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Thermal diffuse scattering in harmonic and nonharmonic crystals

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The total thermal-diffuse-scattering intensity is calculated as a function of temperature for a series of harmonic and nonharmonic chains. The intensity forms walls in reciprocal space, the widths of the walls being approximately inversely proportional to the pair-displacement correlation length. For the harmonic chains the wall width is constant with temperature, but for the nonharmonic chains the width decreases dramatically as the temperature approaches zero, reflecting the approach to infinity of the correlation length. The maximum intensity for the walls decreases approximately linearly with temperature for the harmonic systems. For the nonharmonic chains a slower decrease or an increase in peak intensity occurs for decreasing temperature and may be regarded as evidence of mode softening associated with a displacive phase transition at zero temperature.

I. INTRODUCTION

Thermal-diffuse-scattering (TDS) intensities, measured as a function of temperature by x-ray, γ-ray, or electron diffraction, can provide information about the pair-displacement correlations and, ultimately, the vibrational Hamiltonian for the system. Thus, for example, x-ray TDS intensities[1] in the commensurate phase of Rb_2ZnCl_4 have been used to obtain the critical exponents associated with the correlation length and the static susceptibility.

In certain cases the measured TDS indicates that the atomic thermal vibration is correlated along chains[2] or planes. Then the TDS occurs as, respectively, walls or rods of intensity in reciprocal space, while the Bragg peaks are points for a three-dimensional crystal, and so there is no difficulty in separating out the Bragg scattering from the TDS. The presence of chainlike correlations has been deduced from x-ray and electron diffraction TDS for the essentially harmonic system, Si,[3] whereas planar correlations resulting from motion of a nonharmonic character are apparent from the x-ray TDS (Ref. 4) for $KMnF_3$.

Theoretical treatments of TDS (Ref. 5) tend to consider harmonic systems, for which the breakdown of TDS intensity into one- and two-phonon terms, etc., is a natural consequence. For nonharmonic systems, e.g., crystals at temperatures near a displacive phase transition, the phonon concept is less useful and such divisions of the TDS are of dubious validity. In the present paper we consider both nonharmonic and harmonic systems and, accordingly, the total TDS is calculated.

For mathematically tractable nonharmonic crystal systems we are limited to one-dimensional models, for which transfer integral techniques[6] are applicable. Here we treat double-quadratic (DQ), flat-bottomed quadratic (FQ) and harmonic chains (as defined in the next section), with the aim of gaining some insight into the behavior of three-dimensional crystals in which displacement correlations are predominantly along chains. Since both the DQ and FQ chains become ordered at zero temperature, these systems are closely analogous to the high-temperature phase of crystals possessing a displacive structural phase transition.

The remainder of this paper is arranged as follows. In the next section the chain Hamiltonians are defined and expressions are presented for the one- and two-particle probability density functions, the correlation length, and the Bragg and TDS intensities. Then, in Sec. III, results are given for calculations of the TDS intensity for the various types of chains and for strong and weak interparticle coupling in those chains. These results are discussed, with particular reference to the correlation length and to mode softening. A short summary concludes the paper.

II. MATHEMATICAL FRAMEWORK

Detailed treatments of the statistical mechanics of the DQ and related chains already exist,[7–10] so we present here only the basic formulas and some expressions of particular relevance to the derivation of TDS intensities.

A. Hamiltonians

The vibrational Hamiltonian, H, for a monatomic chain containing N atoms, each of which is coupled harmonically to its nearest neighbors, is given by

$$H(\{y\})=\tfrac{1}{2}m\omega_0^2a^2\sum_{p=1}^{N}V(y_p)+\tfrac{1}{2}m\omega_c^2a^2\sum_{p=1}^{N}(y_p-y_{p+1})^2+\tfrac{1}{2}ma^2\sum_{p=1}^{N}\dot{y}_p^{\,2}\ . \qquad (1)$$

Here y_p is the displacement, u_p, of the pth atom from its mean position, scaled by the chain spacing a, so that y_p is dimensionless. The frequencies ω_c and ω_0 are associated with the harmonic nearest-neighbor coupling and the one-particle potential $V(y_p)$, respectively.

The one-particle potentials are, for the harmonic chain,

$$V(y)=y^2\ , \qquad (2)$$

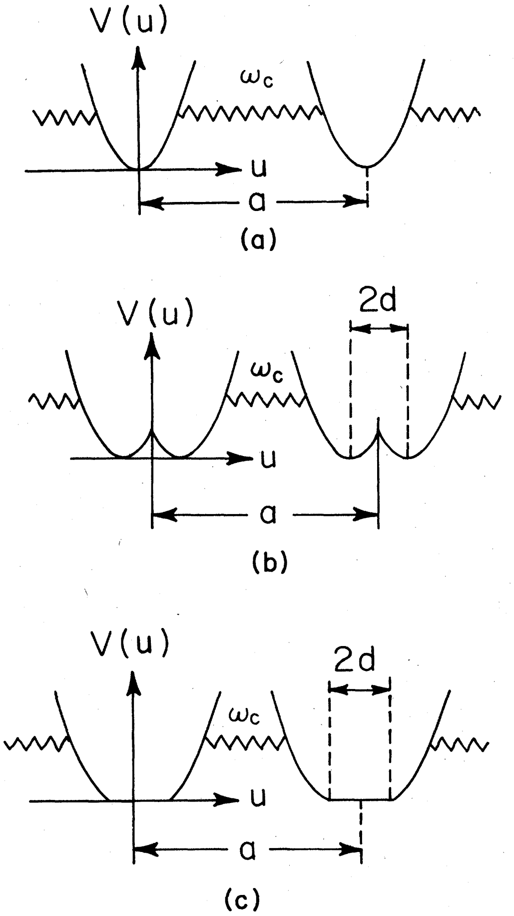

FIG. 1. Schematic representation of the chains, showing one-particle potentials $V(u)$ as a function of displacement of the atoms $u\,(=ay)$ from their equilibrium positions, and harmonic nearest-neighbor coupling for (a) a harmonic chain, (b) a DQ chain, and (c) an FQ chain.

for the DQ chain

$$V(y)=(\,|y|-d/a)^2 , \tag{3}$$

and for the FQ chain

$$V(y)=\begin{cases}(\,|y|-d/a)^2, & |y|\ge d/a\\ 0, & |y|<d/a .\end{cases} \tag{4}$$

The three types of chain are represented schematically in Fig. 1.

B. Probability densities and correlation length

Assuming an infinite chain and periodic boundary conditions, all of the physical properties to be considered may be evaluated using classical statistics in terms of the eigenvalues λ_k and eigenvectors $\phi_k(y)$ of the transfer integral equation[7]

$$\int_{-\infty}^{\infty}\exp\{-U(y,y')/k_BT\}\phi_k(y)dy=\lambda_k\phi_k(y') , \tag{5}$$

where k_B is the Boltzmann constant, T the temperature, and

$$U(y,y')=\frac{m\omega_0^2a^2}{4}\{V(y)+V(y')\}+\frac{m\omega_c^2a^2}{2}(y-y')^2 .$$

Note that the eigenvectors $\phi_k(y)$ are of alternating even and odd parity when ordered according to decreasing magnitude of the corresponding eigenvalues λ_k.

In evaluating the Bragg and TDS intensities, we shall need the one- and two-particle probability density functions $\rho_1(y)$ and $\rho_2(y,y')$. These are given by

$$\rho_1(y)=\phi_1^2(y) , \tag{6}$$

where $\phi_1(y)$ is the eigenfunction corresponding to the largest eigenvalue of Eq. (5), and

$$\rho_2(y_m,y_n)=\sum_{k=1}^{\infty}\left[\frac{\lambda_k}{\lambda_1}\right]^{|m-n|}\phi_k(y_m)\phi_1(y_m)\phi_k(y_n)\phi_1(y_n) , \tag{7}$$

for the mth and nth particles in the chain.

We shall be referring to the correlation length ξ, which we define as the site separation at which the pair-displacement correlation function $\langle yy'\rangle/\langle y^2\rangle$ falls to $\frac{1}{2}$. The correlation functions and the correlation length ξ have been evaluated for all the chains considered here by Johnson and Mair[10] and these results for ξ will be related to the ones for the TDS obtained in Sec. III of this paper.

C. Bragg and TDS Intensities

The total diffracted intensity I_T for a chain of length N atoms is given, in the first Born approximation (single scattering), by

$$I_T=\sum_{p,q=0}^{N-1}\exp[iha(p-q)]\langle\exp[ih(u_p-u_q)]\rangle ,$$

where h is the projection of the scattering vector along the chain and u_p is the displacement of the pth atom ($u_p=ay_p$), assumed to be along the chain. Using $\rho_2(u_p,u_q)$ from Eq. (7) to evaluate the ensemble average, we obtain

$$I_T=\sum_{p,q=0}^{N-1}\exp[iha(p-q)]\sum_{l=1}^{\infty}\left[\frac{\lambda_l}{\lambda_1}\right]^{|q-p|}\int\phi_l(u_p)\phi_1(u_p)\exp(ihu_p)du_p\int\phi_l(u_q)\phi_1(u_q)\exp(-ihu_q)du_q .$$

The terms for $l=1$ are uncoupled in the particle displacements and give the Bragg scattering I(Bragg) as [see Eq. (6)]

$$\begin{aligned}I(\text{Bragg})&=\sum_{p,q=0}^{N-1}\exp[iha(p-q)]\langle\exp(ihu_p)\rangle\langle\exp(-ihu_q)\rangle\\&=\frac{\sin^2(Nha/2)}{\sin^2(ha/2)}\langle\exp(ihu)\rangle^2 ,\end{aligned} \tag{8}$$

i.e., the Bragg scattering is given by the shape function multiplied by the Debye-Waller factor.

The TDS intensity $I(\mathrm{TDS})$ is obtained from the remaining terms as, using Dirac notation,

$$I(\mathrm{TDS})=\sum_{p,q=0}^{N-1}\exp[iha(p-q)]\sum_{l>1}\left[\frac{\lambda_l}{\lambda_1}\right]^{|p-q|}\langle l\,|\exp(ihu_p)\,|\,1\rangle\langle l\,|\exp(-ihu_q)\,|\,1\rangle\ .$$

Substituting $(m+1)$ for l and the sums over p and q by a single sum over s, and recognizing[10] that eigenvectors $\phi_1,\phi_3,\phi_5\ldots$ are symmetric in y, whereas $\phi_2,\phi_4,\phi_6\ldots$ are antisymmetric, we obtain finally

$$I(\mathrm{TDS})=\sum_{m=1}^{\infty}\sum_{s=0}^{N-1}\left[2(N-s)\left[\frac{\lambda_{m+1}}{\lambda_1}\right]^{s}\cos(has)-1\right]\times\begin{cases}\langle m+1\,|\sin(hu)\,|\,1\rangle^2, & m\text{ odd}\\ \langle m+1\,|\cos(hu)\,|\,1\rangle^2, & m\text{ even}\ ,\end{cases}\tag{9}$$

which may be evaluated numerically.

III. RESULTS

Equation (9) describes a distribution of TDS intensity which takes the form of walls in reciprocal space, perpendicular to the chain axis and at separations $1/a$. The wall through the origin of reciprocal space has zero intensity and the other walls vary in width and maximum intensity according to their position in reciprocal space and to the temperature. The zero in the TDS intensity at zero scattering vector may be related to the fact that the atom at the origin "sees" itself as at rest.[11] Intensity distributions through the walls are displayed in Figs. 2—4. They were calculated, to an estimated numerical accuracy of two percent, from Eq. (9) using numerical methods outlined in Appendix 2 of Ref. 7.

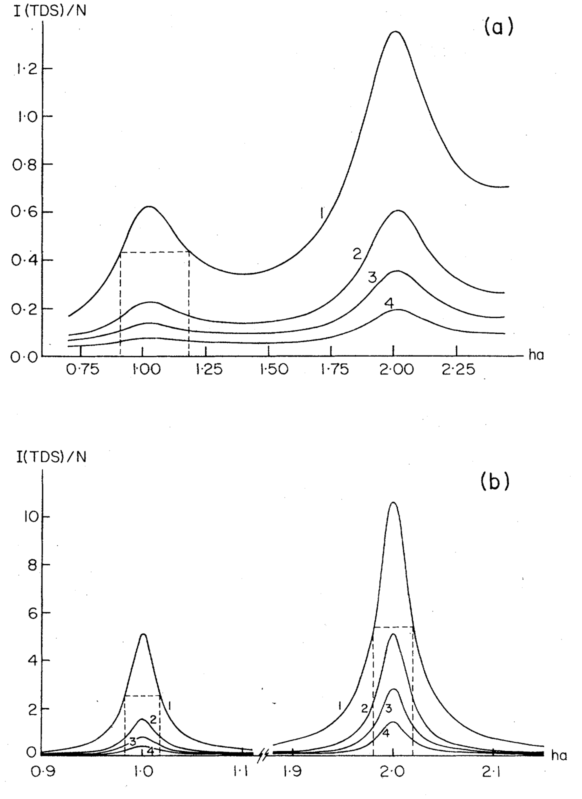

FIG. 2. TDS intensity per atom $I(\mathrm{TDS})/N$ for harmonic chains of 1000 atoms in length along directions parallel to the chain axis. Curves 1, 2, 3, 4 correspond to reduced temperatures $T'(=k_BT/m\omega_0\omega_ca^2)$ of 0.016, 0.004, 0.002, and 0.001, respectively. The broken lines mark the widths σ of the peaks, taken at the estimated half-height of the peak above the unmodulated background. (a) Weak coupling $\omega_c=\omega_0$, (b) stronger coupling $\omega_c=10\omega_0$.

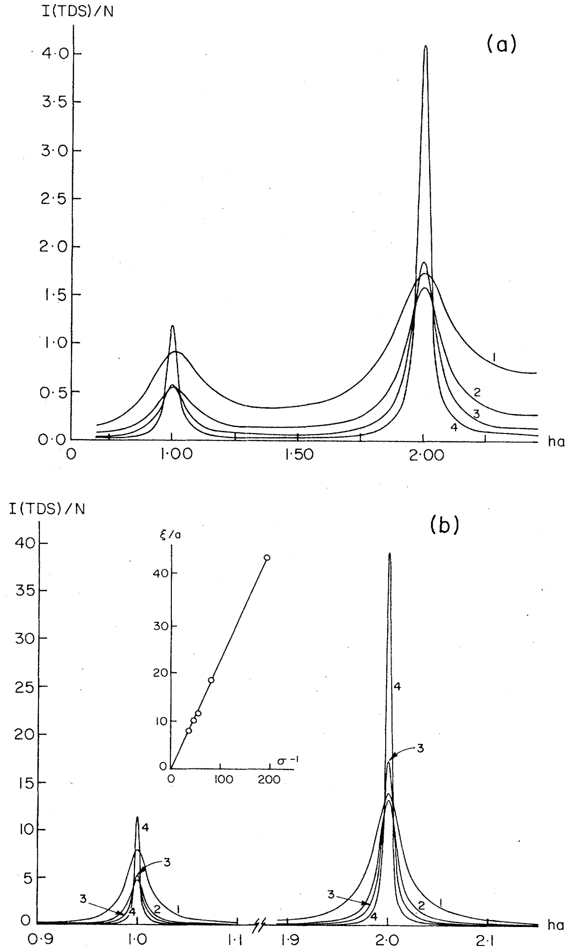

FIG. 3. TDS intensity per atom for DQ chains of 1000 atoms in length. Notation as for Fig. 2. (a) $\omega_c=\omega_0$, (b) $\omega_c=10\omega_0$. The inset to Fig. 3(b) shows the correlation length ξ/a, as calculated in Ref. 10, plotted as a function of inverse peak width at half peak height σ^{-1}.

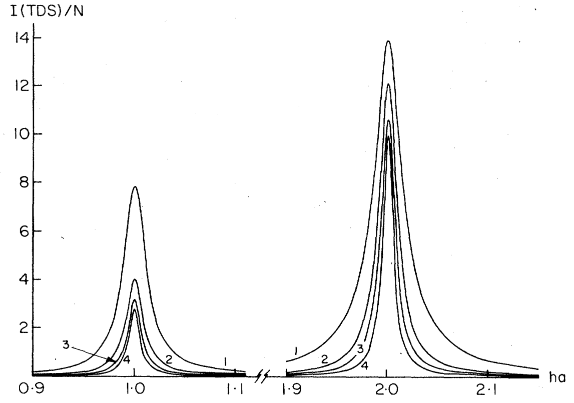

FIG. 4. TDS intensity per atom for an FQ chain of 1000 atoms in length, for coupling $\omega_c = 10\omega_0$. Notation as for Fig. 2.

A. Harmonic chain

The harmonic chains, Figs. 2(a) and 2(b), have overall TDS intensity distributions which get stronger (at least for $ha < 3$) with distance ha from the origin of reciprocal space. The intensity distribution has modulations peaking at $ha = n(n = \pm 1, \pm 2, \pm 3 \ldots)$. This intensity modulation gets weaker as the coupling decreases [cf. Figs. 2(a) and 2(b)] until for a set of Einstein oscillators ($\omega_c = 0$) the modulation disappears altogether. For a harmonic system, the h dependence of I(TDS) is then given by $\{1 - \exp(-h^2 \langle u^2 \rangle)\}$ (see Ref. 11). The peaks in fact result from the presence of correlations in the system and their widths σ are inversely proportional to the correlation length ξ. Figure 2 demonstrates that the peak widths are essentially constant, which is a reflection of the fact that ξ is constant for a harmonic chain (see Ref. 10). For the chain with weaker coupling [Fig. 2(a), $\omega_c = \omega_0$] $\xi/a = 0.7$ and for the other chain [Fig. 2(b), $\omega_c = 10\omega_0$] $\xi/a = 6.9$. Note that the finite length ($N = 1000$ atoms) is effectively infinite for the weakly coupled chain and is only just becoming detectably finite with respect to the sum over s in I(TDS) in the chain with $\omega_c = 10\omega_0$.

The peak heights in Fig. 2 decrease as T decreases. At low temperature the peak heights are almost linear with T, but increase less rapidly at higher temperatures when the Debye-Waller factor component of I(TDS) becomes appreciable. This component of I(TDS) is not obvious in Eq. (9), as written, but is well known in conventional expressions[5] for the harmonic one-phonon TDS [see also Eq. (10) below].

B. Nonharmonic chains

Figures 3 and 4 show the TDS intensity for DQ and FQ chains, respectively. There are two main differences between these nonharmonic results and the harmonic distributions of Fig. 2. The first is that the widths of the peaks are not constant, but decrease as T decreases. As can be seen from the inset to Fig. 3(b), the peak width σ is essentially inversely proportional to the correlation length.[10] The narrowing of the peaks is a reflection of the ordering in the chain as $T \rightarrow 0$. For the DQ chains the peak narrowing is much more rapid than for the FQ chain, in agreement with the slower increase in ξ, as $T \rightarrow 0$, found by Johnson and Mair[10] for the FQ chain.

The second nonharmonic effect is observed in the peak heights which, for the DQ chains, increase with decrease in T for $T' \lesssim 0.004$. For the FQ chain the peak height decreases more slowly than linearly with T, even at the lowest temperatures. This behavior may be interpreted in terms of mode softening if we recall that the peak in the one-phonon TDS I_1^P is proportional to the static susceptibility $\chi(T)$ (Ref. 12),

$$I_1^P \propto T\chi(T)M(T) \,, \tag{10}$$

where $M(T)$ is the Debye-Waller factor and is almost unity for T small. The static susceptibility is inversely proportional to the square of the soft-mode frequency Ω^2 and to $(T - T_c)^\gamma$, where $\gamma \sim 1.0$ and T_c is zero for a nearest-neighbor chain. Thus

$$I_1^P \propto \frac{TM(T)}{\Omega^2} \propto M(T) T^{(1-\gamma)} \,.$$

Insofar as we can apply the one-phonon approximation to the TDS calculations presented here, we can say that both the FQ and DQ chains are showing the effects of mode softening. For the temperature range shown, γ appears to be less than one for the FQ chain and greater than one for the DQ chains.

The effect of coupling strength [cf. Fig. 3(a) with Fig. 3(b)] is similar to that observed for the harmonic chains, smaller coupling resulting in a decrease in the modulation producing the peaks in I(TDS).

IV. SUMMARY

(1) The presence of pair-displacement correlations in chains of spacing a produces modulations in the TDS intensity, in the form of walls in reciprocal space at spacings a^{-1}.

(2) The widths of the walls are inversely proportional to the displacement correlation length. The widths are constant for the harmonic chains, but for the nonharmonic chains they narrow as the temperature approaches zero and the correlation length goes to infinity.

(3) The maximum intensity for the walls varies almost linearly with temperature for harmonic chains at low temperatures, but for the nonharmonic chains the maximum intensity decreases more slowly or even increases as the temperature approaches zero. This may be interpreted as an effect of mode softening.

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[1] S. R. Andrews and M. Mashiyama, J. Phys. C **16**, 4985 (1983).

[2] G. Honjo, S. Kodera, and N. Kitamura, J. Phys. Soc. Jpn. **19**, 351 (1964).

[3] S. Kodera, N. Kitamura, and G. Honjo, J. Phys. Soc. Jpn. **18**, 317 (1963); N. Kitamura, J. Appl. Phys. **37**, 2187 (1966).

[4] R. Comes, F. Denoyer, L. Deschamps, and M. Lambert, Phys. Lett. **34A**, 65 (1971).

[5] M. A. Krivoglaz, *Theory of X-ray and Thermal-Neutron Scattering by Real Crystals* (Plenum, New York, 1969); B. E. Warren, *X-ray Diffraction* (Addison-Wesley, London, 1969); B. Borie, Acta Crystallogr. **A26**, 533 (1970).

[6] D. J. Scalapino, M. Sears, and R. A. Ferrell, Phys. Rev. B **6**, 3409 (1972); J. A. Krummhansl and J. R. Schrieffer, *ibid.* **11**, 3535 (1975); A. R. Bishop, J. A. Krummhansl, and S. E. Trullinger, Physica (Utrecht) **1D**, 1 (1980).

[7] S. L. Mair, J. Phys. C **16**, 4811 (1983).

[8] S. L. Mair, J. Phys. C **16**, 5591 (1983).

[9] S. E. Trullinger and R. M. de Leonardis, Phys. Rev. A **20**, 2225 (1979).

[10] C. H. J. Johnson and S. L. Mair, J. Phys. C (to be published).

[11] J. M. Cowley, *Diffraction Physics* (North-Holland, Amsterdam, 1981), p. 150.

[12] R. A. Cowley, Ferroelectrics **53**, 27 (1984); A. D. Bruce and R. A. Cowley, *Structural Phase Transitions* (Taylor and Francis, London, 1981), p. 31.