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Debye–Waller factors for incommensurate structures

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Abstract. The Debye–Waller factors $\exp[-W]$ for displacive-type incommensurate (IC) structures are calculated taking into account the correlation of the phases of the modulation. It is shown that $W \sim T_i^{1/2}|T - T_i|^{-1/2}$ and that IC satellites should not be observed in the immediate vicinities of transitions.

1. Introduction

The Debye–Waller factors for IC structures have been calculated by Overhauser [1] who showed that they should be very small near the IC transitions and that consequently the IC satellite reflections should not be observable there. However, Axe [2] showed that the values of the Debye–Waller factors should be close to unity even in the immediate vicinities of IC transitions. Later the Debye–Waller factors for the IC structures were also calculated by Krivoglaz [3], who obtained the same result as Overhauser. The discrepancy between the results of Overhauser and Axe arises from the introduction of different variables in these papers for the description of the fluctuations of the phase in the IC structure; this is elucidated in appendix A.

In the present paper we calculate the Debye–Waller factors by taking into account the spatial correlation of the phases of the IC modulation; the necessity for its consideration arises from the discrete character of the crystal structure. Our result differs from those of Overhauser [1], Axe [2] and Krivoglaz [3]. We show that the Debye–Waller factors may be very small for displacive-type IC structures within some temperature range near the transitions (but not as small as was predicted by Overhauser [1]) and hence that, instead of Bragg reflections, a diffuse scattering should be observed. Our result disagrees with the Debye–Waller factor calculation results given by Axe [2] (see appendix 1). The smallness of the Debye–Waller factors for IC structures is a consequence of the anomalous increase (divergence) of the phase fluctuation $\langle\varphi^2(R)\rangle$ on approaching the transition, and the result given by Axe [2] is, in principle, applicable only very far from the transitions.

First, it should be stressed that the result obtained by Overhauser [1] is not as radical as it was interpreted as being. According to our estimates given here, for order–disorder IC phases (which have, generally, small Curie constants and, consequently, large IC amplitudes), satellites are normally not observable in temperature regions of $\sim 10^{-1}$ K around second-order transitions for $T_i \sim 10^2$ K.

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We note the following.

- (i) Most of the observed IC structures are of order–disorder type.
- (ii) Temperature regions as small as 10^{-1} K around transitions are not generally accessible, because of the first-order character of real transitions.
- (iii) Some of the transitions are observed at low temperatures.
- (iv) Even in the case of displacive-type IC transitions, the Curie constant can sometimes be small (such a situation is discussed in section 4 for the IC phase of K_2SeO_4).

For displacive-type IC transitions, the result given by Overhauser indicates that IC satellites are not observable even for temperature regions as large as $\sim 10^2$ K around transitions for $T_i \sim 10^2$ K, while our result indicates that IC satellites are not observable in this case only in much smaller temperature regions of ~ 1 K around the transitions for $T_i \sim 10^2$ K. We also note that the estimates of the Debye–Waller factors are very sensitive to the specific values of the temperature, IC amplitude and other parameters, because of their exponential character and, in principle, the possibility of observation of satellites for displacive-type transitions in temperature regions of about 1 K around the transitions for $T_i \sim 10^2$ K should not be discounted.

In section 4 of this paper, experimental observations for quartz and for crystals of α -CuNSal (α -bis(*N*-methylsalicylideneiminato)copper(II)) are briefly discussed, as examples that provide confirmation of the theory presented.

2. Calculation of the phase fluctuations

The thermodynamic potential expansion for a crystal in the IC phase as a function of the order parameter and its spatial derivatives can be written as

$$\Phi = \int d\mathbf{R} \left\{ \frac{\alpha}{2} \eta^2 + \frac{g}{2} (\nabla \eta)^2 + \frac{g_1}{2} (\nabla^2 \eta)^2 + \frac{b}{4} \eta^4 \right\} \quad (1)$$

where the coefficients $g < 0$ and $g_1 > 0$ determine the value of the IC wavevector k . The IC structure which appears below the transition point may be described by the following modulation function:

$$\eta(\mathbf{R}) = \sqrt{2} \eta_0 \cos(\mathbf{k} \cdot \mathbf{R} + \varphi). \quad (2)$$

Substituting equation (2) into equation (1) and minimizing with respect to k and η_0 , we obtain an explicit expression for the thermodynamic potential for near equilibrium in terms of the IC modulation amplitude η_0 and the phase φ :

$$\Phi = \int d\mathbf{R} \left\{ \frac{\tilde{\alpha}}{2} \delta \eta_0^2 + \frac{\tilde{g}}{2} (\nabla \delta \eta_0)^2 + \frac{D}{2} \eta_0^2 (\nabla \varphi)^2 \right\} \quad (3)$$

where $\tilde{\alpha} = -2(\alpha + gk^2 + g_1k^4) > 0$, $D = g + 6g_1k^2 > 0$, $\tilde{g} = g + 4g_1k^2 > 0$ and the IC vector $k^2 = -g/2g_1$. $\delta \eta_0$ is the deviation of the IC modulation amplitude from its equilibrium value η_0 . In deriving equation (3), the term linear in $\nabla \varphi$ was omitted, since, from the condition $\partial \Phi / \partial k = 0$, i.e., $2g_1k^3 + gk = 0$, it follows that the coefficient of the term $\nabla \varphi$ is equal to zero. In equation (3) the strongly space-oscillating quantities proportional to $\cos(2\mathbf{k} \cdot \mathbf{R} + 2\varphi)$ have been omitted, suggesting that the remaining quantities in equation (3) vary more smoothly in space. This expression has a diagonalized form with respect to the phase and amplitude modes, and coincides with that derived by Golovko and Levanyuk [5].

When performing calculations of the statistical averages of $\varphi(\mathbf{R})$, $\varphi^2(\mathbf{R})$, ... using the potential (3), one should remember that the gradient $\nabla_k \varphi(\mathbf{R})$ in the direction of the IC

wavevector \mathbf{k} cannot be larger than the reciprocal-lattice vector \mathbf{b}_k in the same direction; otherwise the phase difference between two neighbouring lattice sites in the direction of \mathbf{k} would be more than π , and states with this feature do not exist. (Such states correspond to the oscillations of the IC modulation function (2) between two neighbouring lattice sites in the direction of \mathbf{k} . A more detailed discussion of such a situation is given in appendix B.) To incorporate this condition in the calculations, one can use a procedure similar to that followed in the calculations of the Debye correlation energy in plasma [4] (the random-phase approximation). To take into account the condition $|\nabla_k \varphi| \leq |\mathbf{b}_k|$ in the calculation of the continuous statistical integral of $\exp[-\Phi/T_i]$ (where Φ is given by equation (3) and T_i is the temperature under consideration) over $d\varphi(R_1) d\varphi(R_2) \cdots d\varphi(R_N)$, one should in each integration over $d\varphi(R_i)$ multiply the expression under the integral by the factor $\exp[-(\nabla_k \varphi(R_i))^2/(2b_k^2)]$. This factor is close to zero when $(\nabla_k \varphi(R_i))^2 > b_k^2$ and is close to unity when $(\nabla_k \varphi(R_i))^2 < b_k^2$.

So, it can be seen that the above-described procedure (after multiplication by the exponents $\prod_i \exp[-(\nabla_k \varphi(R_i))^2/(2b_k^2)]$ under the statistical integral) leads to the addition of the term $T_i(\nabla_k \varphi(R))^2/(2b_k^2)$ to the expression under the integral in (3). This term corresponds to the phase correlation energy and, as we shall see below, its role is significant in the calculations of the phase fluctuations. Transferring $\varphi(R)$ to the Fourier components, one obtains from equation (3) the thermodynamic potential related to the phase fluctuations for the case in which the IC vector \mathbf{k} coincides with the x -axis:

$$\Delta \Phi = \frac{1}{2} V \sum \left(D\eta_0^2 q^2 + \frac{T_i}{b_k^2} q_x^2 \right) |\varphi_q|^2.$$

Then the phase fluctuations are given by

$$\begin{aligned} \langle |\varphi_q|^2 \rangle &= \frac{T_i b_k^2}{V(Db_k^2 \eta_0^2 q^2 + T_i q_x^2)} \\ \langle \varphi^2(R) \rangle &= \frac{V}{(2\pi)^3} \int d\mathbf{q} \langle |\varphi_q|^2 \rangle \sim \frac{T_i^{1/2} b_k q_0}{D^{1/2} \eta_0} \end{aligned} \quad (4)$$

where q_0 is a certain cut-off parameter of the same order as the reciprocal-lattice vector \mathbf{b} and the integration has been carried out for the case where $Db_k^2 \eta_0^2 \ll T_i$. This condition holds, as we shall see below, for displacive-type transitions with temperatures $T_i \sim 10^2$ K in temperature regions of less than or of the order of 1 K around the transitions, and for order–disorder transitions in narrower temperature regions around the transitions. The temperature dependence of $\langle \varphi^2(R) \rangle$ can be obtained from equation (4), taking into account the fact that $\eta_0^2 \sim |T - T_i|$, and it has the form $\langle \varphi^2(R) \rangle \sim T_i^{1/2} |T - T_i|^{-1/2}$.

As can be seen from equations (4), the phase fluctuations $\langle |\varphi_q|^2 \rangle$ are significantly anisotropic. Since in temperature regions of 1 K around the transitions, η_0^2 takes the value $10^{-4} \eta_{at}^2$ (η_{at} is the amplitude of the IC modulation with displacements of an atomic order of magnitude) for displacive-type transitions and at transition temperatures $T_i \sim 10^2$ K (which is equal to $10^{-2} T_{at}$; T_{at} is of the atomic order of magnitude, $\sim 10^4$ K), the phase fluctuations in equation (4) for the vectors $\mathbf{q} \parallel \mathbf{k}$ and $\mathbf{q} \perp \mathbf{k}$ should differ by two orders of magnitude.

3. Calculation of the Debye–Waller factors

Since the IC modulation function in equation (2) is itself a component of the crystal's electron-density function, one can consider the diffraction (e.g., of x-rays) directly using this function. The scattering amplitude corresponding to the IC Bragg reflection is proportional

to the statistical average of the Fourier component of the modulation function, equation (2):

$$\left\langle \int d\mathbf{R} \eta_0 e^{\pm i(\mathbf{k} \cdot \mathbf{R} + \varphi)} e^{-i\mathbf{Q} \cdot \mathbf{R}} \right\rangle = V \eta_0 e^{-(\varphi^2(R))/2} \quad (5)$$

where the square of the last exponent is the so-called Debye–Waller factor [6], giving the attenuation of the Bragg reflection. (We should point out that the result of averaging in equation (5) is valid not only in the case of the Gaussian phase approximation [2], but also more generally [6].) The square of the function given as equation (5) gives the reflection intensity for the scattering vector $\mathbf{Q} = \pm \mathbf{k}$, which is attenuated due to the phase fluctuations. In equation (5) the fluctuations of the amplitude mode $\delta \eta_0$ are not taken into account, since their contribution to the Debye–Waller factors has the same form for any structural phase transition (not just IC ones) and is generally small.

For the calculation of the intensity of the satellite reflections near the main Bragg reflections (i.e., for large scattering vectors $\mathbf{G} + \mathbf{k}$), one should introduce explicitly the electron-density waves

$$f_G^i \exp[i\mathbf{G} \cdot (\mathbf{R} + \mathbf{u}(\mathbf{R}) + \mathbf{r}_i + \mathbf{u}^{(i)}(\mathbf{R}))]$$

for each sublattice i of the crystal [3], where: the vector \mathbf{R} gives the position of the lattice unit cells in the undistorted crystal; $\mathbf{u}(\mathbf{R})$ gives the displacements of the unit cells induced by the IC modulation (the acoustic displacements); the vector \mathbf{r}_i gives the position of the i th atom in the undistorted unit cell; $\mathbf{u}^{(i)}(\mathbf{R})$ gives the displacement of the i th atom from the site \mathbf{r}_i induced by the IC modulation, which belongs to the group of displacements of the optical mode of η -symmetry; f_G^i is the atomic structure factor; \mathbf{G} is a reciprocal-lattice vector. (We have mainly followed the method of calculation of the scattering amplitude for displacive-type lattice distortions given in reference [3].)

The components of the optical IC wave of displacements $\mathbf{u}^{(i)}(\mathbf{R})$ are proportional to the IC modulation function $\eta(\mathbf{R})$ and the amplitude $u_0^{(i)}$ of such optical modulation is always a linear function of η_0 (it is proportional to η_0). The optical IC wave of displacements generally induces an acoustic wave of IC displacements with the same period, due to some linear gradient acoustic–optical coupling in the thermodynamic potential. The components of such an acoustic IC wave of displacements $\mathbf{u}(\mathbf{R})$ (e.g., u_x and u_y) are modulated like the sine or like the cosine of $(\mathbf{k} \cdot \mathbf{R} + \varphi)$ and the amplitude of the modulation u_0 is proportional to η_0 . In what follows, we assume for simplicity that $\mathbf{u}(\mathbf{R}) = u_0 \cos(\mathbf{k} \cdot \mathbf{R} + \varphi)$, since whether the different components of $\mathbf{u}(\mathbf{R})$ are modulated like a sine or like a cosine is not essential in our consideration.

The electron-density wave can be introduced in the following form [3]:

$$f_G^i e^{i\mathbf{G} \cdot (\mathbf{R} + \mathbf{r}_i + \mathbf{u}(\mathbf{R}))} = f_G^i e^{i\mathbf{G} \cdot (\mathbf{R} + \mathbf{r}_i)} \sum_{n=-\infty}^{\infty} J_n(\mathbf{G} \cdot \mathbf{u}_0) e^{in(\mathbf{k} \cdot \mathbf{R} + \varphi + \pi/2)}.$$

(So as to keep our expressions simple, we have taken into account explicitly just the acoustic wave of displacements $\mathbf{u}(\mathbf{R})$, but the same consideration can be adopted for the optical wave of displacements $\mathbf{u}^{(i)}(\mathbf{R})$.) Taking into account the fact that $\mathbf{G} \cdot \mathbf{u}_0 \ll 1$ (since near the transitions the IC modulation amplitude is generally much smaller than the lattice parameter), one can retain in the above expression just the Bessel functions J_0 and $J_{\pm 1}$, and expand them into a series in $\mathbf{G} \cdot \mathbf{u}_0$ to obtain

$$f_G^i e^{i\mathbf{G} \cdot (\mathbf{R} + \mathbf{r}_i + \mathbf{u}(\mathbf{R}))} = f_G^i e^{i\mathbf{G} \cdot (\mathbf{R} + \mathbf{r}_i)} \left[1 + i \frac{(\mathbf{G} \cdot \mathbf{u}_0)}{2} e^{\pm i(\mathbf{k} \cdot \mathbf{R} + \varphi)} \right].$$

This expression gives the electron-density function in the i th sublattice distorted by the IC modulation in the first-order expansion with respect to the IC acoustic wave of displacements

$\mathbf{u}(\mathbf{R})$. (The same expansion can be used for the case of the optical wave of displacements $\mathbf{u}^{(i)}(\mathbf{R})$.)

To calculate the scattering amplitude, one takes the Fourier component Q of this expansion and carries out statistical averaging. It is easy to show that the averaged scattering amplitude is non-zero only for $Q = G$ (the main Bragg reflection) and $Q = G \pm k$ (IC satellite reflections). As a result of the statistical averaging, and taking into account the scattering from all sublattices, the IC satellite's scattering amplitude takes the form

$$V \left\{ \sum_i f_G^i e^{iG \cdot r_i} \right\} (G \cdot \mathbf{u}_0) e^{-\langle \varphi^2(R) \rangle / 2}$$

which is completely identical to equation (5), since the displacement amplitude $u_0 \propto \eta_0$.

So, the calculation of the Debye–Waller factors always reduces to the averaging of the same exponent: $\langle \exp[i\varphi(R)] \rangle = \exp[-\langle \varphi^2(R) \rangle / 2]$. In fact, the intensity given by the square of equation (5) coincides with the expression for the first-order satellite reflections induced by the IC waves of displacements given in references [1, 3]. However, the calculation of the average of $\langle \varphi^2(R) \rangle$ in the present paper is different from those in references [1, 3].

An alternative way to calculate the scattering amplitude for the IC satellite reflections is as follows [3]. One introduces the electron-density wave for the lattice unit cells, $F_G \exp[iG \cdot (\mathbf{R} + \mathbf{u}(\mathbf{R}))]$, where the vector \mathbf{R} gives the position of the unit cell in the undistorted crystal, $\mathbf{u}(\mathbf{R})$ is the acoustic displacement vector and F_G is the structure factor of the unit cell, which depends on the optical atomic displacements and, in the case of a small displacement, can always be introduced as the expansion $F_G = F_G^0 + \gamma_G \eta$ (F_G^0 is the structure factor of the undistorted unit cell and γ_G is a coefficient of the expansion). In other words, the optical atomic displacements enter the expression for F_G only through the symmetry parameter η [3]. Since the IC modulation function $\eta(R)$ is given by equation (2), the corresponding electron-density wave takes the form

$$F_G^0 e^{iG \cdot (\mathbf{R} + \mathbf{u}(\mathbf{R}))} + \gamma_G \eta_0 e^{i[(G \pm k) \cdot \mathbf{R} \pm \varphi]}$$

(where the acoustic displacements $\mathbf{u}(\mathbf{R})$ are proportional to $\eta(R)$), and the expression for the scattering amplitude and the Debye–Waller factor reduces to the form of equation (5).

Since we have calculated above, equation (4), the mean square of $\varphi(R)$, we can estimate the magnitude of the Debye–Waller factors. For example, at temperatures $T_i \sim 10^2$ K, for the square of the IC modulation amplitude η_0^2 taking the value $10^{-4} \eta_{at}^2$ in temperature regions of 1 K around the transitions in the case of displacive-type transitions, for $b_k \sim q_0$ and for the coefficient D being of the atomic order of magnitude, one obtains an estimate of ~ 10 for the dimensionless quantity $\langle \varphi^2(R) \rangle$ in the exponent of the Debye–Waller factor. We should note that this quantity can indicate attenuation of the satellite reflection by factors varying from 10 to much more than 10^{10} and observation of satellite reflections in such temperature regions around displacive-type IC transitions may thus be almost impossible. (To be more specific, such attenuation, being exponential, is very sensitive to the specific values of the parameters entering the exponent, e.g., the transition temperature and the IC amplitude, and therefore the situation in which the attenuation is by a factor of less than 10 is also possible.) For the order–disorder transitions, the amplitude η_0^2 is generally larger than that for the displacive-type transitions and can be estimated as $10^{-2} \eta_{at}^2$, and hence observation of the satellite reflections is possible even in the closer vicinity of the transition temperature ($\sim 10^{-1}$ K and even less, depending on the specific values of the parameters for each case).

The results for the Debye–Waller factors derived in the work of Overhauser and Krivoglaz [1, 3] can be reproduced from equation (4) if one neglects the phase correlation

in it (omitting the term in q_x^2). In such a case the value of $\langle \varphi^2(R) \rangle$ given by the integral in equation (4) will be $\langle \varphi^2(R) \rangle \sim T_i/\eta_0^2$ (in our notation). At temperatures $T_i \sim 10^2$ K, the mean square value of $\langle \varphi^2(R) \rangle$ will be of the order of 10^2 (for displacive-type structures in temperature regions of ~ 1 K around the transitions), which is much larger than that obtained above which takes into account the phase correlation, and thus the observation of IC satellites would be impossible in most cases. For the order–disorder transitions, using the estimate $\eta_0^2 \sim 10^{-2}\eta_{at}^2$, one obtains for the case considered by Overhauser that $\langle \varphi^2(R) \rangle$ is of the order of ~ 1 (and the satellites are observable) in temperature regions of about 1 K around the transitions for $T_i \sim 10^2$ K.

We shall now show that the Debye–Waller factor may remain small even in the case of a lock-in transition to some commensurate phase if the modulation amplitude is sufficiently small. Let us consider a lock-in transition to a phase with the structure vector $\mathbf{b}/3$. In such a case, a term $\sim \eta_0^3 \cos^3(\mathbf{k} \cdot \mathbf{R} + \varphi)$ should be incorporated in the thermodynamic potential (1). This gives a contribution to the potential (equation (3)) of the form $r\eta_0^3 \cos(3\varphi)$ (r is some coefficient). Such a contribution minimizes the potential (3) in the case where $\varphi = 2\pi/3$ for $r < 0$ and in the case where $\varphi = 2\pi/6$ for $r > 0$. Expanding $\cos(3\varphi)$ near its equilibrium value in terms of $\Delta\varphi = \varphi - 2\pi/3$ (or $2\pi/6$), one will obtain a contribution to the potential (3) of the form $(r/2)\eta_0^3 \Delta\varphi^2(R)$. Then, for the value of $\langle \varphi^2(R) \rangle$, one will obtain, instead of equation (4),

$$\langle \varphi^2(R) \rangle = \frac{V}{(2\pi)^3} \int d\mathbf{q} \frac{T_i b_k^2}{b_k^2 r \eta_0^3 + b_k^2 D \eta_0^2 q^2 + T_i q_x^2} \sim \frac{T_i^{1/2} b_k}{D \eta_0} (\sqrt{D q_0^2} - \sqrt{r b_k^2 \eta_0}). \quad (6)$$

Due to the presence of $\sqrt{\eta_0}$ in the last term of equation (6), $\langle \varphi^2(R) \rangle$ rapidly decreases on cooling, but, as is easy to see, for small values of η_0 it may be large enough to make the satellite reflections invisible. (Generally, the third-order term in the Landau potential expansion induces a strong first-order phase transition with $\eta_0^2 \sim r$, but nevertheless the above-described situation can be realized in the case of a sufficiently small coefficient r .)

To derive equation (6), we have used an expansion of $\cos 3\varphi$ near its equilibrium value, assuming that $\Delta\varphi \ll 1$. But now one can see that, in the immediate vicinities of transitions, the value of equation (6) is greater than unity. Nevertheless, our estimates of the Debye–Waller factor following from equation (6) remain correct, since when the condition $\Delta\varphi \ll 1$ does not hold, the fluctuations $\langle \varphi^2(R) \rangle$ are even larger than those given by equation (6). The latter can be checked by using the function $\cos 3\varphi$ directly (instead of its expansion) to obtain the estimates. The thermodynamic potential (1), containing the term $r\eta_0^3 \cos 3\varphi$ (instead of $r\eta_0^3 \Delta\varphi^2$), now increases less for large fluctuations of φ , since $|r\eta_0^3 \cos 3\varphi| < |r\eta_0^3 \Delta\varphi^2|$ at large values of $\Delta\varphi$. Hence, the fluctuations given by equation (6) are smaller than they should be in this case.

For the higher-order lock-in terms (higher than third order), the corresponding contribution to the Debye–Waller factors should be much smaller, and their behaviour should be more similar to that of the Debye–Waller factors of the IC phases described by equations (4) and (5).

In high-temperature structure studies of the solid solutions $\text{CaF}_2\text{–LnF}_3$ [7] (where Ln is a lanthanide element), undergoing phase transitions involving multiplication of the size of the lattice cell by factors of 7 or 13, instead of satellite reflections a diffuse scattering of x-rays (below the transition) was observed for some elements of the Ln group. The transitions to the 7-fold- and 13-fold-increased lattice cells have been well studied [8] and they originate from the third- and fourth-order lock-in terms in the thermodynamic potential expansion. So, we can see that, even in the case of order–disorder-type transitions, in

view of the lock-in terms in the potential expansion, the above-described effect can be very significant at high temperatures.

4. Discussion

We briefly discuss the spatial distribution of the scattering of x-rays (or neutrons) by phase fluctuations, following from the above development, and the experimental observations for crystals of K_2SeO_4 , $\alpha\text{-CuNSal}$ and quartz.

The intensity of the diffuse scattering of x-rays or neutrons by phase fluctuations [3] in some direction \mathbf{q} is proportional to $\eta_0^2 \langle |\varphi_{\mathbf{q}}|^2 \rangle$. For vectors \mathbf{q} of small magnitude, the intensity $\eta_0^2 \langle |\varphi_{\mathbf{q}}|^2 \rangle$ contributes to the central peak, since the phase fluctuations for small values of q are overdamped [5]. In the case considered by Overhauser [1], the phase fluctuations are $\langle |\varphi_{\mathbf{q}}|^2 \rangle \sim T_i / (D\eta_0^2 q^2)$ and the scattered intensity is proportional to $T_i / (Dq^2)$. If the coefficient D is not small (i.e., is of the atomic order of magnitude), this intensity is of the same order of magnitude as the diffuse intensity induced by acoustic vibrations near any main Bragg reflection: $I \sim T_i / (cq^2)$, where c is of the order of magnitude of the crystal's elastic constants [6]. (The latter contribute to the conventional Debye–Waller factors attenuating the main Bragg reflections.)

As follows from our consideration (see equation (4)), the fluctuations of the phase are significantly anisotropic. For the direction of the IC vector (q_x in equation (4)) the phase fluctuations are given by $\langle |\varphi_{q_{\parallel}}|^2 \rangle \sim 1/q_{\parallel}^2$ and for the direction perpendicular to the IC vector $\langle |\varphi_{q_{\perp}}|^2 \rangle \sim T_i / (D\eta_0^2 q_{\perp}^2)$. So, for the direction of the IC vector, the scattered intensity is proportional to $\sim \eta_0^2 / q_{\parallel}^2$ and it increases with temperature decrease as $\eta_0^2 \sim |T - T_i|$. In the direction perpendicular to the IC wavevector, the corresponding intensity takes the form $\sim T_i / (Dq_{\perp}^2)$ and is expected to be much stronger. For that direction it should have the same order of magnitude as the diffuse scattering near the main Bragg reflections (if the coefficient D is not small).

The IC phase in K_2SeO_4 ($T_i = 130$ K) is interpreted as being of displacement type, although it is the exception [15] in the family of 11 order–disorder IC structures (such as that of Rb_2ZnCl_4). In this crystal, no significant attenuation of the satellites or anomalous diffuse scattering is observed. The temperature of this transition is rather low (130 K) and, in principle, the satellites may not be strongly attenuated. Also, the Curie constant α_0^{-1} (η_0^2 is proportional to $\alpha_0(T_i - T)$) can be relatively small for some displacive-type transitions. In particular, it should manifest itself as a relatively strong fluctuation anomaly over a wide temperature range above T_i , since the first fluctuation correction to the heat capacity is proportional to $T_i^2 \alpha_0^{3/2} |T - T_i|^{-1/2}$. It is interesting to note that the anomaly in the heat capacity of K_2SeO_4 is very strong, like that for a displacive-type transition. It is of the same order of magnitude as the anomaly for typical order–disorder IC transitions in Rb_2ZnBr_4 and Rb_2ZnCl_4 over a wide temperature range of about 10 K above the transition temperature (see figure 1 in the paper by Ishibashi [15]). So, we consider that the satellites in K_2SeO_4 are observed due to the relatively low transition temperature, large IC amplitude (i.e., large α_0) and, consequently, large Debye–Waller factor.

Finally, we briefly comment on two experimental observations, for crystals of $\alpha\text{-CuNSal}$ and quartz, relevant to the present theory. The strong diffuse scattering of x-rays observed in the IC phase of $\alpha\text{-CuNSal}$ was identified [9] as a scattering by phase fluctuations. The intensity of the diffuse scattering by phase fluctuations appeared to be stronger than the scattering near the main Bragg reflections. The IC transition temperature for this crystal is assigned as 305 K. However, we note that a finite value of the IC amplitude is observed

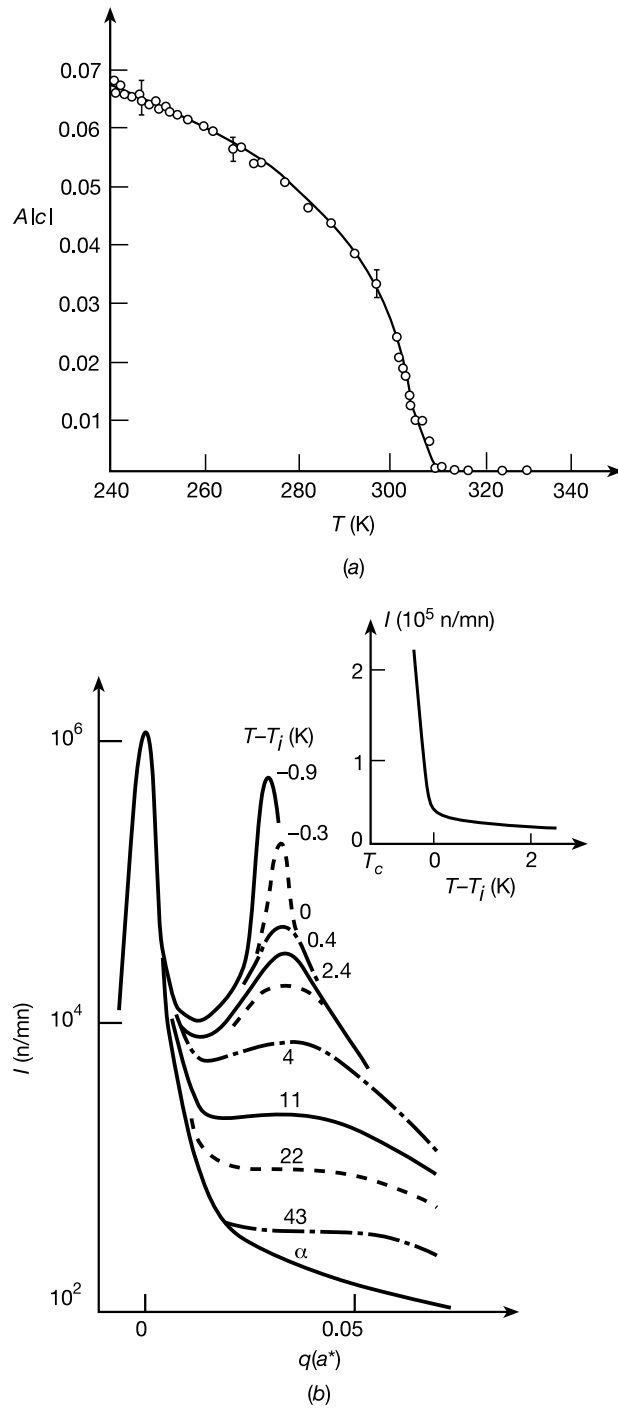


Figure 1. (a) The IC modulation amplitude for α -CuNSal measured by Adlhart *et al* [9] by means of x-ray diffraction. Note that the IC transition temperature is identified as $T_i = 305$ K, although a finite value of the amplitude is observed even at 310 K. (b) The intensity of the quasielastic diffuse scattering of neutrons measured by Dolino *et al* [10] near the (1 1 0) Bragg reflection in quartz. Different peaks correspond to temperatures above and below $T_i = 850$ K.

even at 310 K, as follows from diffraction measurements [9] (see figure 1(a)). As can be seen from figure 3 of [9], the intensity of the diffuse scattering at $T = 323$ K is comparable with the satellite intensity at 303 K. We consider that the IC modulation in this crystal exists at temperatures significantly higher than the value identified, $T_i = 305$ K, but that it is strongly attenuated by the Debye–Waller factor.

In figure 1(b) the neutron scattering peaks observed by Dolino *et al* [10] near the $\alpha \leftrightarrow \beta$ transition of quartz are depicted. These peaks correspond to the IC vector $k \approx 0.035b$. Comparing the intensities of the peaks in figure 1(b), e.g., at $T_i + 0.4$ K (the diffuse scattering) and at $T_i - 0.3$ K (the satellite intensity), one can see that they differ by a factor of only 5.5. (Even for $T_i + 4$ K and $T_i - 0.9$ K, the intensities differ by only a factor of about 40.) However, the intensity of the diffuse scattering is proportional to the scattering volume V , while the intensity of the satellite reflection is proportional to V^2 , and the latter should be much stronger [6]. The IC transition temperature was determined in reference [10] as the point at which the sharp increase of the intensity depicted in the inset of figure 1(b) occurs, and it has the value 850 K. We consider that all of the peaks observed in figure 1(b) correspond to IC satellite reflections strongly attenuated by the Debye–Waller factor and that the IC phase in quartz exists at temperatures higher than $T_i = 850$ K. In other words, since the IC amplitude (the order parameter of the transition) is proportional to $\eta_0 \sim I^{1/2}$, figure 1(b) should be considered as evidence that the value of η_0 is finite (not as small as a fluctuation) at temperatures higher than 850 K also. (Comparing $\eta_0 \sim I^{1/2}$ in figure 1(b) at the temperatures $T_i + 4$ K and $T_i - 0.9$ K, one can see that they differ by factors of only 6–7.)

Existence of the IC phase in quartz at temperatures higher than $T_i = 850$ K is also consistent with the observation in the same temperature range of the central peak [11] and the mode at 355 cm^{-1} in the Raman scattering [12], which are symmetry forbidden for the β -phase.

Appendix A

We reproduce here the procedure for the introduction of variables for the description of fluctuations in the IC phase used by Axe [2] and demonstrate the origin of the discrepancy between the Debye–Waller factors calculated by Axe and those obtained in the present paper (or by Overhauser [1]). The calculations carried out by Axe are based on the description of the phason and amplitude modes given by Bruce and Cowley [13, 14], which is applicable, as we shall see below, only in the case of very small fluctuations of the phase.

The IC displacement wave u_l introduced on page 4185 of the paper by Axe [2] can be presented as follows:

$$u(R) = Q_{q_0} e^{iq_0 \cdot R} + \text{CC} = \eta_1 \cos q_0 \cdot R + \eta_2 \sin q_0 \cdot R. \quad (\text{A1})$$

The variables η_1 and η_2 are introduced in the above equation as the real and imaginary components of the complex amplitude Q_{q_0} .

So, equation (17) in the paper by Axe for the energy of the IC displacement wave in our notation takes the form

$$F = \frac{\tilde{\alpha}}{2}(\eta_1^2 + \eta_2^2) + \frac{b_1}{4}(\eta_1^2 + \eta_2^2)^2 \quad (\text{A2})$$

where the equilibrium value of $\eta_1^2 + \eta_2^2 = -\tilde{\alpha}/b_1$.

The equations of motion for the simplest case of spatially homogeneous fluctuations $\delta\eta_1$ and $\delta\eta_2$ near their equilibrium values η_1 and η_2 can be obtained from the quadratic form of

the variation of the energy:

$$\delta F = b_1(\eta_1 \delta\eta_1 + \eta_2 \delta\eta_2)^2. \quad (\text{A3})$$

This expression can be considered as the potential energy for the spatially homogeneous fluctuations of the phase and amplitude of the IC modulation function (A1) around the equilibrium values of the IC amplitude $\eta_0^2 = \eta_1^2 + \eta_2^2 = -\tilde{\alpha}/b_1$ and a certain phase of the IC wave given by $\varphi_0 = \arctan(\eta_1/\eta_2)$.

So, expression (A3) can be used to obtain the equations of motion for the variables $\delta\eta_1$ and $\delta\eta_2$, as was done by Axe [2] and Bruce and Cowley [13, 14].

For the diagonalization of the equations of motion based on the potential (A3), it is sufficient to diagonalize the quadratic form (A3) and to obtain its eigenvectors as linear combinations of $\delta\eta_1$ and $\delta\eta_2$. As is easy to check, the linear combinations which diagonalize the quadratic form (A3) are

$$\xi_{\parallel} = \frac{\eta_1 \delta\eta_1 + \eta_2 \delta\eta_2}{\sqrt{\eta_1^2 + \eta_2^2}} \quad \text{and} \quad \xi_{\perp} = -\frac{\eta_2 \delta\eta_1 - \eta_1 \delta\eta_2}{\sqrt{\eta_1^2 + \eta_2^2}}. \quad (\text{A4})$$

In the case of spatially homogeneous fluctuations of ξ_{\parallel} and ξ_{\perp} , their frequencies are respectively $\omega^2 = -2\tilde{\alpha}/m$ and $\omega^2 = 0$, which correspond to the amplitude and phason modes. (In the notation of Bruce and Cowley [13, 14], $\xi_{\parallel} = P_1$ and $\xi_{\perp} = P_2$.)

However, using the notation $\eta_1 = \eta_0 \cos \varphi$ and $\eta_2 = \eta_0 \sin \varphi$, one can see that for the simplest case, $\delta\eta_0 = 0$ (i.e., considering only fluctuations of the phase at the fixed amplitude η_0), expressions (A4) take the form

$$\xi_{\parallel} = \eta_0[\cos(\varphi - \varphi_0) - 1] \quad \xi_{\perp} = \eta_0 \sin(\varphi - \varphi_0). \quad (\text{A5})$$

Representing $\cos(\varphi - \varphi_0)$ as $1 - (\varphi - \varphi_0)^2/2 + \dots$, one can see that the mode ξ_{\parallel} is independent of the fluctuations of the phase only to lowest order of the expansion in terms of $\varphi - \varphi_0$; i.e., on taking the expansion to higher order, the energy becomes dependent on the absolute value of the phase φ . This means that the variables $\delta\eta_1$ and $\delta\eta_2$ used by Axe [2] and by Bruce and Cowley [13, 14] are formally acceptable for the description of the fluctuations of the IC modulation only in case of small fluctuations of the phase, $\langle(\varphi - \varphi_0)^2\rangle \ll 1$.

We note that the energy of the IC modulation should always be independent of the absolute value of the phase, and this is the case not only in the harmonic approximation. The variables ξ_{\parallel} and ξ_{\perp} are non-linear functions of φ (they are linear functions of $\cos(\varphi - \varphi_0)$ and $\sin(\varphi - \varphi_0)$), and hence the harmonic approximation in terms of the variables ξ_{\parallel} and ξ_{\perp} is automatically anharmonic as a function of φ . In other words, the expression for the energy (A3) is diagonalized not with respect to the phase and the amplitude, but with respect to some non-linear functions of the phase and amplitude.

So, the introduction of the variables $\delta\eta_1$ and $\delta\eta_2$ as the normal coordinates for the fluctuations of the IC modulation is incorrect from the outset, since it does not give a gapless dispersion law for the phason mode and does not allow one to apply successive perturbation theory for the anharmonic corrections (since the energy depends on the absolute value of the phase in each order of expansion in terms of ξ_{\parallel}).

Introducing new notation based on $\eta_0 \cos(\mathbf{k} \cdot \mathbf{R} + \varphi) = \eta_0 \cos \mathbf{k} \cdot (\mathbf{R} + \mathbf{T})$, where $\varphi = \mathbf{k} \cdot \mathbf{T}$ and the vector \mathbf{T} gives the displacement of the IC wave as a whole, one can see that the form of the energy expression (3) appears to be equivalent to that in classical elasticity theory (it depends only on the spatial derivatives of the displacement vector \mathbf{T}). In other words, the introduction of the phase into the energy expression is similar to the introduction of the acoustic displacements in the elastic energy. This being so, the approach used by Bruce and Cowley [14] appears to be an alternative to that followed in classical elasticity

theory and can be interpreted as follows. Let us consider a crystal with the undistorted electron-density function $\rho_0(\mathbf{R}) = \sum F_G \exp[i\mathbf{G} \cdot \mathbf{R}]$. The acoustic displacements \mathbf{u} distort the function $\rho_0(\mathbf{R})$ and they are equivalent to the changes in the phases φ_G of the complex amplitudes F_G given by $\Delta\varphi_G = \mathbf{u} \cdot \mathbf{G}$. The approach used by Bruce and Cowley [14] introduces into the energy expression, instead of the acoustic displacements, the real and the imaginary components $\delta F'_G$ and $\delta F''_G$ of the fluctuations of the complex amplitude F_G (similar to $\delta\eta_1$ and $\delta\eta_2$ in equation (A3)). However, these variables are never used as the normal coordinates for description of the acoustic phonons (see also the procedure for the introduction of the variables in Landau theory) and such an approach does not give a gapless dispersion law for the acoustic phonons. To demonstrate the latter, it is sufficient to consider a simple case, i.e., a crystal with the electron-density function $\rho_0(\mathbf{R})$ having only one non-zero amplitude F_G , and to expand its energy (like in equations (A2), (A3)) in terms of $\delta F'_G$ and $\delta F''_G$ for a fixed value of the modulus $|F_G| = \text{constant}$.

To calculate the statistical sum or statistical averages in terms of the variables ξ_{\parallel} and ξ_{\perp} , the Jacobian of the transformation from the normal coordinates $\delta\eta_0$ and φ to ξ_{\parallel} and ξ_{\perp} should be included under the statistical integral. The averaging procedures in the paper by Axe [2] are carried out directly, without calculation of the Jacobian, but the non-linear dependence of the coordinates ξ_{\parallel} and ξ_{\perp} on the normal coordinate φ would have a significant impact on such calculations. In particular, the statistical averaging of the exponent in equation (5) (and in the calculations by Axe [2]) is subject to the validity of Wick's theorem [6], which should not hold (in general) for the variables used by Axe. The latter should be considered as the main reason for the discrepancy between the result obtained by Overhauser and that obtained by Axe.

Appendix B

The necessity for the introduction of the phase correlation in the calculations can be demonstrated as follows. The fluctuations of the phase (without taking into account the phase correlation) were calculated by Golovko and Levanyuk [5] and they have the form

$$\langle |\varphi_q|^2 \rangle = \frac{T_i}{VD\eta_0^2 q^2} \quad (\text{B1})$$

in our notation. One can calculate the statistical mean value of

$$\langle (\nabla\varphi(R))^2 \rangle = \frac{V}{(2\pi)^3} \int d\mathbf{q} q^2 \langle |\varphi_q|^2 \rangle \sim \frac{T_i q_0^3}{D\eta_0^2} \quad (\text{B2})$$

and see that it increases very strongly on approaching the phase transition. However, as was already mentioned (see also below), the value of $\langle (\nabla\varphi(R))^2 \rangle$ in the direction of the IC vector cannot be very large and this restriction should be invoked in the calculation of the statistical averages. In other words, the calculation of the statistical averages of $\langle |\varphi_q|^2 \rangle$ by Golovko and Levanyuk [5] is valid only if the condition $\langle (\nabla_k\varphi(R))^2 \rangle < b$ holds, i.e., far from the displacive-type transition temperature.

A similar situation never arises for conventional (not IC) phase transitions, since for the order parameter η the condition of smallness of $\langle (\nabla\eta(R))^2 \rangle$ always holds; that is,

$$\langle (\nabla\eta(R))^2 \rangle = \frac{T_i}{(2\pi)^3} \int d\mathbf{q} q^2 \frac{1}{\alpha + gq^2} \sim \frac{T_i q_0^3}{g} \quad (\text{B3})$$

can be estimated as T_i/T_{ar} , which is always smaller than 10^{-2} , and the corresponding contribution (correction) to the potential is negligibly small, in contrast with that of the mean square $\langle (\nabla\varphi(R))^2 \rangle$.

To show that $\langle (\nabla\varphi(R))^2 \rangle$ cannot be very large in the direction of the IC vector (although this is not the case for other directions), we consider first a one-dimensional linear chain of N atoms in the x -direction, with the IC modulated displacements $u(R) = u_0 \cos(kx + \varphi_1)$. It is obvious that for two neighbouring atoms in the positions x_i and x_{i+1} with the phases $\varphi_1(x_i)$ and $\varphi_1(x_{i+1})$, changes in $\varphi_1(x_{i+1}) - \varphi_1(x_i)$ by $2\pi, 4\pi, \dots$ do not change the state. So, for the calculation of the statistical sum for the linear atomic IC chain, to avoid multiple counting of the same states, one should introduce the restriction $|\partial\varphi/\partial x| < b$ in the calculation procedure.

In the case of two parallel linear chains, modulated as $u(R) = u_0 \cos(kx + \varphi_1)$ and $u(R) = u_0 \cos(kx + \varphi_2)$ respectively, the restriction of the smallness of the fluctuation, $|\partial\varphi/\partial x| < b$, remains valid, but there should be no restriction on the difference $\varphi_1(x_i) - \varphi_2(x_i)$ between the phases of two parallel chains. For example, in the case where $\varphi_1(x) = 0$ and $\varphi_2(x) = ax$ (a is some coefficient), the difference $\varphi_2(x_i) - \varphi_1(x_i) = ax_i$ can be very large for large x_i .

Since a crystal is composed of $N \times N$ linear atomic chains, it is now obvious that the restriction should be introduced only for the fluctuations $\langle (\nabla\varphi(R))^2 \rangle$ along the direction of the IC vector, as was done in the calculations leading to equation (4).

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