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ЛАБОРАТОРИЯ ТЕОРЕТИЧЕСКОЙ ФИЗИКИ

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THEORY OF COHERENT NEUTRON SCATTERING BY HYDROGEN-BONDED FERROELECTRICS AT LOW TEMPERATURES

I. General Expression for Inelastic Coherent Scattering of Slow Neutrons and Effective Thermal Factors

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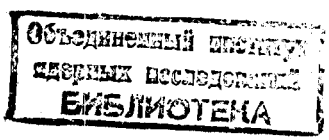

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E4-6171

Теория когерентного рассеяния нейтронов на сегнетоэлектриках с водородной связью при низких температурах (I)

Рассмотрено дифференциальное сечение неупругого когерентного рассеяния медленных нейтронов на сегнетоэлектриках с водородными связями при низких температурах. Вычислены квазиспиновые формфакторы на основе модели Блинца. Учитывается взаимодействие протонов (дейтронов) с решеткой и вводится эффективный фактор Дебая-Валлера.

Сообщения Объединенного института ядерных исследований

Дубна, 1971

Stamenković S.

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Theory of Coherent Neutron Scattering by Hydrogen-Bonded Ferroelectrics at Low Temperatures I. General Expression for Inelastic Coherent Scattering of Slow Neutrons and Effective Thermal Factors

The differential cross section for inelastic coherent scattering of slow neutrons scattered by hydrogen-bonded ferroelectrice at low temperatures has been evaluated. The quasi-spin form factors have been calculated using the Blinc's model. The proton (deuteron)-lattice interaction is taken into account and an effective Debye-Waller factor is introduced.

Communications of the Joint Institute for Nuclear Research.

Dubna, 1971

1. Introduction

The ferroelectric mode in hydrogen-bonded ferroelectrics was extensively theoretically /1-8/ studied as well as experimentally - using the neutron scattering method /9-16/. The theory suggests that the ferroelectric mode should be observed by neutron scattering, although it is expected to be overdamped in the whole energy spectrum especially at high temperatures. Moreover, some theoretical predictions and comparisons of the results obtained by various experimental techniques /9-22/ show that the collective motion of protons or deuterons can be predominantly observed by neutron scattering.

From the theoretical point of view Tokunaga's /2/ differential cross section for coherent neutron scattering, derived on the basis of a suitable quasi-spin relaxation function, is qualitative in the same sense as De Gennes's cross section for incoherent neutron scattering /1/. However, the dynamical consequences due to the presence of the heavy ions are not taken into account while the Fourier transforms of the scattering potential and the quasi-spin form factors of De Gennes are not written

explicitly as functions of momentum transfer. Some of the above requirements are recently taken into account in two exhaustive papers by Cochran /23/ and Novaković et al./24/. Cochran consistently applied the method of Van Hove /25/ to a "mixed phonon" and tunnelling model Hamiltonian /3,4/ so that the main feature of his paper was the introduction of a wave-number and frequency dependent susceptibility $X(\vec{k}, \omega)$ and its relation to the Fourier transformed pair distribution function $S(\vec{k}, \omega)$ which contains the scattering properties of the ferroelectric system. Starting from the same general theory of Van Hove /25/ Novaković et al./24/used the method of an effective proton mass.In addition,as a correction of the familiar quasi-spin Hamiltonian, which is consistent with the idea that the motion of protons develops adiabatically in a rigid crystal lattice, these authors introduced a residual coupling through the same quasi-spin components thus describing an effective interaction of protons with heavy ions. However, in both these papers only the critical scattering was discussed in terms of lattice dynamics.

In the present paper we shall evaluate the differential cross section for inelastic coherent neutron scattering by the KD_2PO_4 crystal at low temperatures since the intensity of coherent scattering on the hydrogeneous prototype KH_2PO_4 is very small. To write it explicitly as a function of scattering momentum and energy transfers, in the "quasi-spin-lattice interaction" formalism we shall use the model of deuteron potential with two harmonic wells/26-29/and a standard procedure analogous to derivations of the magnon differential cross section at low temperatures /30,31/.

II. The Differential Cross Section

The scattering of slow neutrons on KDP type ferroelectric crystals can be described with high accuracy by a pure nuclear interaction while the other interactions are negligible as being the effects of considerably less order of magnitude.

Generally, the differential cross section per unit solid angle and unit interval of outgoing energy for the nuclear scattering of slow neutrons by the KD_2PO_4 ferroelectric can be expressed in the concise form of Van Hove/25/. However, to obtain the final expression for this cross section it is more convenient, in our case, to write immediately equivalent expression by introducing correlation functions /31/

$$\frac{d^2\sigma}{d\Omega\, dE_{p'}} = \frac{m_n^2}{(2\pi)^3 h^5}\,\frac{p'}{p}\sum_{ij}\sum_{\mu\nu}\int_{-\infty}^{+\infty} dt\, e^{i/\hbar\,(E_{p'}-E_p)t} \langle a_{i\mu}\, e^{-i\vec{q}\vec{R}_{i\mu}(0)}\, a_{i\nu}\, e^{i\vec{q}\vec{R}_{i\nu}(t)}\rangle . \quad (1)$$

Here m_n is the neutron mass, $\vec{q} = \vec{p} - \vec{p}'$, $E = E_{p'} - E_p$ is momentum and energy transfers and $\vec{p}, E_p$ and $\vec{p}', E_{p'}$ are initial and final wave vectors and energies, respectively. The index i denotes N unit cells in the crystal. In the i-th cell α designates both the various ions and the three coordinates x, y, z so that α runs from 1 to 3n; the deuterons are labelled by the index r ($1 \le r \le n'$). The corresponding position vectors are marked by $\vec{R}_{i\alpha}$ and $\vec{R}_{i,r}$, respectively. The indicies μ and ν are connected with the indicies α and r: $\mu, \nu = \alpha\,(1 \le \alpha \le 3n)$ or $3n + r\,(1 \le r \le n')$.

$a_{i\mu} = A_{i\mu} + B_{i\mu}\,(\vec{I}_n \vec{I}_{i\mu})$ are the scattering amplitudes of nuclei ($\vec{I}_n$, $\vec{I}_{i\mu}$ - spin operators of neutron and nuclei, respectively, and $A_{i\mu}$ and $B_{i\mu}$ - the corresponding nuclear constants).

In the most recent examinations based on a simplified model for ferroelectric mode /17/ (which, otherwise can be shown to be consistent with a more exact procedure /3,4,7,23/) as well as on the expression for the differential cross section of neutron scattering and the experiment itself /14,15/ it was established that this mode is extremely overdamped. However, it has been studied under small wave vectors by an extrapolation of the scattering intensity to $\vec{q} \to 0$. These experiments were carried out on KD_2PO_4 in the vicinity of the transition temperature T_c, in the paraelectronic phase, where the unstable ferroelectric mode is responsible for the change of the crystal structure /32/. The similar qualitative situation can be expected for the scattering intensity on the polarization mode as well, provided that, with a good energy resolution, one could observe rather sharp scans at low temperature.

As we deal with the scattering at low temperatures we shall use the adiabatic approximation. Since at $\vec{q} = 0$ the "phonon-like" mode is greater than the "deuteron-like" mode ($\omega_0^+ > \omega_0^-$ /3,4,7/) the correlators in (1) of the form

$$< a_{i\alpha} e^{-i\vec{q}\vec{R}_{i\alpha}(0)} \, a_{j\alpha'} e^{i\vec{q}\vec{R}_{j\alpha'}(t)} > \qquad (2)$$

and mixed correlators of deuterons and heavy ions

$$< a_{i\alpha} e^{-i\vec{q}\vec{R}_{i\alpha}(0)} \, a_{j\tau} e^{i\vec{q}\vec{R}_{j\tau}(t)} > \qquad (3)$$

will as a good approximation determine only the Bragg scattering, i.e. a "background" to which the scattering

intensity on the polarization ("deuteron-like") mode would be superposed. According to /14,15/, for the reciprocal lattice point (303) the contribution of deuterium atoms to the scattering structure factor is much greater than that of other atoms. Therefore, in the mode analysis around [010] zone the above approximation is likely adjusted. So for the coherent scattering of unpolarized neutrons we can write

$$\frac{d^2\sigma_{cob}}{d\Omega\, d E_{p'}} = \frac{m_n^2}{(2\pi)^3 h^5}\,\frac{p'}{p}\sum_{ij}\sum_{rr'}\int_{-\infty}^{+\infty} dt e^{i/\hbar\,(E_{p'}-E_p)t}\,\langle\langle \overline{a_{ir}\, a_{jr'}}\rangle\rangle\, \langle e^{-i\vec{q}\vec{R}_{ir}(0)}\, e^{i\vec{q}\vec{R}_{ir'}(t)}\rangle . \quad (4)$$

Here the symbol $\langle\langle \ldots \rangle\rangle$ denotes the averaging over hydrogen isotopes as well as over deuteron spin orientations, and the line above denotes the averaging over the initial orientations of neutron spins x/.

To calculate the correlator in (4) it is necessary to find the equivalent correlator of quasi-spins. With this aim let us perform decomposition of the (ir)-th deuteron position vector

$$\vec{R}_{ir} = \vec{R}_i + \vec{R}^{\,0}_{ir} + \vec{u}^{\,0}_{ir} + \vec{u}_{ir} , \quad (5)$$

where $\vec{R}^{\,0}_{ir}$ refers to the middle point of the (ir)-th $O\text{-}D\ldots O$ bonding line, $\vec{u}^{\,0}_{ir} = \langle \vec{u}^{\,0}_{ir} \rangle + \vec{v}^{\,0}_{ir}$ is the displacement of the (ir)-th deuteron potential centre from the equilibrium position above the Curie point due to deuteron-phonon

x/ Such independent averaging is justified by a negligible interaction between ions and quasi-spins with real deuteron spins.

interaction ($\vec{v}^{\,0}_{ir}$ – the deviation $\vec{u}^{\,0}_{ir}$ from the average value $\langle \vec{u}^{\,0}_{ir} \rangle$ at a given temperature)[x] and $\vec{u}_{ir} = \langle \vec{u}_{ir} \rangle + \vec{v}_{ir}$ is the displacement of the (ir)-th deuteron with respect to the centre of its potential above the Curie point ($\vec{v}_{ir}$ – the deviation from the average value $\langle \vec{u}_{ir} \rangle \approx 0$ at a given temperature).

Further, according to De Gennes /1/ we can write

$$e^{i\vec{q}\vec{v}_{ir}} = \alpha_q^{ir} + 2\beta_q^{ir} S_{ir}^x + 2\gamma_q^{ir} S_{ir}^z + 2\delta_q^{ir} S_{ir}^y , \qquad (6)$$

where the quasi-spin form factors α_q^{ir} , β_q^{ir} and γ_q^{ir} are given by

$$\begin{aligned} \alpha_q^{ir} &= \frac{1}{2} \int [\Psi^2_{L,ir}(\vec{R}) + \Psi^2_{R,ir}(\vec{R})]\, e^{i\vec{q}\vec{R}} d\vec{R} , \\ \beta_q^{ir} &= \int \Psi_{L,ir}(\vec{R})\, \Psi_{R,ir}(\vec{R})\, e^{i\vec{q}\vec{R}} d\vec{R} , \qquad (7) \\ \gamma_q^{ir} &= \frac{1}{2} \int [\Psi^2_{L,ir}(\vec{R}) - \Psi^2_{R,ir}(\vec{R})]\, e^{i\vec{q}\vec{R}} d\vec{R} . \end{aligned}$$

The basis functions, $\Psi_{L,ir}$ and $\Psi_{R,ir}$ (associated with the two minima of the deuteron potential well), are assumed to be real, in which case $\delta_q^{ir} = 0$.

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[x] Here a change in position of the middle potential point due to deuteron-deuteron interactions is descarded.

By decomposition (5) and an expansion of deviation $\vec{v}^{\,0}_{ir}$ in power of deviations $\vec{v}_{ia}$ (introducing normal coordinates $b^{\pm}_{qa}$ for phonons)[x/]

$$\vec{v}^{\,0}_{ir} = \sum \lambda^{ja}_{ir} \vec{v}_{ir} + \ldots \tag{8}$$

(the constants λ^{ja}_{ir} being written explicitly hereafter), as well as by neglecting some mixed scattering events when both collective deuteron modes and phonons are excited, the presence of heavy ions can be taken into account up to an effective Debye-Waller factor denoted below as $e^{-2W^{r}_{q}}$. In this way another of the adiabatic approximation is made in addition to that already performed by replacing the "pure" deuteron mode ω_{qr} by the hybridized ("mixed") mode $\bar{\omega}_{qr}$.

Rejecting the "Bragg background" (from (2) and (3)), and after applying the standard procedure analogous to that used for derivation of the magnon differential cross section /30,31/, in the vicinity of the reciprocal lattice vector $\vec{g}$ one obtains

$$\frac{d\sigma^{\pm}_{cob}}{d\Omega\, dE_{p'}} = \frac{N}{\pi}\sigma_{cob}\frac{p'}{p}\sum_{r} e^{-2W^{r}_{g}} |F^{r}_{g}|^{2} \frac{H_{r}}{\bar{\omega}_{qr}} \times$$

$$\times [n_{r}(\vec{q}) + \frac{1}{2} \pm \frac{1}{2}] \frac{\Gamma_{qr}}{[(E_{p'} - E_{p}) \pm \hbar\bar{\omega}_{qr}]^{2} + \Gamma^{2}_{qr}}, \tag{9}$$

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x/ We neglect variations in the shape of unit cell with temperature, i.e. we work with a clamped crystal ($\vec{v}_{ia} = \vec{u}_{ia} - \langle\vec{u}_{ia}\rangle$; $\vec{u}_{ia}$ are the displacements from equilibrium position above T_c and $\langle\vec{u}_{ia}\rangle$ its mean values at a given temperature).

where $$\sigma_{coh} = \frac{m_n^2}{(2\pi)^3 \hbar^4} \langle a \rangle^2 ; \qquad \langle a \rangle = \sum_s a_s c_s , \tag{10}$$

c_s - the concentration of H - isotopes for which $a_{i,} = a_s$. Here, the above sign (+) refers to the scattering with emission and the lower (-) to the scattering with absorption of the quasi-spin wave. $\omega_{q,}^{-}$ and $\Gamma_{q,}$ are the collective frequency and energy width of the deuteron-like mode of the type r, respectively (given in refs. /3,4,7,8/), while H, is the deuteron molecular field and

$$n_{,}(\vec{q}) = [\, e^{b\omega_{q,}^{-}/k_B T} - 1 \,]^{-1} \tag{11}$$

is the boson distribution function for the average numbers of deuteron-like modes in the state ($\vec{q}$, r)x/. The effective quasi-spin form factor $F_q^{'}$ represents a peculiar thermal factor which is due to the interference of neutron waves in the region of deuteron localization ($\sim l$ = 0.34Å)/9,12,13,28/, and together with the effective Debye-Waller factor e^{-2W_q} can be related to the very anisotropic

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x/ Note that following the Holstein-Primakoff /33/ (or the Tošić-Agranovich representation /34/) we can make the familiar quasi-spin-wave approximation at zero temperature /3,8/ which allows us to express the quasi-spin variable in terms of boson creation and annihilation operators $b_{i,}^{\pm}$ and their Fourier transforms.

structure factor introduced in /15/. For the sake of simplicity the both effective factors are assumed to be independent of index i.

III. The Quasi-Spin Form Factor

The effective quasi-spin form factor in (9)

$$F_q^r = \beta_q^r \cos\theta - \gamma_q^r \sin\theta \; ; \quad (\sin\theta = H_x/H, \; \cos\theta = H_z/H), \tag{12}$$

where the molecular field intensity

$$H = [H_x^2 + H_z^2]^{1/2} \tag{13}$$

(H_x and H_z being its components/3,4,8/ assumed to be independent of indices i and r), can be calculated in the approximation of two interacting linear oscillators x/. We take the basis functions for every i and r in the form /26,28/

$$\Psi_{L,R}(x) = \pi^{-1/4} b^{-1/2} \exp\{-\frac{x_{L,R}^2}{2}\}, \tag{14}$$

where

$$x_L = b^{-1}(x + l/2), \qquad x \leq d \tag{15}$$

$$x_R = b^{-1}(x - l/2), \qquad x \geq d \; ;$$

$b = (\frac{h}{m_d \omega})^{1/2}$ and ω is the classical frequency of a single linear oscillator which is theoretically and experimentally

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x/ We did not take here more exact eigenfunctions expressed in terms of a parabolic cylinder function /35/.

estimated in refs. /5,9,36/; $d = d_{ir} = H_z / m_d \omega^2 l$ is the parameter of deuteron potential asymmetry, l is the distance between the two minima inside the (ir)-th double potential well and m_d is the mass of deuteron. Then the above form factor becomes

$$F_g^r = [e^{-(\frac{l}{2b})^2 \cos\theta} + i \sin(\frac{l g_r}{2}) \sin\theta] e^{-\frac{b^2 g_r^2}{4}}, \tag{16}$$

$$g_r = |\vec{g}| \cos(\vec{g} \cdot ort \vec{l}_r).$$

IV. The Effective Debye-Waller Factor

On the basis of the expansion (8) and after the usual procedure /31/ the exponent of the Debye-Waller factor $2W_a^r$ in (9) can be written in the form

$$2W_q^r = \Sigma |\lambda_{ir}^{ia}|^2 \, 2W_q^a. \tag{17}$$

The constants λ_{ir}^{ia} (i.e. λ_{ir}^{ja} from the expansion (8)) can be found from the equivalency of "coordinate" and "quasi-spin" representation of deuteron-phonon interaction, i.e. from the requirement that the corresponding matrix elements of these two representations are equal:

$$\sum_{ijar} \Phi_{ij}^{ra} (\vec{v}_{ir} \vec{v}_{ja}) \quad <\Longrightarrow> \quad \sum_{ijar} s_{ir}^z (\vec{A}_{ij}^{ra} \vec{v}_{ja}), \tag{18}$$

where

$$A_{ij}^{ra} \approx (2e^{*2} |l_{ir}| / |\vec{R}_{ij}^{ra}|^3) \cdot ort \vec{R}_{ij}^{ra},$$

$$\Phi_{ij}^{ra} = k_{ir}\lambda_{ir}^{ja}[2\theta(v_{ir} - d_{ir}) - 1]; \quad \theta(x) = \begin{cases} 1, & x \geq 0 \\ 0, & x < 0 \end{cases}; \qquad (19)$$

$k_{ir} = m_d\omega^2$ is the force constant of the single linear oscillator, $e^{*2} \approx (1 \div 0{,}5)e^2$ is the square of an effective charge measuring the Coulomb interaction between deuterons and heavy ions and $\vec{R}_{ij}^{ra}$ is the vector connecting the centre of the (ir)-th deuteron-bond and the position of the (ja)-th heavy ion.

One obtains that these constants are proportional to the coupling constants of the deuteron-lattice interaction A_{ij}^{ra} (19):

$$\lambda_{ij}^{ja} = \frac{(\vec{A}_{ij}^{ra} \cdot ort\,\vec{u}_{ja})}{(ort\,\vec{l}_{ir} \cdot ort\,\vec{u}_{ja})}\, I^{-1}, \qquad (20)$$

$$I = \frac{2dlh\omega}{\sqrt{\pi}}\{e^{-[f^2+(\frac{H_z}{2fh\omega})^2]}sh(\frac{H_z}{h\omega}) + \qquad (21)$$

$$+ 2\sqrt{\pi}f[1 - \frac{1}{2}\phi(f + \frac{H_z}{2fh\omega}) + \frac{1}{2}\phi(f - \frac{H_z}{2fh\omega})]\}; \quad f = \frac{m_d\omega l^2}{4h}$$

and $\phi(x) = 2/\sqrt{\pi}\int_0^{\infty} e^{-t^2}dt$ is the Gauss function.

In the expression (17) $2W_q^a$ is the familiar exponent of the Debye-Waller factor which corresponds to the a -th phonon branch

$$2W_q^a = \frac{h}{Nm_a} \sum_{\vec{k}a'} \frac{[\vec{q}\cdot\vec{\epsilon}_a^{a'}(\vec{k})]^2}{\lambda_{a'}(\vec{k})} [n_{a'}(\vec{k}) + \frac{1}{2}]; \qquad (22)$$

m_a stands for the ion mass, $\lambda_{a'}(\vec{k})$ is the frequency of the a' -th phonon branch, $\epsilon_a^{a'}(k)$ is the a' -th projection of the polarization vector of the a -th phonon branch and

$$n_{a'}(\vec{k}) = [e^{b\lambda_{a'}(\vec{k})/k_B T} - 1] \qquad (23)$$

is the distribution function for the average numbers of phonons in the state $(\vec{k}, a')$.

For the real structure of the KDP crystal the calculation of exponents (22) is practically unfeasible. However, with some simplifications the contributions of acoustical and optical (phonon-like) branches can be estimated. Thus the arrangement of the $[K - PO_4]$ complexes and their associated deuterons can be approximated by the simple Bravais lattice /3-5,7,8/. We also assume one quasi-spin per unit cell coupled with one phonon branch only /3,4,7,8/. Then the contribution of the phonon-like branch in (17) is

$$2W_q^+ = 2W_q^{opt} \approx \frac{h[\vec{q}\cdot ort\,\vec{c}]}{m^+\omega_0^+} [1 + 2e^{-\frac{b\omega_0^+}{k_B T}}], \qquad (24)$$

where m^+ stands for the reduced mass of the $[K-PO_4]$complex.

The contribution of acoustic branches can be estimated in the Debye approximation (on condition that the above Bravais lattice is nearly cubic) /31/:

$$2W_q^{ac} = \frac{3h^2q^2}{m^+\tau}\left[\frac{1}{4} + D(\tau/k_BT)\left(\frac{k_BT}{\tau}\right)^2\right], \qquad (25)$$

$\tau = h\omega_{max}^{ac} = v_z\sqrt[3]{6\pi^2 n/v_0}$ is the Debye temperature in energy units, v_z is the sound velocity, v_0 is the volume of the unit cell and

$$D(\tau/k_BT) = \left(\frac{k_BT}{\tau}\right)^2 \int_0^{\tau/k_BT} \frac{x\,dx}{e^x - 1} \qquad (26)$$

is the function expressed numerically which in our case can be approximated by the expression

$$D(\tau/k_BT) \approx \frac{\pi^2}{6}\left(\frac{k_BT}{\tau}\right)^2, \quad k_BT \ll \tau. \qquad (27)$$

In the conclusion we would like to point out that in the second part of this paper (reffered to as II) we shall use the presented approach to study the characteristics of quasy-elastic neutron scattering in more detail. The interpretation of the tunnelling quasi-spin model, the nature of the low temperature ferroelectric state as well as the deuterium vibrations along the c -crystal axis will also be discussed with reference to the refined neutron scattering properties at small angles.

References

1. P.G. De Gennes. Solid State Commun., 1 , 132 (1963).
2. M. Tokunaga and T. Matsubara. Progr. Teor. Phys., (Kyoto) 35, 581 (1965); M.Tokunaga.Progr.Teor.Phys., (Kyoto) 36, 857 (1966).

3. J. Villain and S.Stamenkovic. phys. stat. sol., 15, 585 (1966).

4. K.K. Kobayashi. J. Phys. Soc. Japan, 24, 497 (1967). Phys. Letters, (Netherlands) 26A , 55 (1967).

5. L. Novakovic. J. Phys. Chem. Solids, 27, 1469 (1966); Boris Kidric Bull. 18, 23 (1967); J.Phys.Chem.Solids, 31, 431 (1970).

6. R. Brout, K.A. Muler, H.Thomas. Solid State Commun., 4, 507 (1966); E.Pytte and H.Thomas. Phys.Rev., 175, 610 (1968).

7. И.В. Стасюк, Р.Р. Левицкий, УФЖ, 15, 460 (1970), УФЖ, 14, 110 (1969).

8. S. Stamenkovic and L. Novakovic. phys.stat.sol., 41, 135 (1970).

9. G. Bacon and R. Pease. Proc. Roy. Soc., A230, 359 (1955).

10. I. Pelah, I.Lefkovitz,W.Kley, E. Tunkello. Phys.Rev. Lett., 2, 94 (1959).

11. Y.Imry, I.Pelah, E.Wiener. J. Chem. Phys.,43, 2332 (1965); Y.Imry, I.Pelah, E.Wiener, H.Zafrir. Solid State Commun., 5, 41 (1967).

12. C.Schenk, E.Wiener, B.Weckermann, W.Kley. Phys. Rev., 172, 172 (1968); C. Schenk, B.Weckermann. Phys. Lett., (Netherlands), 27A, 582 (1968).

13. H.Grimm, H.Stiller, Th. Plesser. Proceed, Europ. Meeting on Ferroelectricity, p. 47, Saarbrucken (1969); Th. Plesser, H.Stiller. Solid State Commun., 7, 323 (1969).

14. W.J.Buyers, R.A.Cowley, G.L.Paul, W.Cochran. Neutron Inel.Scatt., p. 267, 1, ed. IAEA Vienna (1968).

15. J.Scalyo, Jr., B.C.Frazer, G.Shirane. Phys. Rev., B 1, 278 (1970).

16. M. Zivanovic et al., to be published in Phys. Rev., B (1971).

17. I.P. Kaminow, R.C.Leite, S.P.S.Porto. J. Phys. Chem., Solids, 26, 2085 (1965); I.P.Kaminow, T.C.Damen. Phys. Rev. Lett., 20, 1105 (1968).

18. А. Стеханов, Е.А. Попова. ФТТ, 7, 3530 (1965), 10, 415 (1968).

19. М. Арефьев, П.А. Бажулин, Т.В. Михальцева, ФТТ, 7, 2413 (1965).

20. R.Blinc, M.Pintar, I.Zupancic. J. Phys. Chem. Solids, 28, 405 (1967); R.Blinc, P.Cevc, M.Shara.Phys. Rev., 159, 411 (1967).

21. B.Lavrencic, I.Levstek, B.Zeks. Chem.Phys.Lett., 5. 411 (1970).

22. M.Arsic - Eskinja, H.Grimm, H.Stiller. First Europ. Conf. on the Phys. of Condens. Matter, Florence (1971).

23. W.Cochran. Advan.Phys., 18, 157 (1969).

24. L.Novakovic, S.Stamenkovic, A.Vlahov. J. Phys. Chem., 32, 487 (1971).

25. L. Van Hove. Phys. Rev., 95, 249 (1954).

26. R.Blinc, D.Hadzi. Molecul. Phys., 1, 391 (1958).

27. Е.А. Пшеничнов, Н.Д. Соколов, ОПТ.Спектр, 11, 16 (1961).

28. С. Стаменкович. ФТТ, 10, 861 (1968).

29. H.Stiller, Ber.Bunsenges. Phys.Chem., 72, 94 (1968).

30. L. Van Hove. Phys. Rev., 95, 1374 (1954).

31. Ю.А. Изюмов. УФН, 80, 41 (1963).

32. L.D. Landau, E.M.Lifshitz. Statistical Physics, Pergamon Press, Oxford (1958).

33. T.Holstein, H.Primakoff. Phys.Rev., 58, 1098 (1940).

34. В.М. Агранович, Б.С. Тошич. ЖЭТФ, 53, 149 (1967).

35. E.Merzbacher. Quantum Mechanics, Chap. 5, John Willey, New York (1970).

36. C.J.Reid. J. Chem.Phys., 30, 182 (1959).

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