Debye-Waller factors for incommensurate structures

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Overhauser has predicted that thermal fluctuations in the phase of the modulation wave will give rise to large Q-independent Debye-Waller factors for incommensurate diffraction satellites. We show that a key to understanding this surprising result is a spatial modulation of the fluctuation of atomic positions in an incommensurate solid. The range of validity of Overhauser's assumptions is discussed and an alternate calculation which should be valid over a larger range of relative fluctuation amplitude is presented. This new calculation predicts the existence of fluctuation- and displacement-dominated regimes, in which higher-order diffraction satellites display qualitatively different behavior.

I. INTRODUCTION

There are by now many known examples of solids in which the regular crystalline spatial arrangement has been disturbed by small-amplitude static displacements of the atoms with a period incommensurate with the underlying crystalline periodicity.[1] For the purposes of this paper, we say that such materials have "incommensurate structures" although the more cumbersome terminology "displacively modulated incommensurate structures" is more proper, acknowledging the possibility of composition and magnetic modulation and of incommensurate intergrowth or overlayer structures with which the present paper is not concerned.

In the absence of impurity and surface-pinning effects, the phases of the modulation waves relative to the lattice are not fixed by energetic considerations in incommensurate structures. This means that an excitation consisting of a uniform phase shift is a zero-energy "Goldstone mode" of the system. Furthermore, it can be shown that the energy necessary to create a spatially slowly varying change in the local phase of the modulation goes to zero as the inverse of the wavelength of distortion. In other words, there should exist in incommensurate structures one or more lattice excitation branches with linear dispersion, $\omega(q) \sim q$, *in addition to* the three normal acoustic phonon branches. Since these modes, which have inevitably been termed "phasons," represent a new and characteristic feature of incommensurate structures, and since their gapless nature guarantees their substantial thermal excitation, it is necessary to investigate their influence on various thermal and transport properties.

In 1971, Overhauser[2] briefly discussed the influence of phason modes on the thermal fluctuations of the atoms as manifested in diffraction experiments and came to some surprising conclusions. In a normal solid, the effect of phonon fluctuations is to reduce the intensity of Bragg reflections by a "Debye-Waller (DW) factor" e^{-2W}, where $W = \frac{1}{3}\langle(\vec{Q}\cdot\vec{u})^2\rangle$, u is the magnitude of the fluctuation of atomic position, and Q is the length of the reciprocal lattice vector specifying the Bragg reflection. Making a number of seemingly plausible assumptions, Overhauser found that phason fluctuations should have *no effect* upon the parent Bragg reflections, i.e., those reflections which arise from the underlying unmodulated lattice. However, the modulation gives rise to a series of satellite reflections and Overhauser concluded that the effect of phason fluctuations on these satellites was of the familiar exponential form $e^{-2W'}$, but with W' *independent of* Q and given approximately by $W' \approx (n^2/Q^2A^2)W$, where A is the amplitude of the static modulation wave and n the order of the satellite. This result is surprising not only for the unusual functional form, but because it implies DW corrections that are not only large, but which, as Overhauser pointed out, could easily reduce the satellite intensities below the limit of observability.

While Overhauser's calculation is mathematically straightforward, the result is not easy to understand; i.e., it is not readily assimilated in terms of our familiar conceptions of how thermal fluctuations ought to behave, and thus seems "mysterious." And to the extent that it is difficult to see the underlying physics, it is also difficult to assess the true role of the various assumptions on which the calculation is based. These assumptions are, as we have stated, rather plausible, but we shall see that they are not uniquely so. Also at present there are a number of examples, unknown in 1971, of incommensurate structures for which it is believed that $(QA)^2 \sim \frac{1}{100}$, for which satellite reflections have been observed, arguments of the preceding paragraph notwithstanding. This again suggests that a reexamination of the question of DW factors for incommensurate structures is in order.

In Sec. II we rederive in a somewhat different way Overhauser's basic results. The fundamental assumption involved is seen to be that the relevant thermal fluctuations act in such a way as to cause the modulation of every atom to experience a random phase having a Gaussian distribution. It is possible to gain additional insight into the nature of the results of this random Gaussian phase approximation (GPA) by a comparison with a conventional expansion of the DW factor in powers of atomic displacements. More specifically, a consideration of the behavior of the mean-square fluctuation of the individual atoms provides the key to understanding the peculiar features of Overhauser's results.

The conventional expansion procedure leads naturally to a different approximation scheme, that of random Gaussian displacements (GDA). This approximation, which is developed in Sec. III, has a number of attractive features. Unlike the GPA, it has a well-defined theoretical basis. It is easily modified to include the effect of simultaneous but independent fluctuations of amplitude and phase of the modulation wave.

In Sec. IV, we compare the GPA and GDA predictions. The predictions are identical in the small-Q, small-fluctuation limit. There are both quantitative and qualitative differences for large fluctuations. In particular, the GDA predicts a new regime in which the $n \geq 2$ satellite intensities are dominated by spatial modulation of the fluctuations. We conclude with a few brief comments on existing experiments.

II. THE GAUSSIAN PHASE APPROXIMATION

In the spirit of Overhauser's original discussion, we simplify the problem by supposing that we are dealing with (a) a Bravais lattice (one atom per unit cell) and (b) mean displacements that can be specified by a single sinusoidal modulation wave. The second restriction is more serious in that it is now known that "umklapp" potential terms exist which inevitably distort simple sinusoidal modulation by adding higher harmonic modulations. The period of the modulation is also pulled toward that of the commensurate umklapp-potential value. However, an analysis[3] of this effect in the continuum approximation shows that significant nonsinusoidal distortion occurs only if the observed spatial period is quite close to a simple (i.e., low-order) commensurate one, either accidentally or through the pulling effect of a strong umklapp potential. Thus, while in principle the nonsinusoidal nature of the modulation may greatly complicate the problem, in reality there will be many instances in which the sinusoidal approximation should be practical and adequate.

The intensity and location in reciprocal space of Bragg scattering is determined by the elastic structure factor $F(\vec{Q})$, the Fourier transform of the atomic density. If we denote the instantaneous position of the lth atom (the atom assigned to the lattice site $\vec{l} = \sum_i l_i \vec{a}_i$, where $\vec{a}_i$ are primitive lattice vectors) by

$$\vec{x}_l = \vec{l} + \vec{u}_l , \qquad (1)$$

then

$$\begin{aligned} F(\vec{Q}) &= \int d^3x \, \langle \rho(\vec{x}) \rangle e^{i\vec{Q}\cdot\vec{x}} \\ &= \int d^3x \left\langle \sum_l \delta(\vec{x}-\vec{x}_l) e^{i\vec{Q}\cdot\vec{x}} \right\rangle \\ &= \sum_l e^{i\vec{Q}\cdot\vec{l}} \langle e^{i\vec{Q}\cdot\vec{u}_l} \rangle , \end{aligned} \qquad (2)$$

where $\langle \cdots \rangle$ denotes the usual thermodynamic ensemble average. Again, following Overhauser, we assume that the effect of the thermal fluctuations of the modulation occurs in the phase rather than in the amplitude A of the modulating function. This leads us to write

$$u_l = A \cos(\vec{q}_0 \cdot \vec{l} - \phi_l - \theta_0) = A \cos(\theta_l - \phi_l) , \qquad (3)$$

where $\theta_l = (\vec{q}_0 \cdot \vec{l} - \theta_0)$. [We shall usually write relations for the magnitude of the displacement vector $\vec{u}_l = u_l \vec{e}$. In this way, we reserve the notation $\vec{A}$ for the complex vector (Fig. 1)]. The thermal fluctuations are specified by ϕ_l, assumed to have a Gaussian distribution, i.e., for any quantity $f(\phi_l)$,

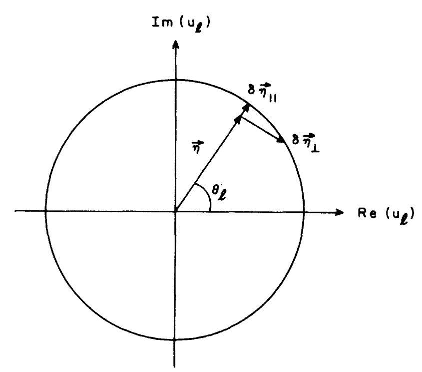

FIG. 1. Geometrical representation of the complex variables used to describe displacement fluctuations in an incommensurate structure. The circle of radius A is drawn in to emphasize that even if the amplitude A does not fluctuate, the magnitude of the vector $\vec{\eta}$, which defines the mean displacement $\langle u_l \rangle = \eta \cos\theta_l$, will in general be less than A.

$$\langle f(\phi_l)\rangle = \int P(\phi_l) f(\phi_l) d\phi_l$$

with (4)

$$P(\phi_l) = (2\pi\langle\phi^2\rangle)^{-1/2} \exp[-\tfrac{1}{2}(\phi_l^2/\langle\phi^2\rangle)] ,$$

so that $\langle f(\phi_l)\rangle$ is independent of l and specified by a single parameter $\langle\phi^2\rangle$, the mean-square fluctuation in ϕ_l. Because of its unique status as the Goldstone variable, we have in Eq. (3) explicitly singled out an overall uniform phase shift θ_0. We must, at the end of the calculation, separately consider the distribution of θ_0. (This situation is exactly analogous to that of a Heisenberg magnet, where we must separately consider the distribution of moment directions as they change from one macroscopic domain to the next.)

We cannot give a complete microscopic justification of the GPA, i.e., of Eqs. (3) and (4), a fact which must be taken as a serious weakness of the approximation. We will see in the following section that there are circumstances in which phase fluctuations are much more important than amplitude fluctuations, although this is not always the case. But as to the Gaussian distribution of ϕ_l, we can only make the following plausible argument. Suppose that the proper elementary excitations are collective Bloch wave phasons, so that

$$\phi_l = \sum_{\vec{q}} \phi(\vec{q}) e^{i\vec{q}\cdot\vec{l}} .$$

By the central limit theorem, $P(\phi_l)$ will tend to a Gaussian distribution, irrespective of the details of the distribution $P(\phi(\vec{q}))$, as long as the number of $\phi(\vec{q})$ is large and they are statistically independent. However, this statistical independence may be expected to break down for large-amplitude fluctuations.

To calculate $F(\vec{Q})$, we make use of the identity

$$e^{iz\cos\phi} = \sum_{n=-\infty}^{\infty} i^n J_n(z) e^{in\phi}$$

to write

$$F(\vec{Q}) = \sum_{\vec{l},n} (ie^{-i\theta_0})^n J_n(\bar{Q}A) \langle e^{in\phi_l}\rangle e^{i(\vec{Q}+n\vec{q}_0)\cdot\vec{l}}$$

$$= \sum_n (ie^{-i\theta_0})^n J_n(\bar{Q}A) e^{-n^2\langle\phi^2\rangle/2} \Delta(\vec{Q}+n\vec{q}_0) , \qquad (5)$$

where $\Delta(\vec{Q}') = \sum_{\{\vec{G}\}} \delta(\vec{Q}'-\vec{G})$ is the familiar periodic delta function, $\{\vec{G}\}$ being the complete set of vectors in the lattice reciprocal to $\{\vec{l}\}$, and we introduce $\bar{Q} = (\vec{Q}\cdot\vec{e})$ to denote the component of $\vec{Q}$ along $\vec{u}_l$. Equation (5) demonstrates the well-known result that every parent Bragg reflection is decorated by an endless series of diffraction harmonic satellites, the one of nth order displaced from $\vec{G}$ by $n\vec{q}_0$. We assume that θ_0 is constant over a region of the sample large compared to the coherence length of the scattering radiation so that we average the *intensity* $I(\vec{Q}) = |F(\vec{Q})|^2$ over θ_0. Then

$$I(\vec{Q} = \vec{G} + n\vec{q}_0) = J_n^2(\bar{Q}A) e^{-n^2\langle\phi^2\rangle}$$

showing that (within the GPA) the effect of thermal phase fluctuations is to reduce the intensity of the nth-order satellite by a "DW factor" $e^{-n^2\langle\phi^2\rangle}$, which is independent of $\vec{Q}$ and which vanishes for parent $n=0$ reflections. [Expressions for $F_n(Q)$ obtained using other approximations will appear subsequently. In all of them, the overall phase θ_0 occurs only in the trivial factor $e^{i\theta_0}$. Since this is the case, in all that follows we choose $\theta_0 = 0$ in order to simplify the expressions.]

We defer for the moment from the discussion of numerical estimates of $\langle\phi^2\rangle$ and turn instead to our attempt to understand the basic result. Among the points to be clarified is this: Although the above calculation results in a DW factor for any given reflection, it does so by sidestepping the consideration of thermal smearing of the positions of the individual atoms. The calculation, in other words, avoids the question of *atomic* DW factors. This can be further considered by proceeding along more conventional lines, writing

$$\vec{x}_l = \vec{l} + \langle\vec{u}_l\rangle + \delta\vec{u}_l ,$$

where from Eq. (3),

$$\langle u_l\rangle = \langle A(\cos\theta_l \cos\phi_l + \sin\theta_l \sin\phi_l)\rangle$$

$$= A\langle\cos\phi\rangle \cos\theta_l \equiv \eta \cos\theta_l \qquad (6)$$

and

$$\delta u_l = u_l - \langle u_l\rangle$$

$$= A[(\cos\phi_l - \langle\cos\phi\rangle)\cos\theta_l + \sin\phi_l \sin\theta_l] . \qquad (7)$$

Then Eq. (2) becomes

$$F(\vec{Q}) = \sum_l e^{i\vec{Q}\cdot(\vec{l}+\langle\vec{u}_l\rangle)} \langle e^{i\vec{Q}\cdot\delta\vec{u}_l}\rangle \qquad (8)$$

and the last factor in this equation can be identified as the DW factor of the lth atom. [We write $\langle f(\phi_l)\rangle$ as $\langle f(\phi)\rangle$ to emphasize its l independence.]

The first extremely important point to note from Eq. (6) is that phase fluctuations reduce the effective amplitude of the mean modulation. [This has an obvious geometrical interpretation which can be seen by inspection of Fig. 1, in which the magnitude of the physical displacement $\langle u_l\rangle$, is represented as the real component of a complex vector with amplitude A. Fluctuations about the mean phase θ_l have no effect on $\langle u_l\rangle$ for $\theta_l = \pi/2$, but reduce $\langle u_l\rangle$ (by order ϕ_l^2) for $\theta_l = 0$.] It is necessary to introduce the renormalized effective amplitude η at this point in this line of development since *the fluctuations in displacement occur about* $\eta\cos\theta_l$, *not* $A\cos\theta_l$.

The DW factor $\langle \exp i(\vec{Q}\cdot\delta\vec{u}_l)\rangle$ is not trivial to evaluate. To see this, we consider the separate terms in the expansion

$$\langle e^{i\vec{Q}\cdot\delta\vec{u}_l}\rangle = \langle [1 + i\vec{Q}\cdot\delta\vec{u}_l - \tfrac{1}{2}(\vec{Q}\cdot\delta\vec{u}_l)^2 - (i/6)(\vec{Q}\cdot\delta\vec{u}_l)^3 + \cdots]\rangle\,, \tag{9a}$$

$$\langle(\vec{Q}\cdot\delta\vec{u}_l)\rangle = 0\,, \tag{9b}$$

$$\langle(\vec{Q}\cdot\delta\vec{u}_l)^2\rangle = (\vec{Q}\cdot\vec{A})^2[(\langle\cos^2\phi\rangle - \langle\cos\phi\rangle^2)\cos^2\theta_l + \langle\sin^2\phi\rangle\sin^2\theta_l]\,, \tag{9c}$$

$$\langle(\vec{Q}\cdot\delta\vec{u}_l)^3\rangle = (\vec{Q}\cdot\vec{A})^3[\langle x^3\rangle\cos^3\theta_l + 3\langle xy^2\rangle\cos\theta_l\sin^2\theta_l]\,, \tag{9d}$$

$$\langle(\vec{Q}\cdot\delta\vec{u}_l)^4\rangle = (\vec{Q}\cdot\vec{A})^4(\cdots)\,, \tag{9e}$$

where $x = \cos\phi_l - \langle\cos\phi\rangle$ and $y = \sin\phi_l$. [In general, $\langle(\vec{Q}\cdot\delta\vec{u}_l)^n\rangle$ appears to be of order $\langle\phi^2\rangle^{n/2}$ for n even and $\langle\phi^2\rangle^{(n+1)/2}$ for n odd if $\langle\phi^2\rangle$ is small.] The GPA is thus fundamentally different from a conventional harmonic phonon theory in that the atomic DW factors involve terms in $Q^n(n>2)$.

Equation (9c) for the mean-square thermal fluctuation is interesting to consider. It shows that the thermal smearing effect of phase fluctuation modes is fundamentally different from that of normal (e.g., acoustic) phonons in yet another way. These latter excitations make a contribution to $\langle\delta u_l^2\rangle$ which is l independent, whereas phason modes cause a *spatial modulation of* $\langle\delta u_l^2\rangle$ with a modulation wave vector $2\vec{q}_0$. From Eq. (7),

$$\begin{aligned}\langle\delta u_l^2\rangle &= (\langle\delta\eta_\parallel^2\rangle\cos^2\theta_l + \langle\delta\eta_\perp^2\rangle\sin^2\theta_l)\\ &= \tfrac{1}{2}[(\langle\delta\eta_\perp^2\rangle + \langle\delta\eta_\parallel^2\rangle) - (\langle\delta\eta_\perp^2\rangle - \langle\delta\eta_\parallel^2\rangle)\cos 2\theta_l]\,,\end{aligned} \tag{10}$$

where we have introduced the notation (see Fig. 1)

$$\langle\delta\eta_\parallel^2\rangle = A^2(\langle\cos^2\phi\rangle - \langle\cos\phi\rangle^2)\,, \tag{11a}$$

$$\langle\delta\eta_\perp^2\rangle = A^2\langle\sin^2\phi\rangle\,. \tag{11b}$$

Thus although $\langle\phi_l^2\rangle$ is independent of l, $\langle u_l^2\rangle$ is sinusoidally modulated. This is obvious by inspection of Fig. 1. For θ_l near 0 or π, phase fluctuations have little effect, and the effect is maximal for θ_l near $\pi/2$ or $3\pi/2$. That every atom in an incommensurate structure has its own uniquely different $\langle\delta u_l^2\rangle$ is, of course, consistent with the lack of translational symmetry in a modulated structure.

We are now in a position to focus on the key question in our attempt to understand Overhauser's result. How can it come about that by summing Eq. (8) (in which each term in the expansion of $\langle e^{i\vec{Q}\cdot\delta\vec{u}_l}\rangle$ depends explicitly upon $\vec{Q}$) over l, we obtain a result that is $\vec{Q}$ independent? Since the result is $\vec{Q}$ independent, it must be true for small $\vec{Q}$ [more precisely, for small values of $(\bar{Q}A)$] and must therefore be manifest even in the leading-order corrections [of order $(\bar{Q}A)^2$] terms in Eq. (9). Retaining only these terms, Eq. (2) becomes

$$F(\vec{Q}) \approx \sum_{\vec{l},k} i^k J_k(\bar{Q}\eta)[(1-w') + w''\cos 2\vec{q}_0\cdot\vec{l}\,] \times e^{i(\vec{Q}+k\vec{q}_0)\cdot\vec{l}}\,, \tag{12}$$

where

$$w' = \tfrac{1}{4}\bar{Q}^2(\langle\delta\eta_\perp^2\rangle + \langle\delta\eta_\parallel^2\rangle)\,, \tag{13a}$$

$$w'' = \tfrac{1}{4}\bar{Q}^2(\langle\delta\eta_\perp^2\rangle - \langle\delta\eta_\parallel^2\rangle)\,. \tag{13b}$$

Equation (12) makes explicitly clear that the phase fluctuations modify the elastic scattering in two distinctly different ways. The uniform term $w'(Q)$ reduces the intensity of a given reflection in the same way as do normal phonon contributions. The spatially modulated fluctuations, on the other hand, represented by $w''(Q)$ have the effect of *mixing the diffraction harmonic contributions of order* $J_k(\bar{Q}\eta)$ *and* $J_{k\pm 2}(\bar{Q}\eta)$. By rearranging Eq. (11) to facilitate comparison with Eq. (5), we find that to lowest order in $(\bar{Q}\eta)$

$$F_n(\vec{Q}) \approx i^n J_n(\vec{Q}\cdot\vec{A})\Delta(\vec{Q}+n\vec{q}_0) \times\left\{\frac{J_n(\bar{Q}\eta)}{J_n(\bar{Q}A)}\right\}\left\{1 - \frac{w''}{2}\left(\frac{J_{n-2}(\bar{Q}\eta)}{J_n(\bar{Q}\eta)}\right)\right\}\,, \tag{14}$$

where here, and in all that follows, we shall assume $n \geq 0$, which is permissible since $F_{-n}(\vec{Q}) = F_n(\vec{Q})^*$.

Written in this way, we see that there are two kinds of corrections to the static scattering amplitude $J_n(\vec{Q}\cdot\vec{A})$ (the two terms in curly brackets). The second, just mentioned, is due to spatial modulation of the mean-square displacements. The first is due to the renormalization of the effective mean-displacement amplitude from A to η. Both of these correction terms contain Q-independent contributions, as can be most easily seen by expanding for small $(\bar{Q}A)$ and small $\langle\phi^2\rangle$ in which case $w'' \approx \frac{1}{4}(\bar{Q}A)^2\langle\phi^2\rangle$, and to leading (zero) order in Q

$$\frac{w''}{2}\frac{J_{n-2}(\bar{Q}\eta)}{J_n(\bar{Q}\eta)} \approx \frac{1}{2}\frac{(\frac{1}{2}\bar{Q}\eta)^2\langle\phi^2\rangle}{(\frac{1}{2}\bar{Q}\eta)^2}n(n-1) = \tfrac{1}{2}n(n-1)\langle\phi^2\rangle$$

and

$$\frac{J_n(\bar{Q}\eta)}{J_n(\bar{Q}A)} \approx \left(\frac{\eta}{A}\right)^n = 1 - \tfrac{1}{2}n\langle\phi^2\rangle + \cdots ,$$

so that the product of the terms in Eq. (14) becomes

$$(1 - \tfrac{1}{2}n\langle\phi^2\rangle + \cdots)[1 - \tfrac{1}{2}n(n-1)\langle\phi^2\rangle + \cdots] = (1 - \tfrac{1}{2}n^2\langle\phi^2\rangle + \cdots)$$

which is in agreement with the expansion of $e^{-n^2\langle\phi^2\rangle/2}$, as we should expect from Eq. (5).

Seen in this light, the $e^{-n^2\langle\phi^2\rangle/2}$ DW factor which results from the GPA is deceptively simple, involving even in the lowest (harmonic) order in Q, strict cooperation on the part of terms arising from two seemingly different physical effects. Obviously similar but increasingly more complicated cancellations between the moments of δu_l and the renormalization of A must occur both within *and between* the higher-order terms in Eq. (9a) to ensure that Eq. (5) is valid for all values of $(\bar{Q}A)$. This last observation brings us to a new point, namely that the $e^{-n^2\langle\phi^2\rangle/2}$ result can be expected to fail, and do so in rather unpredictable ways for deviations in the distribution of ϕ_l away from Gaussian. Since it seems natural to question the reliability of this Gaussian assumption more closely the larger the value of $\langle\phi^2\rangle$, it is now appropriate to consider numerical estimation of this quantity. We may, with Overhauser, reason that the contribution to the mean-square atomic *displacements* of a given phason mode will be roughly equal to that made by an acoustic phonon of identical frequency. If we also assume equal numbers of phason and phonon modes and since excitation amplitude scales inversely with excitation frequency, we should therefore expect that

$$\langle\delta u_l^2(\text{phason})\rangle \approx A^2\langle\phi^2\rangle \approx \langle\delta u_l^2(\text{phonon})\rangle(v_p^2/v_\phi^2)$$

or

$$\tfrac{1}{2}\langle\phi^2\rangle \approx [w(\text{phonon})/Q^2A^2](v_p^2/v_\phi^2) ,$$

where $w(\text{phonon}) = \frac{1}{2}Q^2\langle u^2(\text{phonon})\rangle$ and $v_{p,\phi}$ is the velocity of the excitation on the appropriate branch. The results for incommensurate structures for which reasonably detailed studies exist suggest that $v_\phi^2/v_p^2 \approx 1$ and $A \approx 0.05-0.5$ Å. Coupling these estimates with typical values for $\langle u^2(\text{phonon})\rangle \approx 0.001-0.03$ Å^2, we find plausible values of $\langle\phi^2\rangle$ to lie in the range $0.004 < \langle\phi^2\rangle < 1.0$ when A has attained its low-temperature saturation value. However, $\langle\phi^2\rangle$ is certainly estimated to be ≥ 1 for materials which have normal-incommensurate phase transformations since, near the phase boundary, certainly η, if not A, tends to zero. In cases where $\langle\phi^2\rangle \approx 1$ we are entitled to view the GPA result with considerable skepticism, and to look for a smaller parameter upon which to make a Gaussian approximation. Fortunately, such a parameter, $\langle\delta u_l^2\rangle$ itself, is readily at hand. We will develop this random Gaussian displacement approximation (GDA) in Sec. III.

III. GAUSSIAN DISPLACEMENT APPROXIMATION

A phenomenological Landau theory provides a reasonably satisfactory way of discussing the stability of incommensurate structures in very general terms. Similar treatments have appeared before,[4-6] so we only sketch below the principal features. We specify atomic displacements relative to the parent unmodulated structure in terms of normal coordinates Q_{qj},

$$u_l = \sum_{qj} Q_{qj} e^{i\vec{q}\cdot\vec{l}} ,$$

where

$$Q_{qj} = Q^*_{-qj} = |Q_{qj}| e^{-i\phi(qj)} .$$

In the most elementary case, we concern ourselves with a single branch so that the branch index j can be suppressed. We expand the free energy (again with respect to the unmodulated parent structure),

$$F = \sum_{q,q',q'',\ldots} \left(\frac{1}{2!} U_2(q) Q_q Q_{q'} \Delta(q+q') + \frac{1}{3!} U_3(q,q',q'') Q_q Q_{q'} Q_{q''} \Delta(q+q'+q'') + \frac{1}{4!} U_4(q,q',q'',q''') \times Q_q Q_{q'} Q_{q''} Q_{q'''} \Delta(q+q'+q''+q''') + \cdots \right) . \tag{15}$$

Neglect (initially) fluctuation effects and stabilize sinusoidal static displacements by postulating

$$U_2(q) = [\Omega_0^2 + v_\phi^2(q-q_0)^2] . \tag{16}$$

The static free energy $\bar{F}$ in this approximation is given simply by

$$\bar{F} = U_2(q_0) Q_0^2 + \tfrac{1}{4} U_4 Q_0^4 , \tag{17}$$

where we have set

$$Q_{q_0} = Q_0 e^{-i\theta_0} , \tag{18}$$

which will give static displacements of the form $\eta\cos(\vec{q}_0\cdot\vec{l} - \theta_0)$ with $\eta = 2\langle Q_0\rangle$. We also neglect q dependence of U_4. Minimizing $\bar{F}$ with respect to Q_0 gives for the equilibrium static amplitude

$$\langle Q_0\rangle^2 = -2(\Omega_0^2/U_4) , \tag{19}$$

a solution which is stable for $\Omega_0^2 < 0$, U_4 and $v_\phi^2 > 0$.

We now calculate the energy $\delta F = F - \bar{F}$ caused by adding to the static modulation $\langle Q_{q_0}\rangle$, a spatial fluctuation Q_{q_0+q}. In addition to harmonic terms of the type $U_2(q_0+q)Q_{q_0+q}Q_{-q_0-q}$, there are fourth-order terms, e.g., proportional to

$$(Q_{q_0}Q_{-q_0}Q_{q_0+q}Q_{-q_0-q}) \text{ and } (Q^2_{-q_0}Q_{q_0+q}Q_{q_0-q})\,.$$

To lowest order these terms renormalize the *harmonic* stiffness since we may replace Q_{q_0} by its static value $\langle Q_0\rangle$. The net effect of all of the fourth-order terms is to produce a renormalized stiffness matrix $\underline{V}_2(\vec{q})$:

$$\underline{V}_2(\vec{q}) = \begin{pmatrix} \alpha & \beta^* \\ \beta & \alpha \end{pmatrix} \qquad \begin{aligned} \alpha &= U_2(\vec{q}_0+\vec{q}) + U_4\langle Q_0\rangle^2\,, \\ \beta &= \tfrac{1}{2}\langle Q_0\rangle^2 e^{2i\theta_0} \end{aligned}$$

in terms of which δF to lowest order takes the quadratic form

$$\delta F = \tfrac{1}{2}\sum_q \tilde{Q}^*(q)\cdot \underline{V}_2(\vec{q})\cdot \tilde{Q}(\vec{q})\,, \quad \tilde{Q}(\vec{q}) = \begin{pmatrix} Q_{q_0+q} \\ Q_{-q_0+q} \end{pmatrix} \tag{20}$$

$$= \tfrac{1}{2}\sum_q \left[\Lambda_\parallel(\vec{q})|\xi_\parallel(\vec{q})|^2 + \Lambda_\perp(\vec{q})|\xi_\perp(\vec{q})|^2\right]. \tag{21}$$

Equation (21) follows from Eq. (20) by a principal axis transformation which has eigenvalues,

$$\Lambda_\parallel(q) = -2\Omega_0^2 + v_\phi^2(q-q_0)^2\,, \tag{22a}$$

$$\Lambda_\perp(q) = v_\phi^2(q-q_0)^2\,, \tag{22b}$$

where we use the self-consistent value [Eq. (19)] for $\langle Q_0\rangle$. In terms of the eigenmodes $\xi_\parallel(\vec{q})$ and $\xi_\perp(q)$, the fluctuating displacements around the static value $\eta\cos(\vec{q}_0\cdot\vec{l} - \theta_0)$ become

$$\delta u_l = \frac{1}{\sqrt{2}}\sum_q \left[\cos(\vec{q}_0\cdot\vec{l} - \theta_0)\xi_\parallel(q) + \sin(\vec{q}_0\cdot\vec{l} - \theta 0)\xi_\perp(q)\right]e^{i\vec{q}\cdot\vec{l}}\,. \tag{23}$$

Among the points to be noted in the above development are the following:

(i) The static free energy $\bar{F}$ contains no cubic contributions and is independent of the overall phase θ_0.

(ii) Quartic terms in F mix plane-wave modes with wave vectors differing by $\pm 2\vec{q}_0$, giving rise to new normal modes $\xi_\parallel(q)$ and $\xi_\perp(q)$.

(iii) From Eq. (23), $\xi_\parallel(q)$ modes represent (for small $\vec{q}$) long-wavelength modulation of the static displacements, $\eta\cos(\vec{q}_0\cdot\vec{l} - \theta_0)$, and may thus be legitimately called amplitude fluctuation modes. The orthogonal $\xi_\perp(q)$ modes are only *approximately* (to first order in displacement) phase-fluctuation modes. (The notation $\parallel$ and $\perp$ are again obvious by inspection of Fig. 1.)

(iv) $\xi_\perp(q)$ represent true Goldstone modes since, from Eq. (22b), their stiffness $v_\phi^2(q-q_0)^2$ vanishes at $\vec{q} = \vec{q}_0$. In this sense, it is still appropriate to describe them as phasons, in spite of the inaccuracy in this term noted in (iii).

(v) From Eq. (21), $\xi_\parallel(q)$ and $\xi_\perp(q)$ are statistically independent and have a Gaussian distribution. Therefore, we again find a modulation of the mean-square fluctuations

$$\langle\delta u_l^2\rangle = \langle\delta\eta_\parallel^2\rangle\cos^2\theta_l + \langle\delta\eta_\perp^2\rangle\sin^2\theta_l$$

of the same form as Eq. (10). In addition, we have the explicit expressions

$$\langle\delta\eta_\parallel^2\rangle = \tfrac{1}{2}\sum_q\langle\xi_\parallel^2(q)\rangle = \sum_q \tfrac{1}{2}kT/\Lambda_\parallel(q)\,, \tag{24a}$$

$$\langle\delta\eta_\perp^2\rangle = \tfrac{1}{2}\sum_q\langle\xi_\perp^2(q)\rangle = \sum_q \tfrac{1}{2}kT/\Lambda_\perp(q)\,. \tag{24b}$$

(vi) It is not necessary for our purposes to discuss the time dependence of δu_l, but in the absence of damping this model predicts that the phase and amplitude modes are harmonic (constructed from linear combinations of phonon modes) with frequencies whose squares are given by $\Lambda_\parallel(q)$ and $\Lambda_\perp(q)$, respectively. From this point of view, the incommensurate structure is the result of an unstable soft-phonon mode of the unmodulated parent structure with wave vector $\vec{q}_0$ and $\omega^2 = \Omega_0^2 < 0$.

It is now straightforward to calculate DW factors within the GDA. Since *displacements* now have a Gaussian distribution

$$\langle e^{i\vec{Q}\cdot\delta\vec{u}_l}\rangle = e^{-(1/2)\bar{Q}^2\langle\delta u_l^2\rangle} = e^{-w'}e^{w''\cos 2\theta_l}$$

$$= e^{-w'}\sum_m I_m(w'')e^{2im\theta_l}\,,$$

where $I_m(z) = i^{-m}J_m(iz)$ are modified Bessel functions of imaginary argument and w' and w'' [defined in Eq. (13)] are now given by Eq. (24) rather than Eq. (11). Combining this result with the Bessel function expansion for $e^{i\vec{Q}\cdot\langle\vec{u}_l\rangle}$ used previously, we find

$$F(\vec{Q}) = \sum_l e^{i\vec{Q}\cdot\vec{l}}e^{i\vec{Q}\cdot\langle\vec{u}_l\rangle}\langle e^{i\vec{Q}\cdot\delta\vec{u}_l}\rangle$$

$$= \sum_{lkm} e^{-w'}i^kJ_k(v)\,I_m(w'')e^{i[\vec{Q}+(k+2m)\vec{q}_0]\cdot\vec{l}}\,,$$

where

$$v = \bar{Q}\eta$$

and we have again chosen $\theta_0 = 0$ to simplify our expressions. To put this relation into a convenient final form, we sum on l and look for the contribution at $\vec{Q} = \vec{G} - n\vec{q}_0$ $(n = k + 2m)$:

$$F_n(\vec{Q}) = \Delta(\vec{Q} + n\vec{q}_0)i^n e^{-w'}\sum_{m=0,\pm1,\pm2\cdots}(-1)^m J_{n-2m}(v)I_m(w'')\,. \tag{25}$$

For some purposes it is desirable to introduce two new parameters

$$y = \langle \delta\eta_\perp^2 \rangle / \eta^2 \text{ and } \Phi = (\langle \delta\eta_\perp^2 \rangle - \langle \delta\eta_\parallel^2 \rangle)/\langle \delta\eta_\perp^2 \rangle$$

in terms of which

$$w' = \tfrac{1}{4} v^2 y (2 - \Phi) \text{ and } w'' = \tfrac{1}{4} v^2 y \Phi .$$

The anisotropy parameter Φ can be evaluated for the model described in this section by performing the indicated sums in Eqs. (24) over the range $0 < (q - q_0) < k_m$, with the result

$$\Phi = \frac{\kappa}{k_m} \tan^{-1}\left(\frac{k_m}{\kappa}\right), \quad (26)$$

where $\Omega_0^2 \equiv v_\phi^2 \kappa^2$, and k_m is an (arbitrary) wave-vector cutoff.

IV. DISCUSSION

Any comparison of GDA and GPA results is complicated by inclusion within the GDA of independent longitudinal and transverse fluctuations. In the GPA, $\eta_\perp$ and $\eta_\parallel$ are not independent but are instead related through the equations $\langle \delta\eta_\perp^2 \rangle = \eta^2 \sinh\langle \phi^2 \rangle$ and $\langle \delta\eta_\parallel^2 \rangle = \eta^2 (\cosh\langle \phi^2 \rangle - 1)$, which means that the anisotropy parameter Φ assumes the special value

$$\Phi^0 = 1 - \tanh(\tfrac{1}{2} \langle \phi^2 \rangle) . \quad (27)$$

It is probable that this "constant-amplitude" assumption for Φ represents something like the minimum physically plausible ratio of $\langle \delta\eta_\parallel^2 \rangle / \langle \delta\eta_\perp^2 \rangle$ and it seems reasonable to adopt it in the GDA at least for the purpose of making comparisons with the GPA. Specifically, w' and w'' are calculated using $\Phi = \Phi^0$ and introducing $\langle \phi^2 \rangle$ parametrically through the relation $y = \sinh\langle \phi^2 \rangle (\approx \langle \phi^2 \rangle$ for $y \leq 1)$.

The results of the comparison can be summarized as follows:

(*a*) $v < 1$, $n^2 \langle \phi^2 \rangle \ll 1$. In this regime, which is easily realizable in practice, GPA and GDA make essentially identical predictions for F_n. In particular, in the small-v limit we can write generally for all n

$$F_n(v \to 0, \langle \phi^2 \rangle) = (\tfrac{1}{2} v)^n d_n(\langle \phi^2 \rangle) , \quad (28)$$

where $d_0 = 1$ and for $n^2 \langle \phi^2 \rangle \ll 1$ the DW factor d_n $(n \geq 1)$ is given by the GPA result

$$d_n^0 = e^{-n(n-1)\langle \phi^2 \rangle / 2} . \quad (29)$$

(It is important to note that d_n^0 written in this way is equivalent to Overhauser's result [Eq. (5)], but expressed in terms of the average amplitude variable $v = \overline{Q}\eta$ rather than the unobservable quantity $\overline{Q}A (= v \langle \cos\phi \rangle^{-1} = v e^{\langle \phi^2 \rangle / 2})$. We prefer to write it in this manner as it is in keeping with the traditional idea of expanding about the mean position.)

(*b*) $v > 1$, $n^2 \langle \phi^2 \rangle \ll 1$. Here quantitative differences appear in the two approximations. Most notable are shifts in the positions of the nodes and extrema of $F_n(Q)$ from the GPA result $F_n(\overline{Q}) \sim J_n(QA)$. Much of this effect can be traced to the replacement of the variable $\overline{Q}A$ by $v = \overline{Q}\eta$, i.e., to the renormalization of the static displacement by the fluctuations just discussed. A comparison of the two predictions for $F_4(v)$ for $\langle \phi^2 \rangle = 0.1$ shown in Fig. 2(a) is typical.

(*c*) $n^2 \langle \phi^2 \rangle \gtrsim 1$. Even at small v, strikingly different behaviors are predicted by the two approximations for $n > 2$. The cause of this can be seen most clearly by examining the GDA result, Eq. (26), in the $v \to 0$ limit. Retaining only those terms which give contributions to leading order in v,

$$F_n(v \to 0) = [J_n(v) I_0(w'') - J_{n-2}(v) I_1(w'')]_{v \to 0} . \quad (30)$$

The meaning of the two terms is the same as has already been explained in Sec. II. The first term is the nth-order diffraction harmonic of the static displacement wave. The second term results from

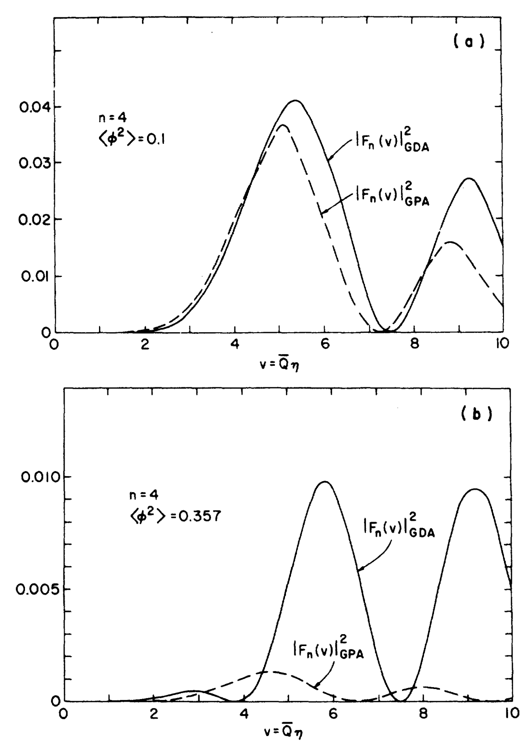

FIG. 2. Comparison of predicted satellite intensities $|F_n(v, \langle \phi^2 \rangle)|^2$ using the GDA and GPA. (a) $\langle \phi^2 \rangle = 0.1 < \langle \phi^2 \rangle_{\text{crit}}$. (b) $\langle \phi^2 \rangle = 0.357 > \langle \phi^2 \rangle_{\text{crit}}$. The additional node at $v \approx 0.38$ for the GDA curve marks the transition to fluctuation-dominated behavior.

a modulation of the $(n-2)$nd diffraction harmonic by the spatial periodicity of the fluctuation $\langle \delta u_l^2 \rangle$.

There is a critical value of $y\Phi = (\langle \delta\eta_\perp^2 \rangle - \langle \delta\eta_\parallel^2 \rangle)/\eta^2$ below which the $J_n I_0$ term is larger in magnitude than the $J_{n-2} I_2$ term and above which the converse is true. In the limit $v \to 0$ its value is easily shown to be $(y\Phi)_{\text{crit}} = 2[n(n-1)]^{-1}$, or in terms $\langle \phi^2 \rangle$

$$\langle \phi^2 \rangle_{\text{crit}} = \ln\{[1 - 2/n(n-1)]^{-1}\}$$
$$\approx 2[n(n-1)]^{-1} \quad \text{for } n \le 3 . \qquad (31)$$

$(y\Phi)_{\text{crit}}$ separates the behavior of F_n into two regions which we will call displacement dominated (DD) and fluctuation dominated (FD) regimes, respectively. The locus of the boundary between the two types of behavior is readily extended throughout the $(\langle \phi^2 \rangle, v)$ plane by determining the location of the roots of the equation $F_n(v, w', w'') = 0$. The approximate results for $n = 3$ and 4 are plotted in Fig. 3.

The index $n = 2$ is marginal in the sense that for $n > 2$, crossover from DD to FD behavior occurs at finite $\langle \phi^2 \rangle_{\text{crit}}$. At $n = 2$, $\langle \phi^2 \rangle_{\text{crit}} = \infty$ and FD behavior is excluded for $n < 2$. This marginal behavior at $n = 2$ depends critically on the assumed anisotropy $\Phi = \Phi_0$. A slight further suppression of $\langle \delta\eta_\parallel^2 \rangle$ gives a finite $\langle \phi^2 \rangle_{\text{crit}}$ for $n = 2$, and complete suppression $\langle \delta\eta_\parallel^2 \rangle = 0$, gives $y_{\text{crit}} = 1$ or $\langle \phi^2 \rangle_{\text{crit}} = 0.88$ for $n = 2$. It nevertheless seems likely that well away from the normal-incommensurate phase boundary that $\langle \phi^2 \rangle_{\text{crit}}$ is not easily exceeded for $n = 2$ satellites; i.e., under most conditions secondary satellites are probably safely within the DD regime, but the situation is surely reversed

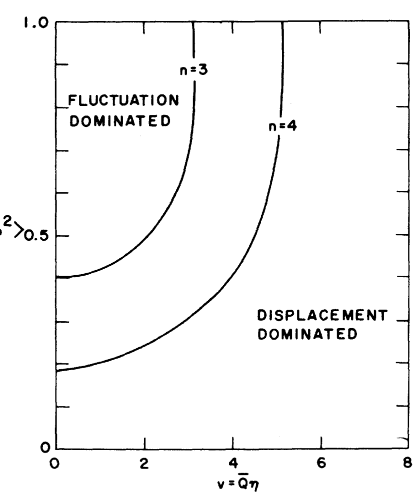

FIG. 3. The area to the upper left of the appropriate boundary is the fluctuation-dominated regime for the nth-order satellites; the area to the lower left, the displacement-dominated regime.

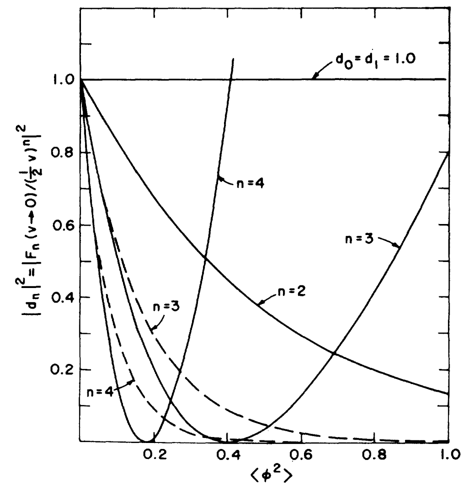

FIG. 4. Comparison of factors for nth-order satellites as calculated in GDA (solid lines) and GPA (dashed lines) in the limit $v = \vec{Q}\eta \to 0$. Both approximations give identical results for $n = 0$, 1, and 2 for this particular choice of the anisotropy parameter $\Phi = \Phi^0$.

at some point for higher satellites. (Note that satellites with n as high as 6 have been observed in Na_2CO_3.[7])

The significance of the crossover from DD to FD behavior is well illustrated by Fig. 4 which compares $d_n(\langle \phi^2 \rangle)$ [defined in Eq. (28)] calculated in the GDA with the GPA results d_n^0, for intermediate values of $\langle \phi^2 \rangle$. In this $v \to 0$ limit the GDA and GPA results are in precise agreement for $n = 0$, 1, and 2. For $n \ge 2$ the two results agree asymptotically as $\langle \phi^2 \rangle \to 0$, as we have already stated; but whereas d_n^0 tends monotonically to zero at large $\langle \phi^2 \rangle$, the GDA result passes through zero at $\langle \phi^2 \rangle_{\text{crit}}$ and further increases in $\langle \phi^2 \rangle$ (i.e., in the fluctuations) causes the diffracted intensity to *increase*. This seemingly odd behavior is entirely reasonable once the concept of a FD regime is grasped.

It is not possible to succinctly characterize the differences in the two approximations at large values of v. However, it is useful to compare Fig. 2(a) where $\langle \phi^2 \rangle$ is small enough as to be everywhere in the DD regime with Fig. 2(b) where $\langle \phi^2 \rangle > \langle \phi^2 \rangle_{\text{crit}}$. Note that in addition to the extra node in the GDA result at $v \sim 3.8$, which marks the boundary between FD and DD behavior, the GDA result is less attenuated than the GPA result even in the DD (large-v) regime.

(*d*) $v \to 0$, $\langle \phi^2 \rangle \gg 1$. This remaining region must be singled out for special study because it is most likely to occur in the vicinity of a second-order normal-incommensurate phase boundary, where $\langle \phi^2 \rangle$ (or $\langle \delta\eta_\perp^2 \rangle / \eta^2$) diverges because $\eta \to 0$. As might have been expected, there is some subtlety involved in this limit. Consider, for example, the fundamental inequality

$$\frac{\langle\delta\eta_\perp^2\rangle - \langle\delta\eta_\parallel^2\rangle}{\eta^2} > \frac{2}{n(n-1)},$$

which must be exceeded to observe FD behavior in nth-order satellites. It is not difficult to show that with the constant-amplitude assumption $\Phi=\Phi^0$, both η^2 and $(\langle\delta\eta^2\rangle - \langle\delta\eta^2\rangle)$ go to zero (as $e^{-\langle\phi^2\rangle}$) for large $\langle\phi^2\rangle$ such that their ratio $\Phi^0 y \to 1$. This is again the statement that $\langle\phi^2\rangle_{\text{crit}} \to \infty$ at $n=2$, which we saw was critically dependent on placing $\Phi=\Phi^0$. Clearly, a better assumption for Φ near the phase boundary (and, in fact, the only one fully compatible with the quasiharmonic nature of the GDA model) are those of classical mean-field theory, for which $(\langle\delta\eta_\perp^2\rangle - \langle\delta\eta_\parallel^2\rangle) \sim \kappa \sim (T_c - T)^{1/2}$ [from Eq. (25)] and $\eta^2 \sim (T_c - T)$, so that the left side of the above inequality diverges as $T \to T_c$. Thus, the mean-field-GDA model predicts that there is *no escape* from a crossover to FD behavior even for $n=2$ (and, of course, for $n>2$ as well) as one approaches the phase boundary.

In general, mean-field predictions of critical behavior are not to be trusted and, in particular, Bruce and Cowley[8] have exploited correspondences with xy spin systems together with scaling arguments to show that mean-field theory is not expected to adequately describe the behavior of incommensurate systems near the normal phase boundary. Bruce[9] has recently analyzed the expected behavior of $n=1$ and 2 satellite intensities near the phase boundary. It is not appropriate to discuss these results here in detail, but his analysis indicates that the mean-field GDA results given here do in fact fail in the critical region, and do so in a way that cannot be remedied by simply replacing the mean-field exponents for η and κ by their xy-model values. Interestingly enough, although the asymptotic behavior of $n=1$ satellites is controlled by the order-parameter exponent β, the $n=2$ satellite intensity is governed by a crossover exponent associated with energy-density fluctuations. The relationship of this predicted fluctuation dominated behavior for $n=2$ satellites to that predicted by the mean-field GDA model for $n \geqslant 2$ requires some clarification, but the result is provocative. It may also be remarked that these new results do not in the least imply that the mean-field results have no region of validity, but only that they must be treated with increasing skepticism the more closely the phase boundary is approached.

We conclude with some comments on pertinent experimental observations. No special consideration of "unusual" DW factors has been accorded to most data on incommensurate satellite intensities. Overhauser[10] states that DW effects (calculated in the GPA) lower the apparent transformation temperature of $K_2Pt(CN)_4Br_{0.3}$ (KCP), as judged by the growth of the $n=1$ satellite intensity some 40% below the actual onset of the incommensurate phase. This interpretation is complicated by the now widespread belief that random impurity-pinning effects prevent KCP from ever attaining true incommensurate long-range order.

There is, however, a more fundamental point to be made. By applying a DW factor $e^{-\langle\phi^2\rangle/2}$ to the $n=1$ satellite, we are really just renormalizing the mean amplitude so that if, as a result, the satellite intensity vanishes, it is because $\eta \to 0$, and there would seem to be no sense in which the incommensurate phase could be thought to exist beyond this point. It is to avoid such misinterpretations that we prefer the alternative definition for which $d_n^0 = e^{-n(n-1)\langle\phi^2\rangle/2}$.

Recently, a Mössbauer x-ray scattering experiment was carried out which was designed to detect low-lying inelastic phason scattering which might be present in copious amounts near incommensurate satellite positions and "mistaken" for elastic scattering in a conventional experiment.[11] No such effect was found and the authors concluded from this that "phasons do not make anomalously large contributions to the DW factors." Although this conclusion may be too strong (it is not clear whether the experiment sampled a sufficiently large region of reciprocal space to be able to set an interesting limit), the results are at least not in contradiction to notions set forth here.

In the present context, perhaps the most interesting result to date is a careful crystallographic refinement of the structure of Na_2CO_3 by Hogervorst *et al.*[12] using intensities of several hundred satellites for each of the orders $n=1$–4. Using conventional DW factors, they find that the calculated $n=2$–4 satellites intensities are systematically high and that an additional *Q-independent* reduction factor of the form $(1-n^2\langle\phi^2\rangle)$ with $\langle\phi^2\rangle = 0.012$ greatly improves the fit. They speculate that this correction is necessary because of random fluctuations in the phase of the modulation wave. It is not clear whether the authors have static or dynamic fluctuations in mind. It is also interesting to note that in spite of the chosen form of the reduction factor, Hogervorst *et al.* are careful not to attribute any directly measurable anomalous reduction to $n=1$ satellites, which is of course in accord with the present reformulation of Overhauser's result. It would be worthwhile to test whether or not a reduction factor of the form $[1-n(n-1)\langle\phi^2\rangle]$ would fit their results more accurately. (See Note added in proof.)

V. SUMMARY

(1) As first pointed out by Overhauser, the effect of phase fluctuations on incommensurate satellite intensities requires special treatment. The form of the corrections are of a fundamentally different form from that given by a normal Debye-Waller factor. This remains true despite the assumption of harmonic fluctuations.

(2) The explanation of (1) involves two distinctly different physical processes. Phase fluctuations (a) reduce the mean amplitude of the atomic displacements and (b) produce spatially modulated fluctuations of the atomic displacements.

(3) In the small-Q, small-fluctuation limit ($\bar{Q}\eta \ll 1, n^2\langle\phi^2\rangle \ll 1$) the effect of phase fluctuations alone on the structure factor of the nth-order satellite can be approximated by a Q-*independent* Debye-Waller factor

$$F_n(\vec{Q}) = d_n J_n(\bar{Q}\eta)\,,$$

where

$$d_n(\langle\phi^2\rangle) = \begin{cases} e^{-n(n-1)\langle\phi^2\rangle/2}, & n \geq 2 \\ 1, & n = 0, 1\,. \end{cases}$$

This result is mathematically equivalent to Overhauser's result

$$F_n(Q) = \begin{cases} e^{-n^2\langle\phi^2\rangle/2} J_n(\bar{Q}A), & n \geq 1 \\ 1, & n = 0\,. \end{cases}$$

However, in using this version it is essential to understand that the distinction set forth in (2) is ignored and that the argument of J_n refers not to the actual mean displacement amplitude but rather to a fictitious amplitude A, which the modulation would assume in the absence of fluctuations.

(4) Wherever the GPA and GDA results differ (and, in particular, for $n^2\langle\phi^2\rangle \gtrsim 1$), the latter approximation is probably preferable. The most notable difference between the two treatments is that the latter predicts that for any value of $n \geq 2$ and $\bar{Q}\eta$, there is a critical value of $\langle\phi^2\rangle$ above which a further increase in $\langle\phi^2\rangle$ serves to increase rather than diminish the satellite intensity.

(5) In any actual case, one must also be prepared to assess the importance and make appropriate allowances for amplitude as well as phase fluctuations as well as fluctuations from other normal phonon branches. Likewise, the existence in real materials of several sublattices (i.e., non-Bravais parent lattices) cause further practical complications although these effects are formally straightforward to include.

Note added in proof. Professor de Wolff has kindly informed me that the intensity data of Ref. 12 are indeed better described by a $[1 - n(n-1)\langle\phi^2\rangle]$ reduction factor than by $(1 - n^2\langle\phi^2\rangle)$. These results are not regarded as conclusive, however, as the magnitudes of the reduction factors are small in Na_2CO_3 in any case. Professor de Wolff also cautions that the data have not been corrected for inelastic scattering which could conceivably alter the resulting comparison. [Of course, such corrections should include contributions from phason modes as well as acoustic phonons and the relative weights of such contributions for higher order satellites ($n \geq 2$) have yet to be explored.]

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