Multiphonon coherent scattering of neutrons in a naphthalene crystal

A. I. Kolesnikov, E. L. Bokhenkov, and E. F. Sheka

Institute of Solid State Physics, USSR Academy of Sciences

(Submitted 26 October 1982)
Zh. Eksp. Teor. Fiz. **84**, 2180–2193 (June 1983)

The temperature and angular dependences of single- and multiphonon inelastic incoherent neutron scattering (IINS) are considered. The partial cross sections and cross sections are calculated by solving the complete dynamic problem for a naphthalene crystal. Good qualitative agreement is observed between the total spectra and the results of IINS experiments at 5 and 80 K in the entire range of transfer of energy ε to the neutrons (to 1500 cm^{-1}) and at 296 K for $\varepsilon \geqslant 300$ cm^{-1}. A strong influence of multiphonon scattering at all temperatures is revealed at $\varepsilon \geqslant 300$ cm^{-1}. A difference between the angular dependences of the ratio of the useful signal to the background at low and high energy is demonstrated and may prove to be useful in neutron spectroscopy experiments. The spectra of the single-phonon IINS are separated and the anharmonicity effects in the density of the phonon states are analyzed.

PACS numbers: 61.12.Fy, 61.65. + d, 63.20.Dj

1. INTRODUCTION

Spectroscopy of inelastic incoherent scattering of neutrons (IINS) of low energy, as a method of investigating the dynamics of molecular crystal, has intensively progressed in the past few years. Owing to the very large cross section for incoherent scattering by hydrogen atoms and to the low mass of the latter, this method is particularly useful when applied to hydrocarbons. The list of investigated subjects is therefore growing rapidly: naphthalene,[1–4] benzene,[5] anthracene,[6] biphenyl,[7] hexamethylenetetramine,[8] polyethylene,[9] and others. By modern techniques one can obtain IINS spectra in a wide energy-transfer range (up to 3500 cm^{-1} with the high-flux reactor of the Laue and Langevin Institute[8,9]) and in a wide range of temperatures and scattering angles.

Despite this great success in obtaining various experimental results, there has been no comparable decrease in the difficulty of extracting information on the phonon spectrum of the crystal. The scattering spectrum, usually measured by the time-of-flight method, is the result of an integral convolution of the scattering cross section with the instrumental function of the apparatus, in the form

$$N(t,\ T,\ \varphi)=\sigma^{\mathrm{inc}}(T,\ \varphi,\ \varepsilon)\infty F(t,\ \varepsilon), \tag{1}$$

where σ^{inc} describes the total cross section for IINS as a function of the energy transferred to the neutrons given the temperature T and the scattering angle φ, $F(t,\varepsilon)$ is the instrumental function of the spectrometer, and t is the time of flight of the neutron over a fixed distance.[1] The sought quantity is the cross section σ_1, of the incoherent1) single-phonon process, since this function is most directly connected with the density $g(\omega)$ [more accurately, with the density $G^{\mathrm{H}}(\omega)$ weighted over the squares of the zero-point oscillations of the hydrogen atoms] of the phonon states of the crystal.[10–12]

Thus, in the quantitative interpretation of the IINS spectra we encounter two problems: 1) separation, from the experimental spectrum $N(t)$, the part $N^{(1)}(t)$ due only to single-phonon process, and 2) establishment of the connection between σ_1 and the spectrum $N^{(1)}(t)$.

The first problem pertains to the general problem of analyzing the structure of the phonon wings that accompany zero-phonon lines in the emission, absorption, or scattering spectra of various particles (photons, γ-ray or x-ray quanta, electrons, neutrons, etc.). Phonon expansion, as a method of solving this problem, was initially formulated in fact for IINS,[11,13] but was not developed further there. At the same time, it was successfully used to obtain information from phonon wings in optical spectra.[14,15] As for the experimental IINS spectra, it is usually assumed that they are single-phonon, although the need of taking multiphonon process has been occasionally mentioned.

Definite progress was made in the solution of the second problem by using the method of the direct spectral problem.[1] In this method, the cross sections σ_1 and the spectra $N^{(1)}(t)$ of single-phonon IINS can be calculated on the basis of the dynamic model. By comparing these spectra with the experimental ones one can assess the degree to which the single-phonon approximation is sufficient and how well the dynamic problem was solved.

The object investigated in greatest detail by inelastic neutron scattering method is the naphthalene crystal.[1–4,6,16–22] It was shown that at a temperature 5 K the calculated spectra of single-phonon coherent and incoherent neutron scattering agree with the experimental one with accuracy not worse that 10–15% for the band positions and 20–30% for the intensities. With rising temperature, the experimental IINS spectra change noticeably, and their agreement with the calculated single-phonon harmonic spectra becomes worse. The phonon anharmonicity and multiphonon scattering should be regarded as the main causes of their variation. As shown recently,[22] the main anharmonic effect in the phonon spectrum of the naphthatlene crystal, even at high temperature, is the strain due to the thermal expansion of the crystal, and can be taken into account in the quasi-harmonic approximation.

The satisfactory description of the temperature-in-

0038-5646/83/061270-09$04.00

duced frequency shifts notwithstanding, the spectra $N^{(1)}$ of the single-phonon IINS still agree poorly with the experimental ones.[2] This disparity is most noticeable in the high-frequency region, where the experimental spectra show an appreciable growth of the integral scattering intensity with rising temperature. This behavior of the spectra raises the question of allowance for multiphonon scattering processes.

In the present paper, multiphonon scattering of neutrons (MPNS) is considered within the framework of the direct spectral problem[1] for the naphthalene crystal, using the complete 108-mode phonon spectrum calculated in the entire energy range (0–3100 cm^{-1}) of their existence.[16] The problem was solved for the first time on the basis of an exact expression for the MPNS cross section. The hitherto available calculations of the MPNS spectra (e.g., Ref. 23) were approximate and used simplified models of the phonon spectrum.

2. MULTIPHONON SCATTERING CROSS SECTION

For MPNS calculations it is convenient to use the phonon expansion of the incoherent-scattering cross section, which takes in the harmonic approximation the form (see, e.g., Ref. 24)

$$\sigma=\frac{d^2\sigma}{d\Omega\, d\varepsilon}=\frac{k}{2\pi\hbar k_0}\exp\left(-\frac{\varepsilon}{2k_\mathrm{B}T}\right)$$

$$\times\sum_{\mathrm{H}}(b_\mathrm{H}^{\mathrm{inc}})^2F_\mathrm{H}\int_{-\infty}^{\infty}d\tau\exp\left(-\frac{i\varepsilon\tau}{\hbar}\right)$$

$$\times\exp\left\{\frac{1}{N_c}\sum_{j\mathbf{q}}\frac{\hbar}{2M_\mathrm{H}\omega_{j\mathbf{q}}}\frac{\exp(-\hbar\omega_{j\mathbf{q}}/2k_\mathrm{B}T)}{1-\exp(-\hbar\omega_{j\mathbf{q}}/k_\mathrm{B}T)}|\mathbf{Q}\mathbf{e}_{j\mathbf{q}}^{\mathrm{H}}|^2\right.$$

$$\left.\times[\exp(-i\omega_{j\mathbf{q}}\tau)+\exp(i\omega_{j\mathbf{q}}\tau)]\right\} \qquad (2)$$

where F_H is the Debye–Waller (DW) factor for the hydrogen atom H,

$$F_\mathrm{H}=\exp\left[-\frac{1}{N_c}\sum_{j\mathbf{q}}\frac{\hbar|\mathbf{Q}\mathbf{e}_{j\mathbf{q}}^{\mathrm{H}}|^2}{2M_\mathrm{H}\omega_{j\mathbf{q}}}\operatorname{cth}\frac{\hbar\omega_{j\mathbf{q}}}{2k_\mathrm{B}T}\right]. \qquad (3)$$

Here N_c is the number of unit cells in the crystal, $\mathbf{Q}=\mathbf{k}-\mathbf{k}_0$ is the change of the neutron momentum, while $\omega_{j\mathbf{q}}$ and $\mathbf{e}_{j\mathbf{q}}^{\mathrm{H}}$ are the frequency and polarization vector of the jth phonon mode with wave vector $\mathbf{q}$ for the H atom. The remaining notation is standard.[24]

The mean squared displacement of the H atom is written in the form[25]

$$\langle(\mathbf{u}^\mathrm{H})^2\rangle=\sum_{j\mathbf{q}}\langle(\mathbf{u}_{j\mathbf{q}}^{\mathrm{H}})^2\rangle$$

$$=\frac{\hbar}{2N_cM_\mathrm{H}}\sum_{j\mathbf{q}}\mathbf{e}_{j\mathbf{q}}^{\mathrm{H}}(\mathbf{e}_{j\mathbf{q}}^{\mathrm{H}})^{*}\frac{1}{\omega_{j\mathbf{q}}}\operatorname{cth}\frac{\hbar\omega_{j\mathbf{q}}}{2k_\mathrm{B}T}=u_\mathrm{H}^2, \qquad (4)$$

as a result of which expression (3) can be reduced to the form

$$F_\mathrm{H}=\exp\left(-Q^2\sum_{j\mathbf{q}}\langle(\mathbf{u}_{j\mathbf{q}}^{\mathrm{H}})^2\rangle\cos^2\eta_{j\mathbf{q}}^{\mathrm{H}}\right), \qquad (3a)$$

where $\eta_{j\mathbf{q}}^{\mathrm{H}}$ is the angle between $\mathbf{Q}$ and the vector of displacement of the atom under the influence of the phonon ($j\mathbf{q}$).

Expanding $\exp\{\ldots\}$ in (2) in a series, integrating the resultant expression, and replacing the sum over $\mathbf{q}$ by an integral over reciprocal space

$$\sum_{j\mathbf{q}}\to\sum_{j}\frac{N_cv}{(2\pi)^3}\int d\mathbf{q},$$

where v is the volume of the unit cell, we obtain the doubly differential cross section represented in the form of a sum of the scattering cross sections: elastic σ_0 and inelastic—single-phonon σ_1 and a series of multiphonon σ_n:

$$\sigma_0=\sum_{\mathrm{H}}(b_\mathrm{H}^{\mathrm{inc}})^2F_\mathrm{H}\delta(\varepsilon), \qquad (5)$$

$$\sigma_1=\frac{k}{k_0}\sum_{\mathrm{H}}(b_\mathrm{H}^{\mathrm{inc}})^2F_\mathrm{H}$$

$$\times\sum_{j}\int d\mathbf{q}B[(\mathfrak{N}+1)\delta(\varepsilon-\hbar\omega_{j\mathbf{q}})+\mathfrak{N}\delta(\varepsilon+\hbar\omega_{j\mathbf{q}})], \qquad (6)$$

$$\sigma_2=\frac{k}{k_0}\sum_{\mathrm{H}}(b_\mathrm{H}^{\mathrm{inc}})^2F_\mathrm{H}$$

$$\times\sum_{j_1j_2}\int d\mathbf{q}_1\, d\mathbf{q}_2B_1B_2\left\{\frac{1}{2}(\mathfrak{N}_1+1)(\mathfrak{N}_2+1)\delta[\varepsilon-\hbar(\omega_1+\omega_2)]\right.$$

$$\left.+(\mathfrak{N}_1+1)\mathfrak{N}_2\delta[\varepsilon-\hbar(\omega_1-\omega_2)]+\frac{1}{2}\mathfrak{N}_1\mathfrak{N}_2\delta[\varepsilon+\hbar(\omega_1+\omega_2)]\right\}, \qquad (7)$$

$$\sigma_3=\frac{k}{k_0}\sum_{\mathrm{H}}(b_\mathrm{H}^{\mathrm{inc}})^2F_\mathrm{H}$$

$$\times\sum_{j_1j_2j_3}\int d\mathbf{q}_1\, d\mathbf{q}_2\, d\mathbf{q}_3B_1B_2B_3\left\{\frac{1}{6}(\mathfrak{N}_1+1)(\mathfrak{N}_2+1)(\mathfrak{N}_3+1)\cdot\right.$$

$$\times\delta[\varepsilon-\hbar(\omega_1+\omega_2+\omega_3)]$$

$$+\frac{1}{2}(\mathfrak{N}_1+1)(\mathfrak{N}_2+1)\mathfrak{N}_3\delta[\varepsilon-\hbar(\omega_1+\omega_2-\omega_3)]$$

$$+\frac{1}{2}(\mathfrak{N}_1+1)\mathfrak{N}_2\mathfrak{N}_3\delta[\varepsilon-\hbar(\omega_1-\omega_2-\omega_3)]$$

$$\left.+\frac{1}{6}\mathfrak{N}_1\mathfrak{N}_2\mathfrak{N}_3\,\delta[\varepsilon+\hbar(\omega_1+\omega_2+\omega_3)]\right\} \qquad (8)$$

etc., where

$$B_i=\frac{v}{(2\pi)^3}\frac{\hbar Q^2|\mathbf{e}_{j_i\mathbf{q}_i}^{\mathrm{H}}|^2\cos^2\eta_{j_i\mathbf{q}_i}^{\mathrm{H}}}{2M_\mathrm{H}\omega_i},$$

$$\mathfrak{N}_i=1/[\exp(\hbar\omega_i/k_\mathrm{B}T)-1], \qquad \omega_i=\omega_{j_i\mathbf{q}_i}. \qquad (9)$$

The $\mp$ signs in the δ functions preceding ω_i correspond to processes with phonon creation and annihilation.

3. CALCULATION OF THE IINS SPECTRA

The results that follow were calculated by the following procedure:

Lattice dynamics Scattering cross section Scattering spectrum

$$\omega_{j\mathbf{q}},\ \mathbf{e}_{j\mathbf{q}}^{\mathrm{H}} \longrightarrow \sigma_n \longrightarrow N^{(n)}(t)$$

The frequencies $\omega_{j\mathbf{q}}$ of the 108 phonon modes of the naphthalene crystal and the polarization vectors $\mathbf{e}_{j\mathbf{q}}^{\mathrm{H}}$ were obtained by solving the harmonic (at 4.7 K) and quasi-harmonic (at 293 K) dynamic problems at 7600 points of the Brillouin zone, using the BENZ[2)] program.[25] We used the "6-exp" interatomic-interaction potential with the Williams parameters[26] and the structure data for 4.7 K (see Ref. 17) and 296 K (Ref. 27).

The scattering cross sections σ_n for $n = 1, 2,$ and 3 were calculated from Eqs. (6)–(8) as applied to polycrystals. The calculation becomes more complicated with increasing n and at $n \geqslant 4$ it takes too much computer time to be realistic. The calculations for such n were therefore made in the Sjölander approximation.[28] This approximation is based on the fact that by convoluting n times a function of arbitrary form, we obtain for the energy at large n a Gaussian (central limit theorem of probability theory) with a mean value E and a variance Δ, which are n times larger than the mean value and variance of the energy for the initial function.

The cross section for MPNS in the Sjölander approximation is written in the form

$$\sigma_{\text{Sjöl}} = \frac{k}{k_0}\sum_{\mathrm{H}} (b_{\mathrm{H}}^{\mathrm{inc}})^2 F_{\mathrm{H}} \exp(E_{\mathrm{H}}\omega/\Delta_{\mathrm{H}}^2)\frac{1}{\Delta_{\mathrm{H}}}\Phi(z_{\mathrm{H}}, x_{\mathrm{H}}),$$

$$\Phi(z_{\mathrm{H}}, x_{\mathrm{H}}) = \sum_{n=n_0}^{\infty}[z_{\mathrm{H}}^{n}/(2\pi n)^{1/2} n!]\exp(-x_{\mathrm{H}}^2/2n),$$

$$z_{\mathrm{H}} = \frac{1}{3}\exp(-E_{\mathrm{H}}^2/2\Delta_{\mathrm{H}}^2)\int_0^{\infty}\frac{\hbar Q^2}{2M_{\mathrm{H}}\omega}G^{\mathrm{H}}(\omega)[2\mathfrak{N}(\omega)+1]\,d\omega,$$

$$x_{\mathrm{H}} = \omega/\Delta_{\mathrm{H}}, \tag{10}$$

$$E_{\mathrm{H}} = (\langle\hbar\omega\rangle)_{\mathrm{H}} = \int_0^{\infty} G^{\mathrm{H}}(\omega)\,d\omega \Big/ \int_0^{\infty}\frac{G_{\mathrm{H}}(\omega)}{\omega}[2\mathfrak{N}(\omega)+1]\,d\omega,$$

$$\Delta_{\mathrm{H}}^2 = [\langle(\hbar\omega)^2\rangle]_{\mathrm{H}} - E_{\mathrm{H}}^2$$

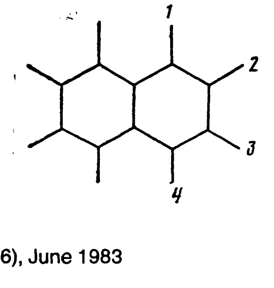
$$= \int_0^{\infty} G^{\mathrm{H}}(\omega)\,\omega[2\mathfrak{N}(\omega)+1]\,d\omega \Big/ \int_0^{\infty}\frac{G^{\mathrm{H}}(\omega)}{\omega}[2\mathfrak{N}(\omega)+1]\,d\omega - E_{\mathrm{H}}^2.$$

The values of E_{H} and Δ_{H} for the naphthalene crystal at 78 and 293 K are listed in Table I. It can be seen that with rising temperature the mean value and variance of the energy, which determine the MPNS, vary very strongly, with $\Delta_{\mathrm{H}} > E_{\mathrm{H}}$ everywhere. It follows from the last circumstance that the MPNS cross section in the Sjölander approximation is a rather smooth function of energy. Therefore, as will be shown below, the use of this approximation turns out to be most justified when processes are described starting with a sufficiently large phonon content. For small n_0, its use leads to incorrect results.

A serious problem in the calculation of the scattering cross sections is the calculation of the DW factors for inelas-

TABLE I. Temperature dependence of the mean squared displacements of the hydrogen atoms [in Å^2] and of the mean values and variances of the energy [cm^{-1}], which determine the MPNS in the Sjölander approximation, for a naphthalene crystal.

Number of molecules in unit cell	Number of atoms in molecule	T, K						
		4.7	78			293		
		u_{H}^2	u_{H}^2	E_{H}	Δ_{H}	u_{H}^2	E_{H}	Δ_{H}
1	1	0.0642	0.0969	516	752	0.2991	168	496
	2	0.0696	0.1083	462	722	0.3500	143	459
	3	0.0695	0.1082	463	723	0.3490	144	460
	4	0.0644	0.0971	515	751	0.2987	168	496
2	1	0.0641	0.0960	521	754	0.2944	170	499
	2	0.0695	0.1079	464	723	0.3477	144	461
	3	0.0694	0.1078	464	724	0.3467	145	461
	4	0.0642	0.0962	520	753	0.2940	170	500



tic processes in polycrystalline samples. Expressions (5)–(8) are valid for scattering from a single crystal. For scattering from polycrystalline samples it is necessary to average over the sample orientations. It is difficult to solve this problem in the general case, and the isotropic approximation is customarily used, in which the DW factor does not depend on the orientation of the sample and is equal, for any n-phonon process,

$$F_{\mathrm{H}}^{\mathrm{isotr}} = \exp(-{}^{1}/{}_{3}Q^{2}u_{\mathrm{H}}^{2}). \tag{11}$$

Therefore in this approximation the averaging of the quantity

$$\prod_{i=1}^{n} \cos^{2} \eta^{\mathrm{H}}_{\lambda_i q_i}$$

which depends on the sample orientation, leads to the appearance of a coefficient $(1/3)^n$ in σ_n. As applied to the naphthalene crystal, the isotropic approximation can be regarded as good in view of the low anisotropy of the ellipsoid of the thermal vibrations of the atoms. The mean squared displacements of the hydrogen atoms were calculated in accord with (4) over the entire phonon spectrum. The obtained values of u_{H}^{2} are listed in Table I.

The results that follow were compared with the IINS spectra of a naphtalene crystal, obtained with the KDSOG-1 spectrometer.[1] The MPNS spectra were therefore calculated with account taken of the instrumental function of just this instrument. This function falls off practically to zero at energy transfers $\varepsilon \geqslant 1500\ \mathrm{cm}^{-1}$ (Ref. 1). Consequently the MPNS spectra were calculated in a region bounded by this value on the high-energy side. The calculations reported were made, unless otherwise stipulated, in energy steps of 1 cm^{-1}. Account was taken of all the possible phonon creation and annihilation processes.

The results have shown that the IINS spectra depend on temperature and on angle. It is convenient to consider these dependences separately.

4. TEMPERATURE DEPENDENCE OF THE SCATTERING SPECTRA

The temperature dependence of the MPNS spectra was considered for scattering through an angle 90°. The cross section for single-phonon IINS from a naphthalene polycrystal at three temperatures, calculated in accord with (6), is shown in Fig. 1. The spiked structure is due to the structure of the density of states of the phonon spectrum of the crystal.[16] With increasing temperature the cross section increases in the region to 150 cm^{-1} (at 293 K the cross section in this region is decreased in Fig. 2 by a factor 5) and decreases for $\varepsilon > 300\ \mathrm{cm}^{-1}$, since it is acted upon, according to (6) by two opposing factors. The first is that the phonon population (mostly of low frequency) increases with temperature, and the second, the Debye–Waller factor, decreases exponentially, since the atom displacements increase (see Table I). At energies $\sim 200\ \mathrm{cm}^{-1}$ these competing factors cancel each other, and the cross section remains constant from helium to room temperature.

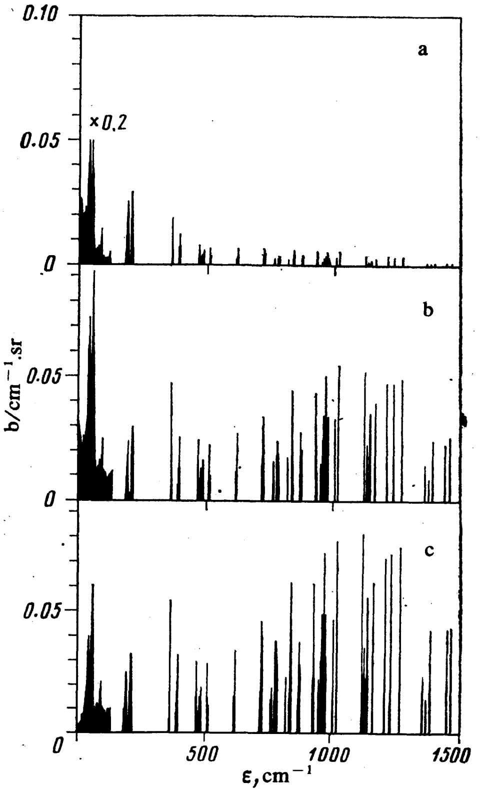


FIG. 1. Calculated cross sections of single-phonon IINS from a naphthalene crystal: a—293 K; b—78 K; c—4.7 K. Scattering angle 90°.

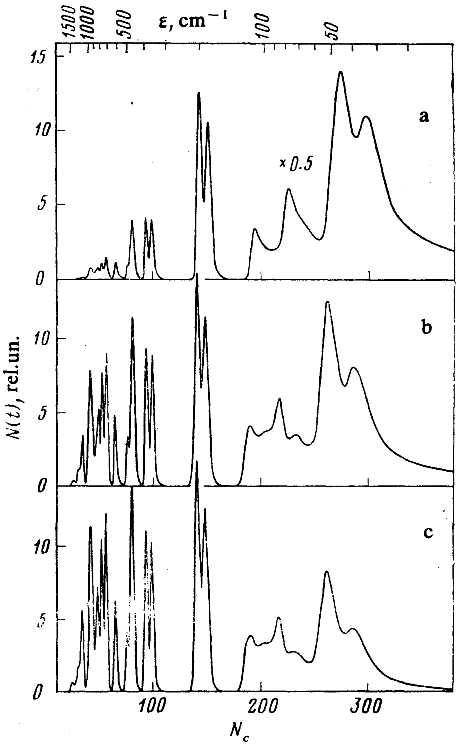


FIG. 2. Calculated spectra of single-phonon IINS: a—293 K, b—78 K, c—4.7 K; scattering angle 90°; N_c is the number of the time-analyzer channel (64 μsec); $N(t)$ is the intensity of the scattered neutrons.

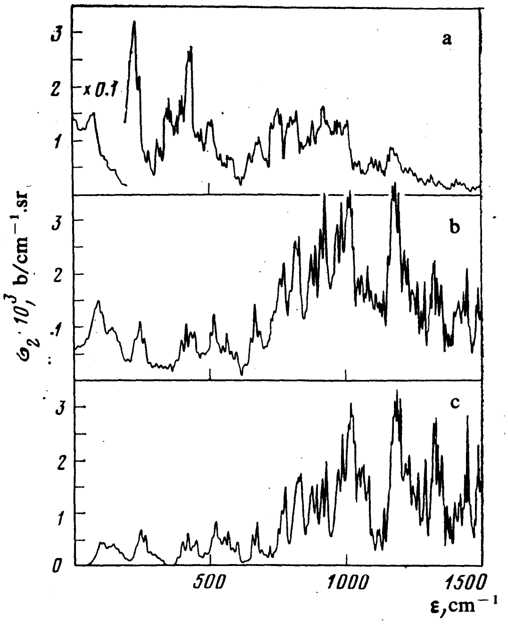


FIG. 3. Calculated two-phonon IINS spectra: a—293 K, b—78 K, c—4.7 K; scattering angle 90°.

The single-phonon IINS spectra are shown in Fig. 2. It can be seen from the figure that with increasing temperature the integrated scattering intensity increases and becomes redistributed in favor of the low-frequency spectrum.

The cross sections for two-phonon IINS, calculated in accord with (7), are shown in Fig. 3. Their structure differs radically from the single-phonon scattering cross section: the number of peaks is considerably larger, they are broader, and the spectrum occupies a continuous energy band. The two-phonon IINS spectra are shown in Figs. 4, a–c. It can be seen from the figure that in the 500–1500 cm^{-1} region the contribution of the two-phonon scattering relative to the maximum intensity amounts to 20–30% of that of the single-phonon scattering at the temperatures 4.7 and 78 K, and even exceeds it at 293 K.

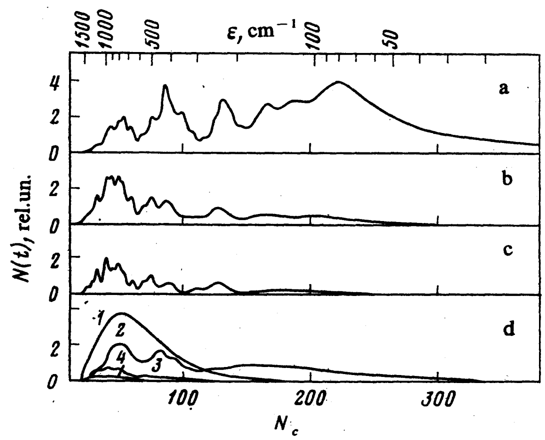


FIG. 4. Calculated spectra of multiphonon IINS through 90°: a,b,c—two-phonon spectra at 293, 78, and 4.7 K; d—multiphonon spectra: 1—scattering spectra with n from 4 to 15; 2,3,4—three-phonon spectra at $T = 293$, 78, and 4.7 K.

The three-phonon IINS cross sections were calculated in accord with (8). To shorten the computer time, energy steps of 25 cm^{-1} were used. Control calculations with 1 cm^{-1} steps have shown that the results are accurate enough. The three-phonon IINS spectra at different temperatures are shown in Fig. 4d (curves 2, 3, and 4). The intensity of the three-phonon scattering at 4.7 K is negligibly small. At 78 K, relative to the intensity maximum, the three-phonon scattering in the high-energy region is $\sim 10\%$ of the single-phonon scattering, and the spectrum is practically without structure. At 293 K the three-phonon scattering is comparable with the two-phonon scattering in the region of the internal modes, and is small in the region of the external ones.

The computational difficulties that increase with increasing n made an exact calculation of the scattering cross sections at $n \geqslant 4$ impossible; these cross sections were therefore calculated in the Sjölander approximation (10). It turned out that at 4.7 and 78 K the contribution from these multiphonon processes is negligibly small. The MPNS spectrum at 293 K is shown in Fig. 4d (curve 1). As seen from the figure, its intensity is quite large and is comparable in order of magnitude with the sum of the two- and three-phonon spectra. The MPNS cross sections for the processes with $n \geqslant 16$ have an amplitude less than 1% of the single-phonon cross section.

The end result of the calculations are the spectra of IINS from a naphthalene crystal at various temperatures, shown in Fig. 5 and constituting the sum of the single-phonon and multiphonon spectra. The darkened regions in this figure show the summary spectra of the MPNS with

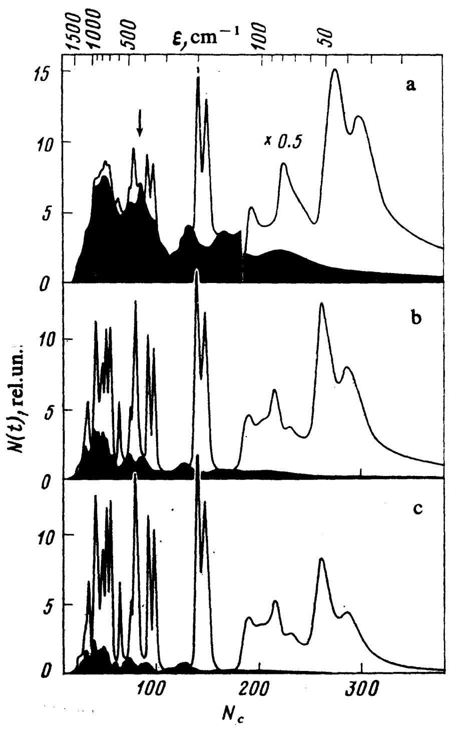


FIG. 5. Calculated IINS spectra with allowance for the single-phonon and all the multiphonon processes: a—293 K, b—78 K, c—4.7 K. Scattering angle 90°. Blackened regions—MPNS spectra.

$n \geqslant 2$. It can be seen from the figure that at 4.7 K the MPNS has low intensity, so that the summary spectrum is in practice single-phonon. The same conclusion can be drawn also for the low-frequency part of the spectrum at 78 K. At large energy transfers, however, the MPNS contribution is comparable with the single-phonon one. At 293 K the MPNS predominates in this region and makes a noticeable contribution also to the low-frequency spectrum. As can be seen from Fig. 5 the MPNS spectrum in the energy-transfer region up to 300 cm^{-1} has no distinct structure and constitutes in the summary scattering spectrum only a background base for the single-phonon, remaining everywhere smaller in intensity. In the region $\varepsilon \gtrsim 400\ \text{cm}^{-1}$, a structure is observed in the MPNS spectrum, in the form of peaks of width comparable with the widths of the peaks in the single-phonon scattering spectrum. The position of one of such peaks, comparable in intensity with the single-phonon ones, is marked by an arrow in Fig. 5.

5. ANGULAR DEPENDENCE OF THE IINS SPECTRA

The angular dependence of the cross sections for n-phonon scattering are determined by a factor that is proportional to Q^{2n} and by the isotropic DW factor (11) which does not depend on n. Naturally, the scattering cross sections, and hence also the scattering spectra, will vary differently at different temperatures as functions of the angle (or of Q^2). For the temperatures 4.7 and 78 K the angular dependence of the total spectrum is determined mainly by the angular dependence of the single-phonon scattering spectrum. At 293 K, as follows from the foregoing, we cannot confine ourselves to such a dependence, and account must be taken of the angular dependence of the MPNS intensity.

Figure 6 shows the angular dependences of the total and single-phonon IINS spectra at 293 K. It can be seen from the figure that the scattering spectrum varies differently at energies ε smaller and larger than 300 cm^{-1}. In the low-frequency region of the spectrum the angular dependence is determined by the changes of the single-phonon spectrum. In this energy region, the Q^2 are small, so that the DW factor is close to unity, therefore the change of the spectrum intensity is determined by the pre-exponential factor Q^2 [see Eqs. (6) and (9)]; an increase of Q^2 on going from a scattering angle 30° to 150° increases the intensity by almost five times.

In the region $\varepsilon > 400\ \text{cm}^{-1}$, the values of Q^2 are already comparable with $1/u_{\text{H}}^2$, so that the increase of the intensity in the single-phonon spectrum, due to the increase of Q^2, is overlapped by the action of the DW factor, leading to a decrease of the spectrum amplitude. The MPNS intensity increases in this case, since the increase of the factor Q^{2n} in expressions (7)–(9) at $n \geqslant 2$ prevails over the exponential decrease of the DW factor. Because of the opposite signs of the intensity changes of the single- and multiphonon spectra, the intensity of the total spectrum at $\varepsilon > 300\ \text{cm}^{-1}$ changes by not more than a factor of two in the considered angle interval.

From the angular dependence of the IINS spectra shown in Fig. 6 follows an important conclusion concerning the comparison of the experimental and calculated spectra in the case when the former are the sum of the spectra for scattering through different angles. The best situation in this case will be one at which the calculated spectrum is also the sum over the angles. The calculated and experimental spectra of the IINS from a naphthalene crystal at 80 K were compared in this manner.[1] If, however, MPNS must be considered, the calculations become very cumbersome and consume much time. A good approximation in this case is comparison of the calculated spectrum of the angle 90° with the total experimental spectrum measured for a set of angles consisting of pairs symmetric about 90° (e.g., 150 and 30°, 110 and 70°, etc.). The intensity of the calculated spectrum should be multiplied by the number of angles from the set. The equality of the doubled cross section at 90° and the sum of the cross sections for the symmetric angles for the single-phonon spectrum follows from expressions (6) and (9) for $F_{\text{H}} \sim 1$. Inasmuch as the single-phonon spectrum predominates in the low frequency region of the total spectrum, replacement of the sum of paired spectra by double the spectrum at 90° seems accurate enough. The validity of this conclusion for the IINS spectra of napthalene at 293 K was verified in the present paper by direct calculation.

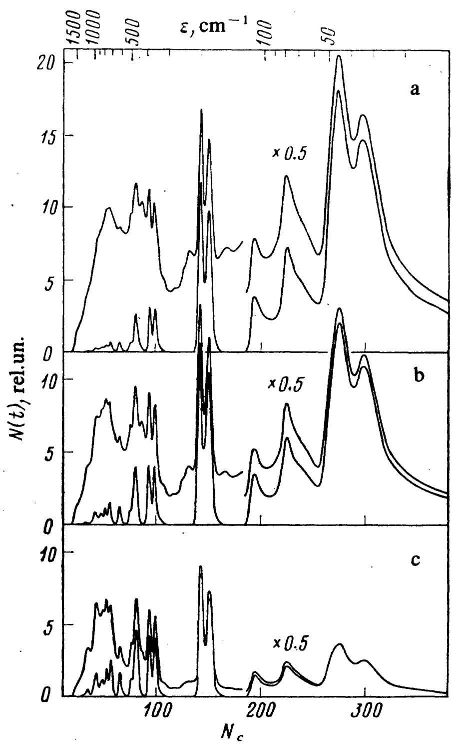


FIG. 6. Calculated IINS spectra at $T = 293$ K for different scattering angles: a—150°, b—90°, c—30°. Lower curves—single-phonon spectra, upper—total spectra.

6. COMPARISON OF CALCULATED AND EXPERIMENTAL DATA

The IINS spectra of a naphthalene crystal were measured by us earlier by the time-of-flight method with a KDSOG-1 inverse-geometry spectrometer on the IBR-1 reactor in the neutron-physics laboratory of JINR at temperatures 5 (Ref. 4), 80, and 296 K (Ref. 1). The total trans-

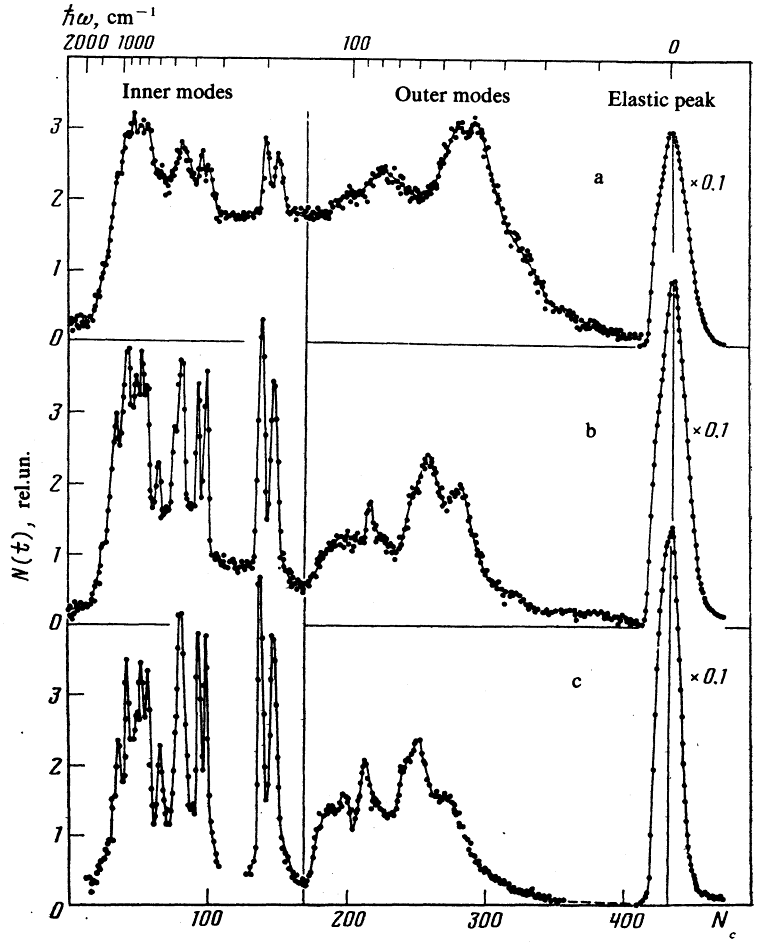


FIG. 7. Experimental IINS spectra of naphthalene crystal: a—296 K, b— 80 K, c—5 K.

mission of neutrons by the sample was 80%. The spectra were recorded at scattering angles 50, 70, 110, 130, and 150° at 80 and 296 K and at angles 30, 50, 70, 90, 110, 130, and 150° at 5 K. To improve the statistics, it is customary to sum the spectra measured at different scattering angles. Such summary scattering spectra are shown in Fig. 7. The spectra were corrected for the background from the cryostat and normalized to equal sample mass and equal measurement time. In accordance with the foregoing, they can be described as a sum of seven 90°-scattering spectra at 5 K and a sum of four 90°-spectra and one 150°-spectrum for 80 and 296 K. Since scattering through 90° predominates in the experimental spectra, we shall compare them with the calculated spectra for 90°.

The calculated MPNS spectra shown in Fig. 5 were obtained for single scattering of the neutrons in the sample. This raises the natural question: what is the fraction of the multiple scattering under the considered experimental conditions? No such calculations were performed for crystals with a complicated atomic cell structure. We have calculated for the first time the spectrum of single-phonon binary scattering in the direct spectral problem, using the method proposed in Ref. 29 to calculate the scattering cross section, for a naphthalene polycrystal with the geometric dimensions described in Ref. 4 (transmission 80%, scattering angle 90°). The intensity of the spectrum at $T = 5$ K is negligibly small in the low-frequency region and reaches ~1% of the intensity of single scattering in the high-frequency region. With increasing temperature, the intensity of double single-phonon scattering increases by approximately three times because of the growth of the phonon states. The question remains of the value of the double MPNS. Owing to the different power-law dependences of the individual MPNS components on Q^{2n}, such a calculation is very complicated. In the subsequent comparison of the calculated and experimental data multiple scattering was not taken into account.

From a comparison of the experimental and calculated IINS spectra (Figs. 5 and 7) it can be seen that at 5 K the total calculated scattering spectrum accounts sufficiently well for the details of the structure and for the intensity distribution observed in experiment. As noted also earlier,[1,4] the IINS spectrum at this temperature is practically single-phonon, and this causes the clearly pronounced structure both in the low- and in the high-frequency region.

When the temperature is raised to 80 K, the changes that take place in the experimental spectrum can be easily tracked also in the calculated one. The total intensity and the background intensity increase in the energy region 100 cm^{-1} and higher; as seen from Fig. 5, this is apparently due to MPNS.

At 296 K, the agreement between the experimental and calculated data is noticeably worse. The calculated spectrum

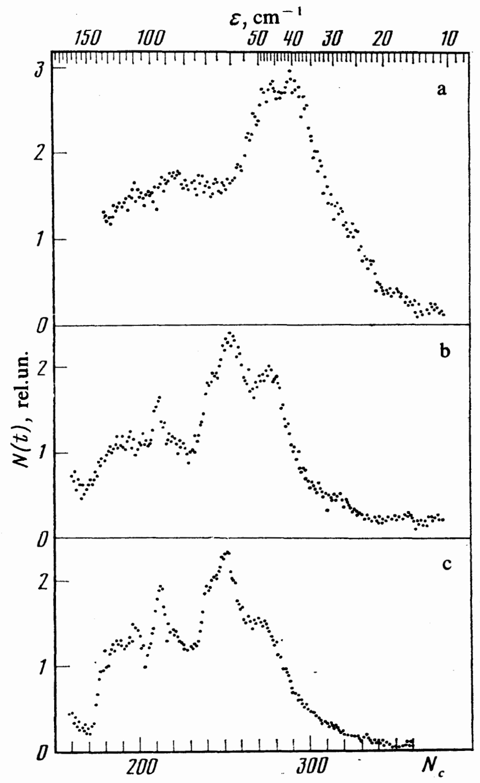


FIG. 8. Single-phonon IINS spectrum obtained from the experimental one by subtracting the MPNS spectrum: a—296 K, b—80 K, c—5 K.

agrees well with the structure of the experimental spectrum in the region of high energy transfers ($\varepsilon \geqslant 300\ \text{cm}^{-1}$), confirming the assumption made earlier[1] that MPNS plays an important role in this region. However, whereas the scattering intensity in the experimental spectrum is approximately the same at all energies, in the calculated spectrum the low-frequency region is twice as intense.

Analysis of the temperature and angular dependences of the calculation results has made it possible to separate in the low-frequency region from the total experimental data the spectra of the single-phonon IINS, as the differences between the experimental and approximating MPNS spectra (see Fig. 8). As shown earlier,[1] the structure of the single-phonon IINS obtained with the KDSOG-1 inverse-geometry spectrometer accounts well in the low-frequency region for the structure (namely, for the position of the singularities) of the density of the phonon states of the crystal. As a result, Fig. 8 shows the change of this structure when the temperature is raised, a change due to the phonon anharmonicity. When the temperature is increased from 5 to 80 K the scattering spectrum hardly changes structure and only shifts towards low frequencies. This behavior is typical of quasi-harmonic phonons, as can be seen from a comparison of spectra *b* or *c* with spectrum *a* in Fig. 2. It corresponds to a uniform ($\Delta\omega/\omega \approx \text{const}$) softening of the phonon frequencies, due to thermal expansion of the crystal.[22] When the temperature is raised to 296 K the spectrum not only continues to soften but is also noticeably restructured. This restructuring reveals a nonuniform variation of the phonon frequencies over the spectrum, as a result of the intrinsically anharmonic shifts.[22] In contrast to the investigation of temperature effects in individual phonon modes in coherent neutron scattering, analysis of the temperature dependence of the spectra of the single-phonon IINS makes it possible to establish the limits of applicability of the quasi-harmonic description and the role of the intrinsic anharmonicity in the total phonon spectrum of the crystal.

Noticeable anharmonicity of the naphthalene-crystal phonons can be the cause of the indicated disparity in the distribution of the intensity in the calculated and experimental IINS spectra at high temperature, because no account was taken in the calculations of the corrections to the DW factor and to the factor $\langle |\mathbf{Q}\cdot\mathbf{u}_{\mathrm{H}}|^{2n}\rangle$.

7. CONCLUSION

So detailed a study of the processes of multiphonon and multiple scattering turned out to be possible for a naphthalene crystal because it was recently the principal object of an extensive program of experimental and theoretical investigations of the dynamic properties of molecular crystals. As in the preceding cases dealing with the development of methods of phonon-spectrum calculations,[16] detailed neutron-spectroscopy research,[1,4,17] and others, the results obtained for this crystal in the present paper can be generalized and lead to a number of important practical (from the point of view of performing experiments and processing their results) and physical conclusions, which can be applied to a large class of crystals without the need for complicated and time consuming computations.

It follows from an analysis of the temperature dependence that at temperatures comparable with or lower than the Debye temperatures ($T_D \sim 100$ K for naphthalene), the IINS spectra are with good degree of accuracy single-phonon up to large ($\sim 700\ \text{cm}^{-1}$) values of the transferred energies. Multiphoton scattering is assuming a noticeable role at $T > T_D$, and increases rapidly at high frequencies, becoming predominant there at $T \sim 3T_D$.

On the basis of this conclusion it becomes possible to determine the MPNS spectra also for crystals whose dynamics has not been sufficiently well investigated for a detailed theoretical analysis analogous to the one presented above. If we bear it in mind that the low-temperature IINS spectrum is single-phonon it is possible, separating the "experimentally weighted density of phonon states" (Ref. 4), to calculate the MPNS spectrum at any temperature. When a similar procedure is used it becomes unnecessary to know exactly the instrumental function of the spectrometer. In the analysis of the temperature of the MPNS, only the anharmonicity of the phonon will not be taken into account.

In conclusion, the authors consider it their pleasant duty to thank I. Natkaniec, I. P. Sadikov, and A. A. Chernyshev for helpful discussions in a discussion of the results.

---

1) The superscript "inc" will hereafter be omitted throughout.

2) The authors take the opportunity to thank Dr. R. Righini for placing the BENZ program at their disposal.

[1] E. L. Bokhenkov, I. Natkaniec, and E. F. Sheka, Zh. Eksp. Teor. Fiz. **70**, 1027 (1976) [Sov. Phys. JETP **43**, 536 (1976)].

[2] E. L. Bokhenkov, E. M. Rodina, E. F. Sheka, and I. Natkaniec, Phys. St. Sol. (b) **85**, 331 (1978).

[3] E. L. Bokhenkov, I. Natkaniec, and E. F. Sheka, Pibid. **75**, 105 (1976).

[4] A. V. Belushkin, E. L. Bokhenkov, A. I. Kolesnikov *et al.*, Fiz. Tverd. Tela (Leningrad) **23**, 2607 (1981) [Sov. Phys. Solid State **23**, 1529 (1981)].

[5] E. L. Bokhenkov, V. G. Fedorov, E. F. Sheka *et al.*, Nuovo Cimento **44B**, 324 (1978).

[6] E. L. Bokhenkov, A. I. Kolesnikov, T. A. Krivenko *et al.*, J. de Phys. **42**, C6–605 (1981).

[7] I. Natkaniec, A. V. Bielushkin, and T. Wasiutynski, Phys. St. Sol. (b) **105**, 413 (1981).

[8] H. Jobic, R. E. Ghosh, and A. Rnouprez, J. Chem. Phys. **75**, 4025 (1981).

[9] H. Jobic, J. Chem. Phys. **76**, 2693 (1982).

[10] G. Placzek and L. van Hove, Phys. Rev. **93**, 1207 (1954).

[11] Yu. Kagan, Zh. Eksp. Teor. Fiz. **40**, 312 (1961); **42**, 1375 (1962) [Sov. Phys. JETP **13**, 211 (1961); **15**, 954 (1962).

[12] P. A. Reynolds, J. K. Kjems, and J. W. White, J. Chem. Phys. **56**, 2928 (1972).

[13] L. S. Kukushkin, Fiz. Tverd. Tela (Leningrad) **7**, 54 (1965) [Sov. Phys. Solid State **7**, 38 (1965)].

[14] R. I. Personov, I. S. Osad'ko, E. D. Godyaev, and E. I. Al'shitz, Fiz. Tverd. Tela (Leningrad) **13**, 2653 (1971) [Sov. Phys. Solid State **13**, 2224 (1972)].

[15] K. P. Meletov and E. F. Sheka, Mol. Cryst. Liq. Cryst. **43**, 203 (1977).

[16] E. L. Bokhenkov, A. I. Kolesnikov, T. A. Krivenko *et al.*, J. de Phys. **42**, C6-566 (1981).

[17] I. Natkaniec, E. L. Bokhenkov, B. Dorner *et al.*, J. Phys. C **13**, 4265 (1980).

[18] R. Righini, S. Califano, and S. H. Walmsley, Chem. Phys. **50**, 113 (1980).

[19] G. A. Mackenzie, G. S. Pawley, and O. W. Dietrich, J. Phys. C **10**, 3723 (1977).

[20] G. S. Pawley, G. A. Mackenzie, E. L. Bokhenkov *et al.*, Molec. Phys. **39**, 251 (1980).

[21] J. Kalus, B. Dorner, V. K. Jindal *et al.*, J. Phys. C **15**, 6533 (1982).

[22] E. F. Sheka, E. L. Bokhenkov, B. Dorner *et al.*, J. Phys. C (1983) (in press).

[23] P. P. Parshin, M. G. Zemlyanov, A. S. Ivanov *et al.*, Fiz. Tverd. Tela (Leningrad) **23**, 2634 (1981) [Sov. Phys. Solid State **23**, 1545 (1981)].

[24] I. I. Gurevich and L. V. Tarasov, Fizika neitronov nizkikh energii (Physics of Low-Energy Neutrons), Nauka, 1965, Chap. 4.

[25] G. Taddei, H. Bonadeo, M. P. Marzocchi, and S. J. Califano, J. Chem. Phys. **58**, 966 (1973).

[26] D. E. Williams, J. Chem. Phys. **45**, 3770 (1966); **47**, 4680 (1967).

[27] D. W. J. Cruickshank, Acta Cryst. **10**, 504 (1957).

[28] A. Sjölander, Arkiv för Fysik **14**, 316 (1958).

[29] A. K. Agrawal, Phys. Rev. **A4**, 1560 (1971).

Translated by J. G. Adashko