THERMAL OSCILLATIONS AND THE MOSSBAUER EFFECT IN THE PHASE TRANSITION REGION IN FERROELECTRICS

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We consider thermal-oscillation anomalies and the probability of Mossbauer absorption in the phase transition region in ferroelectrics. For transitions of the displacement type, the anomalies can be expressed in terms of the dielectric characteristics and some constants defining the low-frequency spectrum of the crystal. An anisotropy of the oscillations below the transition point is obtained. Estimates are presented for order-disorder transitions.

1. INTRODUCTION

IN an earlier paper[1], henceforth cited as I, we considered the thermodynamics and low-frequency oscillation spectra in phase transitions of the displacement type in ferroelectrics. In the present paper we use the methods developed in I to describe the thermal oscillations and the mean square displacements near the transition. These quantities can be investigated experimentally by x-ray or neutron diffraction[2], but the attainable accuracy is apparently insufficient for the study of the temperature dependences. Thermal oscillations in ferroelectrics were investigated recently in a number of experiments with the aid of the Mossbauer effect[3,4], and anomalies were observed in the Debye-Waller factor near the transition. A theoretical discussion of these experiments was limited so far to general considerations concerning the possible influence of the critical oscillation[5], without attempts at a quantitative calculation.

The more detailed analysis presented in this paper shows that important factors in the observed effect, besides the temperature dependence of the critical frequency, are also the piezoeffect and the difference between the first-order and second-order phase transitions. The resultant expression for the anomalous part of the mean displacements contains, besides the known dielectric, striction, and elastic constants, several other constants characterizing the critical oscillations and the degree to which the given ion takes part in them. These same constants determine the spectra of the low-lying excitations (I), so that it is possible to obtain with the aid of the Mossbauer effect information concerning these important characteristics of the crystal. The temperature dependence of the anomaly above the transition is inversely proportional to the square root of the dielectric constant ϵ, and below the transition it is expressed in terms of ϵ and the spontaneous polarization P.

As in I, we are considering an ideal crystal. By way of an example we discuss essentially the case of perovskites with a transition from the cubic phase to the tetragonal phase, although the general formulas are applicable to any transition of the displacement type, and particularly a non-ferroelectric transition. In Sec. 4 we present certain considerations and estimates for the Mossbauer effect near the order-disor-

der phase transitions. In this case, the character of the anomaly in the Debye-Waller factor depends on the relation between the natural width of the Mossbauer line and the relaxation time of the ions in the cells to the equilibrium distribution.

2. GENERAL FORMULAS FOR THE PROBABILITY OF THE MOSSBAUER ABSORPTION

The general expression for the probability of the Mossbauer absorption W in terms of the Debye-Waller factor[6] is obtained by using a harmonic approximation for the lattice oscillations. In the region of the phase transition, the anharmonicity effects are important, and we therefore derive a somewhat more general expression for W than usual.

The probability of absorption of a quantum of frequency ω in the Mossbauer effect is given by the expression[6,7]

$$W(\omega) = \frac{\sigma_0 \Gamma}{2\pi} \int_{-\infty}^{\infty} \exp\{i(\omega - \omega_0)t - \Gamma|t|\} \langle \exp\{iq(u_r(t) - \bar{u})\} \quad (1)$$

$$\times \exp\{-iq(u_r(0) - \bar{u})\}\rangle.$$

Here ω_0 is the resonant frequency, Γ is the natural width of the nuclear level, q is the wave vector of the quantum, $u_H(t) - \bar{u}$ is the Heisenberg operator of the displacement of the nucleus relative to the equilibrium position $\langle u_H \rangle = \bar{u}$:

$$u_r(t) = e^{iHt} u_r e^{-iHt},$$

H is the usual phonon Hamiltonian of the crystal, see, for example, (I.1) and (I.7). The symbol $\langle \ldots \rangle$ denotes statistical averaging:

$$\langle \ldots \rangle = \text{Sp}\left[(\ldots)e^{-\beta H}\right](\text{Sp}\, e^{-\beta H})^{-1};$$

$\beta = 1/T$; σ_0 is the total absorption cross section.

In the considered case of transitions of the displacement type, the times characterizing the motion of the absorbing ion are of the order of the reciprocal of the optical frequencies, and are much shorter than the emission times $\Gamma^{-1} \gtrsim 10^{-9}$ sec. Therefore the expression in the angle brackets in (1) can be averaged, before integration with respect to t, over the time, after which the time-average can be replaced, on the basis of the general statistical theorems, by the statistical average. As a result we get

$$W(\omega) = \frac{\sigma_0}{\pi} f^2 \frac{\Gamma}{(\omega - \omega_0)^2 + \Gamma^2} \quad (2)$$

where the thermal Debye-Waller factor is given by the expression

$$f = |\langle \exp\{i\mathbf{q}(\mathbf{u_r} - \overline{\mathbf{u}})\}\rangle|. \tag{3}$$

In formulas (1)–(3) we neglected the presence of the spin of the nucleus and the associated effects of quadrupole and magnetic splitting. These splittings can be comparably in magnitude with the line width, but are always smaller to the optical frequencies. Allowance for these splittings leads to a replacement of (1) by a sum of several terms with frequencies that depend on the spin state of the nucleus. Integrating this equation over a frequency region that is large compared with the line width but small compared with the optical frequencies, we find that the total probability of the Mossbauer transition, just as in the case described by (2), is equal to $\sigma_0 f^2$.

The factor f in (3) can be easily calculated in the harmonic approximation which, as already mentioned, is not applicable directly to the transition region. However, for transitions of the displacement type, the anharmonicity is small, (I); this makes it possible to obtain for the thermal factor a successive-approximation series, just as for the thermodynamic quantities. Expanding (3) in powers of the exponent, we get

$$f = 1 - \frac{q^2}{2}\langle(u-\bar{u})^2\rangle + \frac{q^4}{4!}\langle(u-\bar{u})^4\rangle - \dots, \tag{4}$$

where u denotes the projection of $\mathbf{u_H}$ on the direction of q.

The second term in (4) is expressed in terms of the temperature Green's function [8,1] $G(\mathbf{k}, i\omega_n)$ as follows:

$$\langle(u_{r\alpha} - \bar{u}_\alpha)(u_{r\beta} - \bar{u}_\beta)\rangle = T \sum_{\mathbf{k}n} G_{\alpha\beta}(\mathbf{k}, i\omega_n). \tag{5}$$

The third term is expressed in terms of the two-phonon Green's function K, which satisfies the Bethe-Salpeter equation [8], which can be written symbolically in the form

$$K = GG + GG\hat{\Gamma}K, \tag{6}$$

where $\hat{\Gamma}$ is the amplitude of two-phonon scattering.

By the methods of Sec. 4 of I we can verify that the ratio of the second of (6) to the first is proportional to the ratio of the temperature T to the atomic energy ϵ_{at}, i.e., to the anharmonicity parameter. Therefore the second term of (6) can make a noticeable contribution to (4) only at very large q, when the total probability $W \sim \exp[-q^2\langle u - \bar{u}\rangle^2]$ is extremely small. For not too large q, it is sufficient to retain the first term of (6), as a result of which the third term of (4) becomes

$$\frac{1}{8}\left[q_\alpha q_\beta T \sum_{n\mathbf{k}} G_{\alpha\beta}(\mathbf{k}, i\omega_n)\right]^2. \tag{7}$$

The remaining terms of the expansion (4) are calculated in similar fashion. As a result we get

$$f = \exp[-\frac{1}{2}q_\alpha q_\beta\langle(u_\alpha - \bar{u}_\alpha)(u_\beta - \bar{u}_\beta)\rangle],$$
$$\langle(u_\alpha - \bar{u}_\alpha)(u_\beta - \bar{u}_\beta)\rangle = \langle u_\alpha u_\beta\rangle - \bar{u}_\alpha \bar{u}_\beta = T\sum_{n\mathbf{k}} G_{\alpha\beta}(\mathbf{k}, i\omega_n). \tag{8}$$

Expression (8) has the usual form [6], but the mean value and G in (8) correspond to the Green's function with allowance for anharmonicity. This formula, as well as the analogous results of I, can be obtained by using the "linear anharmonic approximation" [9], in which the formulas of the harmonic theory are used, but a temperature dependence is introduced into the

Green's function phenomenologically; in the first approximation in $T\epsilon_{at}^{-1}$, such a procedure is correct.

3. ANOMALIES OF THERMAL OSCILLATIONS IN TRANSITIONS OF THE DISPLACEMENT TYPE

The matrix $G_{\alpha\beta}$ in (8) can be taken for the case under consideration from (I.26):

$$G(\mathbf{k}, i\omega_n) = \Big[\mathcal{M}\omega_n^2 + A - \sum_{b,b'}(\omega_n^2\overline{\gamma\mu_b} + V_b + Q_b) \tag{9}$$

$$\times'\Big(\omega_n^2 + S_0^{(b)} + S_{bb'} + \frac{4\pi z_b z_{b'}}{v_c}g^l\Big)^{-1}(\omega_n^2\overline{\gamma\mu_{b'}} + V_{b'}^+ + Q_{b'}^+)\Big]^{-1}.$$

The indices b and b' number here different optical coordinates (critical $\mathbf{x_c}$ and all other $\mathbf{x_H}$), $\omega_n = 2nT$ are the discrete frequencies of the temperature diagram technique [8], the constants μ_b and z_b characterize respectively the effective masses and polarizabilities of the optical branches, v_c is the volume of the unit cell, $g_{\alpha\beta}^l = n_\alpha n_\beta$, and $\mathbf{n} = \mathbf{k}/k$. The constants $S_0^{(b)}$ are proportional to the squares of the optical frequencies as $\mathbf{k} \to 0$, and for the critical coordinate the matrix $S_0^{(c)}$ is the inverse of a dielectric-constant matrix of the clamped crystal ϵ:

$$S_0^{(c)} \equiv S_0 = \lambda/\epsilon, \quad \lambda = 4\pi z_c^2/v_c. \tag{10}$$

The matrices A, V, and S for small values of k are given by formula (I.9) and are proportional to k^2, while the piezoelectric matrix Q, in accordance with formula (I.25), is proportional to k and to the polarization P.

If the temperature is not small compared with the Debye temperature Θ_D, then the main contribution to the integral with respect to k in (8) is made by the region of large k, on the order of the reciprocal lattice constant a^{-1}; the contribution of the region of small k is suppressed with a statistical weight $\sim k^3$. However, this main contribution is a smooth function of the temperature and has no singularities near the transition. As discussed in I, the critical phenomena are insignificant only in the region of small wave vectors $k \sim a^{-1}\epsilon^{-1/2}$. Therefore to find the anomalous part of the displacements from the function $G(\mathbf{k}, i\omega_n)$ in (8) it is possible to subtract the function $G^{00}(\mathbf{k}, i\omega_n)$, which is regular near the transition, and which is obtained from G by putting $S_0 = Q = 0$. The corresponding anomalous part of the displacements will be denoted by $\langle u_\alpha u_\beta\rangle_c$:

$$\langle u_\alpha u_\beta\rangle_c = T\sum_{n\mathbf{k}}(G(\mathbf{k}, i\omega_n) - G^{00}(\mathbf{k}, i\omega_n))_{\alpha\beta}. \tag{11}$$

In the integral (11), the region of small $k \sim a^{-1}\epsilon^{-1/2}$ is already important. Therefore we can use in (9) the expansions of the matrices contained therein for small k. Then, as in Sec. 4 and 5 of I, we can neglect the contribution of all the normal branches $\mathbf{x_H}$, and also the longitudinal critical branch $\mathbf{x_{ck}} \parallel \mathbf{n}$. In addition, if we do not consider the case of extremely small T, the temperature frequencies $\omega_n = 2n\pi T$ in (9) and (11) are much larger than the critical frequencies $\omega_c \sim (\lambda\epsilon^{-1})^{1/2}$, and it is sufficient to retain in the sum over n in (11) the classical term with $n = 0$. As a result we get

$$\langle u_\alpha u_\beta\rangle_c = T\sum_k\Big[\frac{1}{A - (V+Q)(\lambda/\epsilon + S)_l^{-1}(V+Q^+)} - \frac{1}{A - VS_l^{-1}V}\Big]_{\alpha\beta} \tag{12}$$

Here, just as in I, the matrices V, S, and Q without an index correspond to the critical branch, and R_t^{-1}, in accordance with formula (I.30), denotes that we project the matrix R on the subspace orthogonal to n, and that we use in this subspace the matrix inverse to the obtained one:

$$R_t^{-1} = \left[\sum_{\mu,\nu} n_\mu n_\nu A_{\mu\nu}(0) \right]^{-1} \frac{\partial}{\partial \xi} A_{\alpha\beta}(\xi) \Big|_{\xi=0}, \quad (13)$$

where $A_{\alpha\beta}(\xi)$ is the cofactor of the matrix element $R_{\alpha\beta} + \xi n_\alpha n_\beta$.

We shall show that in the region below the transition temperature T_0 it is possible to express the anomalous part of the displacements (12) in terms of the dielectric constant $\epsilon(T)$. For concreteness, we consider henceforth the case of perovskites with a phase transition from the cubic phase to the tetragonal phase. Then the matrices A, V, and S in (12) are given by formulas (I.9), and the matrix Q vanishes when $T > T_0$ in accordance with (I.25).

We introduce in the integration with respect to k in (12) a new variable $x = |k|(\epsilon/\lambda)^{1/2}$, after which the integral becomes

$$\langle u_\alpha u_\beta \rangle_c = -\frac{T}{24\pi^3} \frac{\delta_{\alpha\beta}}{\rho} \left(\frac{\lambda}{\epsilon}\right)^{1/2} \int_0^\infty dx \int dn \, \mathrm{Sp}[\chi(1+x^2\varphi)^{-1} \varphi_t^{-1} \tilde{\chi}]. \quad (14)$$

Here $\rho = \mathcal{M}/v_c$ is the density, dn denotes integration over the angles of the vector n, and the matrices χ and φ depend only on the angles of n:

$$\chi = (a_l g^l + a_t g^t + a_a g^a)^{-1}(v_t g^t + v_a g^a),$$

$$\varphi = s_t g^t + s_a g^a - (v_t g^t + v_a g^a)\chi;$$

$$g_{\alpha\beta}^t = \delta_{\alpha\beta} - g_{\alpha\beta}^l = \delta_{\alpha\beta} - n_\alpha n_\beta, \quad g_{\alpha\beta}^a = \sum_{\sigma=1}^3 e_\sigma^\alpha e_\sigma^\beta (n e_\sigma)^2; \quad (15)$$

e_σ are unit vectors of the principal axes of the crystal; a_i, v_i, and s_i are constants introduced in (I.9); $\tilde{\chi}$ is the transpose matrix of χ.

Thus, above the transition the anomalous part of the displacements increases on approaching T_0, decreasing in absolute magnitude in inverse proportion to the square root of the dielectric constant.

In the tetragonal phase, the permittivity $\epsilon_{xx} = \epsilon_{\parallel}$ along the tetragonal axis x is as a rule smaller than the transverse permittivity $\epsilon_{yy} = \epsilon_{zz} = \epsilon_\perp$. Therefore the transformation of the variables in the integral with respect to k is more conveniently done with the aid of $\epsilon_\perp$: $x = |k|(\epsilon_\perp\lambda^{-1})^{1/2}$, after which (12) is written in the form

$$\langle u_\alpha u_\beta \rangle_c = \frac{T}{8\pi^3\rho} \left(\frac{\lambda}{\epsilon_\perp}\right)^{1/2} \int_0^\infty dx \int dn \left[\left\{ \hat{a} - \left(x\hat{v} + i\hat{q}P \sqrt{\frac{\lambda}{\pi\rho}} \right) \right. \right.$$

$$\times \left. \left(\delta^\perp + \delta^\parallel \frac{\epsilon_\perp}{\epsilon_\parallel} + x^2\hat{s} \right)_t^{-1} \left(x\hat{v} - i\hat{q}P \sqrt{\frac{\lambda}{\pi\rho}} \right) \right\}^{-1} - \{\hat{a} - \hat{v}(\hat{s})_t^{-1}\hat{v}\}^{-1} \right]_{\alpha\beta} \quad (16)$$

Here P is the polarization, and in the coordinate system connected with the axes of the crystal the matrices have, in accordance with I, the form

$$\hat{v} = \begin{pmatrix} v_t + v_a n_1^2 & 0 & 0 \\ 0 & v_t + v_a n_2^2 & 0 \\ 0 & 0 & v_t + v_a n_3^2 \end{pmatrix},$$

$$\hat{q} = \begin{pmatrix} (q_{11} - \tfrac{1}{2}q_{44})n_1 & 0 & 0 \\ q_{12}n_2 & \tfrac{1}{2}q_{44}n_1 & 0 \\ q_{12}n_3 & 0 & \tfrac{1}{2}q_{44}n_1 \end{pmatrix},$$

$$\delta^\perp + \delta^\parallel \frac{\epsilon_\perp}{\epsilon_\parallel} + x^2\hat{s} =$$

$$= \begin{pmatrix} \epsilon_\perp/\epsilon_\parallel + x^2(s_t + s_a n_1^2) & 0 & 0 \\ 0 & 1 + x^2(s_t + s_a n_2^2) & 0 \\ 0 & 0 & 1 + x^2(s_t + s_a n_3^2) \end{pmatrix}; \quad (17)$$

$\hat{a} = a_l g^l + a_t g^t + a_a g^a$ is the matrix of the elastic coefficients, q_{ik} are the striction constants, and the components $(\ldots)_t^{-1}$ are obtained in accordance with the rule (13).

Thus, an anisotropy of the oscillations, $\langle u_x^2 \rangle_c \neq \langle u_y^2 \rangle_c$, appears below T_0. The temperature dependence of the displacements is determined by the temperature variation of the permittivities ϵ and of the polarization P. If the transition is close to a second-order transition, so that the relations $\epsilon \sim (T_C - T)^{-1}$ and $P \sim (T_C - T)^{1/2}$ are sufficiently well satisfied for ϵ and P below T_0, then the anomaly of the displacement is proportional to $|T_C - T|^{1/2}$, just as above the transition.

If the elastic, striction, and dielectric properties of the crystal are known, then expressions (12), (14), and (16) contain four unknown constants, and these can be chosen to be, for example, λs_t^{-1}, $v_t^2 s_t^{-1}$, $s_a s_t^{-1}$, and $v_a v_t^{-1}$. In the low-frequency spectrum of the crystal there enter, besides these constants, also two others, the quantity λ itself, and the mass constant $\mu^{[1]}$. The reduction in the number of constants is due to the discarding of the terms with $n \neq 0$ from the sum over the frequencies ω_n, which corresponds in turn to the classical description of motion, when the factors containing the kinetic energy in the equilibrium distribution function are separated from the terms containing the potential energy, As a result, the mass characteristics contained in the kinetic theory drop out from the mean values of the displacement.

In the general case, the integrals (12), (14), and (16) must be determined numerically. To illustrate and explain the physical picture, let us consider, just as in I, the hypothetical case of an isotropic crystal, in which $a_a = v_a = s_a = 0$. As noted in I, for the considered cubic crystals, such an estimate is apparently fairly accurate also quantitatively. The calculations are more conveniently carried out in this case in a coordinate system, in which one of the axes is directed along k and another is perpendicular to k and to the tetragonal axis. The integration with respect to x in (16) yields for the anomaly of the total mean square of the thermal displacements

$$\langle u_x^2 + u_y^2 + u_z^2 \rangle_c = -\frac{T}{4\pi\rho} \left(\frac{\lambda}{\epsilon_\perp w}\right)^{1/2} \int_0^1 dz \left[\frac{P^2\epsilon_\perp}{\pi\rho} \left(\frac{\xi^2 + \eta^2}{\sqrt{R_1}} + \frac{q_{44}^2 n_1^2}{4a_t^2 \sqrt{R_\perp}} \right) \right.$$

$$\left. - \frac{v_t^2}{w a_t^2}(\sqrt{R_1} + \sqrt{R_\perp}) \right]. \quad (18)$$

Here

$$z = n_1, \quad n_\perp^2 = 1 - z^2, \quad \xi = \frac{n_1}{a_t}\left(\frac{q_{44}}{2} + q_a n_\perp^2\right),$$

$$\eta = \frac{n_\perp}{a_l}(q_{12} + q_a n_1^2), \quad q_a = q_{11} - q_{12} - q_{44}, \quad w = s_t - \frac{v_t^2}{a_t},$$

$$R_1 = n_1^2 + n_\perp^2 \frac{\epsilon_\perp}{\epsilon} - \frac{P^2\epsilon_\perp}{\pi\rho}(a_l\xi^2 + a_t\eta^2), \quad R_\perp = 1 - \frac{P^2\epsilon_\perp}{\pi\rho}\frac{q_{44}^2 n_1^2}{4a_t}.$$

Expression (18) consists of two parts: a striction part, proportional to P^2, and the "properly critical part"—the last term. These terms make different contributions to the anomaly of the displacement. On
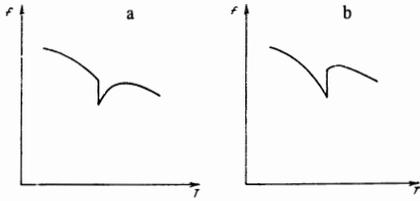
going over to the ferroelectric phase, each of the quantities $\epsilon_\parallel$ and $\epsilon_\perp$ is smaller than the value of ϵ of the high-temperature phase, therefore the stiffness to the critical oscillations below the transition increases jumpwise, a fact leading in the absence of terms with P to a jumpwise decrease of the amplitude of the oscillations and to an increase of the Mossbauer yield. With further lowering of the temperature, ϵ and the oscillation amplitudes continue to decrease, so that the observed temperature dependence of the Debye-Waller factor would have the form shown in Fig. a. However, the term with P^2 describes the growth of the oscillation amplitude as a result of the piezoelectric coupling between the acoustic and the critical branches, which decreases the elastic moduli. Therefore the resultant sign of the jump of the Debye-Waller factor of the point of transition depends on the ratio of the quantities $v_t^2 s_t^{-1}$ and $P^2 \epsilon_\perp$ at $T = T_0$. The subsequent temperature variation is also determined by the competition of these two terms. It can be shown that the described picture with contributions of different signs remains in force also when account is taken of the anisotropic terms s_a, v_a, and a_a.

The experimental results, especially in [3], apparently indicate that the normal situation is that shown in Fig. b, where the jump in the factor f at the transition point is negative, i.e., the striction jump is larger. This is followed by a drop of the amplitudes and by an increase of f, i.e., the second term in (18) increases with decreasing temperature more rapidly than the first.

It would be of interest to obtain more experimental material, so as to understand the degree to which such a situation is general. For the time being we can only note that, for example in the case of $BaTiO_3$, the increase of the second term of (18) relative to the first with decreasing T is natural, since the values of P and $\epsilon_\perp$ in this material vary sufficiently little below T_0, whereas $\epsilon_\parallel$ decreases rapidly [10], so that the ratio $\epsilon_\perp / \epsilon_\parallel$, which enters in R_1, increases rapidly.

We present also an expression for the anisotropy of the oscillations below T_0 in the case when $s_a = v_a = a_a = 0$. In the notation of (19) we have

$$\langle u_z^2 \rangle_. - \langle u_x^2 \rangle_. = \frac{T}{8\pi\rho}\left(\frac{\lambda}{w\epsilon_\perp}\right)^{1/2}\int_0^1 dz\left[\frac{P^2\epsilon_\perp}{\pi\rho}\left(\frac{(\xi n_\parallel - \eta n_\perp)^2 - 2(\xi n_\perp + \eta n_\parallel)^2}{\sqrt{R_1}}\right.\right.$$

$$\left.\left.+ \frac{q_{44}^2 n_\parallel^2}{4a_l^2 | R_\perp} \right) + \frac{v_t^2}{wa_l^2}((2 - 3n_\parallel^2)\sqrt{R_1} - \sqrt{R_\perp}) \right]. \quad (20)$$

The determination of the sign of expression (20) calls for more careful estimates. It can be noted, however, that R_1 increases with increasing $\epsilon_\perp / \epsilon_\parallel$, so that Equation (20) is positive at not too small a value of $v_t^2 s_t^{-1}$. Inasmuch as it is customary to assume that the Ti ion in $BaTiO_3$ is the most strongly coupled with the critical oscillation [10], the result cited in [2] concern-

ing the sign of the anisotropy of the oscillations of Ti agrees with the result expected from (20). However, the magnitude of the anisotropy, $\sim 50\%$, given in [2] seems too large. Estimates with the aid of (20) give for the anisotropy a value on the order of 0.01–0.1.

4. ORDER-DISORDER TRANSITIONS

In order-disorder transitions [10], the ions or the groups of ions have several symmetrical positions of equilibrium in the cell, which are statistically uniformly populated above the transition, and an asymmetry of the population appears below the transition, as in the well-known Ising model. The total potential in which the ion moves can be strongly anharmonic in this case, so that the picture of the transition differs from the case of transitions of the displacement type. We shall show that in this case, too, the probability of the Mossbauer effect can have anomalies in the transition region.

Earlier, in going over from (1) to formulas (2) and (3), we used the fact that the line width Γ is much smaller than the characteristic frequencies of the ion motion, which are the optical frequencies in the case of a transition of the displacement type. In our case, the characteristic time is the time τ within which the distribution of the ions in the cells relaxes to the equilibrium value. The Mossbauer effect will be sensitive to the transition only if the emission time Γ^{-1} is larger than or of the order of τ. In ferroelectrics, the order of magnitude of can be estimated experimentally from data on the dispersion of the dielectric constant [11,12]. The values of τ and Γ^{-1} vary in a wide range and can be commensurate.

For simplicity, we disregard as before the quadrupole and magnetic splittings, and confine ourselves to the case of small q, when the exponentials in (1) can be expanded in powers of qu:

$$W = \frac{\sigma_0\Gamma}{2\pi}\int_{-\infty}^{\infty} dt\exp\{i(\omega - \omega_0)t - \Gamma|t|\} \quad (21)$$
$$\times [1 + q_\alpha q_\beta(\langle u_\alpha(0)u_\beta(t)\rangle - \langle u_\alpha(0)u_\beta(0)\rangle)].$$

For a qualitative description of the phenomena connected with the transition, we assume that the correlation function of the coordinates decreases t in accordance with a simple exponential law, with a relaxation time τ [12]:

$$\langle(u_\alpha(0) - \bar{u}_\alpha)(u_\beta(t) - \bar{u}_\beta)\rangle = \langle u_\alpha(0)u_\beta(t)\rangle - \bar{u}_\alpha\bar{u}_\beta$$
$$= (\langle u_\alpha(0)u_\beta(0)\rangle - \bar{u}_\alpha\bar{u}_\beta)e^{-t/\tau}. \quad (22)$$

Formula (21) then yields

$$W = \frac{\sigma_0}{\pi}\left[\frac{\Gamma}{(\omega - \omega_0)^2 + \Gamma^2} + q_\alpha q_\beta(\langle u_\alpha(0)u_\beta(0)\rangle - \bar{u}_\alpha\bar{u}_\beta)\right.$$
$$\left.\times\left(\frac{\Gamma + 1/\tau}{(\omega - \omega_0)^2 + (\Gamma + 1/\tau)^2} - \frac{\Gamma}{(\omega - \omega_0)^2 + \Gamma^2}\right)\right]. \quad (23)$$

In the case of large relaxation times, $\Gamma\tau \gg 1$, the terms in the round brackets of (23) cancel out. In this case, the atom does not have time to jump from one potential well to the other during the emission time, and the result, naturally, will not be sensitive to the transition point. In the case when $\Gamma\tau \sim 1$, the frequency dependence of the probability is a superposition of two lines of different width. On approaching the transition point, the area of the narrow line, as will be

shown below, decreases somewhat, and the area of the broad line increases. Finally, in the case when $\Gamma\tau \ll 1$, the first term in the brackets is much smaller than the second in the frequency region $|\omega - \omega_0| \ll \tau^{-1}$. Then, just as in the case of transitions of the displacement type, the probability of absorption is expressed in terms of the correlation function of the ions and has a singularity at the transition point.

To clarify the character of this singularity, we shall use the model considered in [12,13], and discuss first the case of a nonferroelectric transition. The Hamiltonian of this model is of the form

$$H = \sum_r \frac{m\dot{x}_r^2}{2} + \sum_r U(x_r) - \frac{1}{2}\sum_{r\neq r'} V(r - r')x_r x_{r'}. \quad (24)$$

For simplicity we consider one-dimensional motion, x_r is the coordinate of the ion relative to the center of the cell, $U(x) = U(-x)$ is the anharmonic potential of the ion in the cell, the potential $V(r)$ is spherically symmetrical and has a large but finite radius of action r_0. The first-order phase transition consists of the appearance of an average displacement relative to the center at $T = T_c$. The transition occurs at high temperatures, so that the motion of the ions can be regarded as classical.

Using the methods of [13,14], the sought value of the correlation function can be written, in first approximation in r_0^{-3}, in the form

$$\langle (x-\bar{x})^2 \rangle = \left\{ \int \prod_l dx_r (x_r - \bar{x})^2 \exp\left[-\beta U(x_r) + \beta V_0 \bar{x}x_r \right.\right.$$
$$\left.+ \frac{\beta}{2}\sum_{r,r'}\tilde{V}(r-r')(x_r-\bar{x})(x_{r'}-\bar{x})\right]\right\}\left\{\int \prod_r dx_r \exp\left[-\beta U(x_r)\right.\right.$$
$$\left.\left.+ \beta V_0\bar{x}x_r + \frac{\beta}{2}\sum_{r,r'}\tilde{V}(r-r')(x_r-\bar{x})(x_{r'}-\bar{x})\right]\right\}^{-1}. \quad (25)$$

Here $V_0 = \sum_r V(r)$, and the effective interaction $\tilde{V}$, which is analogous to the Debye potential [14], takes into account the correlation of the particles in the first approximation:

$$\tilde{V}(r) = \sum_k \frac{V_k}{1 - \beta V_k \langle (x-\bar{x})^2 \rangle_0} e^{ikr}, \quad V_k = \sum_r V(r)e^{-ikr}. \quad (26)$$

The index $\langle \ldots \rangle_0$ denotes that the averaging is carried out at $\tilde{V} = 0$.

In the region of the transition, $\beta\tilde{V}(r)$ is a small quantity of the order of r_0^{-3} [13]. Expanding (25) in powers of $\beta\tilde{V}$, we get

$$\langle (x-\bar{x})^2 \rangle = \overline{x^2(T)} - x_0^2 + \frac{1}{2}[\langle (x-x_0)^4 \rangle_0$$
$$- (\overline{x^2}-x_0^2)^2] \sum_k \frac{\beta V_k}{1-\beta V_k(\overline{x^2}-x_0^2)}, \quad (27)$$

where $x_0 = \overline{x(T)}$ and $\overline{x^2(T)} = \langle x^2 \rangle_0$. In this approximation, the temperature of the transition is $T_c = V_0\overline{x^2(T_c)}$. Therefore in the region of small k and $|T - T_c|$, the denominator of the Green's function in (27) takes the form

$$1 - \beta V_k(\overline{x^2}-x_0^2) = \frac{k^2 r_0^2}{6} + a\frac{T-T_c}{T_c} + \frac{x_0^2}{\overline{x^2}};$$

$$r_0^2 = V_0^{-1}\sum_r r^2 V(r), \quad a = 1 + T_c\frac{d}{dT}\ln\overline{x^2(T)}|_{T=T_c}. \quad (28)$$

Thus, the sum over k in (27) has the same form as in (12), (14), and (16), and the anomaly of the quadratic

displacement is proportional to $|T - T_c|^{1/2}$. The expression in the square brackets of (27) is positive, and therefore the Mossbauer-effect probability always has a minimum at the transition point, in accordance with the decrease of the stiffness for the long-wave fluctuations near T_c. In the case of large r_0 under consideration, the second term in (27), below the transition, is proportional to $T - T_c$ and is larger than the third term by the ratio r_0^3: v_c. Therefore, in the region of applicability of the employed approximation [13], $T_c \gg |T - T_c| \gg v_c^2 r_0^{-6} T_c$, and the Mossbauer absorption probability below T_c is larger than at the same value of $|T - T_c|$ above the transition, and increases linearly with $T_c - T$.

In ferroelectrics, the order-disorder transitions are characteristic of uniaxial crystals. In these cases, the influence of the long-range dipole-dipole interaction is appreciable [12,13]. Thus, when $T > T_c$ the correlation function in the region of small k is given by the expression [13]

$$\langle x_k x_{-k} \rangle = \frac{\overline{x^2}}{k^2 r_0^2/6 + \lambda x^2(1/\varepsilon + n_x^2)/T_c}; \quad \lambda = \frac{4\pi e_{eff}^2}{v_c}, \quad n_x = \frac{k_x}{k}. \quad (29)$$

Here ε is the dielectric constant, which is proportional to $(T - T_c)^{-1}$, e_{eff} is the effective charge of the ion, and it is assumed that k is much larger than the reciprocal dimension of the sample L^{-1}. This formula differs from the analogous expression in (28) in that it has additional terms n_x^2 in the denominator, which suppress the correlation effects at small values of k. As a result, the anomalous part of the quadratic displacements near T_c will have a singularity weaker than a root singularity, namely $\sim |T - T_c| \ln |T - T_c|$:

$$f^2 = f^2(T_c)\left[1 + q^2\frac{\overline{x^4} - (\overline{x^2})^2}{\overline{x^2}}\frac{v_c}{r_0^3}\frac{3\sqrt{6}}{8\pi}\left(\frac{\lambda\overline{x^2}}{T_c}\right)^{1/2}\frac{\ln\varepsilon}{\varepsilon}\right]. \quad (30)$$

We note that in the case of order-disorder transitions, when the anharmonicity is not small, the singular part of f does not contain the small factor $T\varepsilon_{at}^{-1}$, which arises in the case of displacement-type transitions (12). Therefore the singularity, generally speaking, should be more noticeable. This can compensate in part the weaker character of the singularity (30), but a comparison with experiment calls for more careful estimates.

5. CONCLUSION

It is seen from the foregoing discussion that investigations of the Mossbauer effect in the region of phase transitions are of great interest. In the case of transitions of the displacement type, which can be quantitatively described, these investigations make it possible to measure the microscopic constants. In the case of order-disorder transitions, the Mossbauer measurements can give qualitative information concerning the relaxation times and the parameters of the transition.

Great interest attaches also to Mossbauer measurements in the region of nonferroelectric structural first-order transitions in crystals. The dielectric properties have no anomalies in this case. It is therefore not always clear whether the transition is close to a second-order transition, as in the case of displacement-type transitions in ferroelectrics, or else the phases above and below the transition differ

greatly, and the anomalies inherent in second-order transitions are missing.

It is seen from the foregoing that the characteristic minimum in the probability of the Mossbauer yield is connected precisely with the correlation effects, and with the decrease of the stiffness of the system to the long-wave correlations. On the other hand, in the case of a "normal" first-order transition, this probability should in general have only a jump at the transition point, and a kink in the temperature dependence, but it should not have drops on approaching the transition. Therefore relatively simple Mossbauer measurements can yield useful information concerning the character of the transition.

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