J.A., Experimental Neutron Resonance Spectroscopy, Oak Ridge, Tennessee, N.Y., London (1970) 379.
- [28] SOLBRIG Jr., A.W., Amer. J. Phys. <u>29</u> (1961) 257-261; Nucl. Sci. Eng. <u>10</u> (1961) 167-168.
- [29] BORN, M., Optik, Berlin (1933).
- [30] VISSCHER, W.M., Ann. Phys. (N.Y.) 9 (1960) 194-210.
- [31]. NELKIN, M.S., PARKS, D.E., Phys. Rev. 119 (1960) 1060-1068.
- [32] JACKSON, H.E., LYNN, J.E., Phys. Rev. <u>127</u> (1962) 461-486.
- [33] EGELSTAFF, P.A., SCHOFIELD, P., Nucl. Sci. Eng. <u>12</u> (1962) 260-270.
- [34] YOUNG, J.A., Nukleonik <u>12</u> (1969) 205-208.
- [35] BORGONOVI, G.M., HOUSTON, D.H., et al., Phys. Rev. <u>C1</u> (1970) 2054-2059.
- [36] LAJEUNESSE, C., MOORE, W.E., YEATER, M.L., Nucl. Sci. Eng. <u>47</u> (1972) 349-364.
- [37] BUTLAND, A.T.D., Ann. Nucl. Sci. Eng. <u>1</u> (1974) 575.
- [38] LYNN, J.R., RAE, E.R., J. Nucl. Energy 4 (1957) 418-444.
- [39] MOSSBAUER, R.L., Z. Physik. <u>151</u> (1958) 124-143.
- [40] ROWLANDS, J.L., Proc. IAEA Consultants Meeting on Uranium and Plutonium Isotope Resonance Parameters, Vienna (1981) INDC(NDS)-129/GS, 8.
- [41] SEELIGER, D., SEIDEL, K., HERMSDORF, D., et al., Forschungsbericht, TU Dresden (1984).
- [42] LETOKHOV, V.S., MINOGIN, V.G., Zh. Ehksp. Teor. Fiz. <u>69</u> (1975) 1569-1581.
- [43] LETOKHOV, V.S., MINOGIN, V.G., Zh. Ehksp. Teor. Fiz. 70 (1976) 794-804.
- [44] LETOKHOV, V.S., Phys. Rev. <u>A12</u> (1975) 1954-1965.
- [45] BOWMAN, C.D., SCHRACK, R.A., Phys. Rev. <u>C21</u> (1980) 58-64.

- [46] SIBIN, S., "Molecule vibrations and mean square amplitudes" (translated from English into Russian), Mir, Moscow (1971).
- [47] BELYANIN, V.S., "Thermophysical constants for uranium and tungsten hexafluorides", [in Russian], USSR Academy of Sciences, Moscow (1976).
- [48] MEISINGSETH, E., BRUNVOLL, J., CYVIN, S.J., Det. KGL Norske Videnskabers Selskabs Skrifters <u>7</u> (1964) 96.
- [49] BOYLE, E.J.F., BUNBURY, D.S.P., et al., Proc. Phys. Soc (Lond.) <u>76</u> (1960) 165-167.
- [50] PRUDNIKOV, A.P., BRYCHKOV, Yu.A., MARICHEV, O.I., "Integrals and series" [in Russian], Nauka, Moscow (1981).
- [51] BEREZIN, F.A., "The second quantization method" [in Russian], Nauka, Moscow (1965).
- [52] SHAPIRO, F.L., Research Applications of Nuclear Pulsed Systems, Vienna (1967) 176.
- [53] BAND, I.M., FOMICHEV, V.I., Atom. Data Nucl. Data Tables <u>23</u> (1970) 295-314.
- [54] HEILIG, K., STEUDEL, A., Atom. Data Nucl. Data Tables <u>14</u> (1974) 613-638.
- [55] BUNATYAN, G.G., Yad. Fiz. 29 (1979) 10-21; Yad. Fiz. 35 (1982) 16-26.
- [56] "Physical values tables", Reference Book [in Russian] (KIKOIN, I.K., Ed.), Atomizdat, Moscow (1976).