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Computer Simulation of Bragg and Diffuse Scattering Intensities against Temperature for a Structural Phase Transition

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Abstract

Molecular dynamics has been used to estimate the properties of a two-dimensional crystal exhibiting a second-order soft-mode phase transition. Using a vibrational potential for the crystal which is *temperature independent*, the essential features observed experimentally in the coherent scattering from analogous real systems are reproduced in the computer simulation. The potential consists of an effective one-particle component with multiple minima and a harmonic nearest-neighbour coupling component. It is emphasized that the coupling component is essential to reproduce correctly the qualitative features not only of the diffuse scattering, but also of the mean-square displacements as a function of temperature. The condition for appearance of a cusp at T_C in the mean-square displacement *versus* temperature curve is discussed and the formation of superlattice peaks in the diffuse scattering is demonstrated.

Introduction

Crystallographic studies of structural phase transitions can provide information on the nature of the phase change through measurements of:

(*a*) the structure of the high- and low-temperature phases (with associated measurement of order parameters);

(*b*) the temperature factors as a function of temperature; and

(*c*) the diffuse scattering as a function of temperature.

The crystallographic literature contains many examples of such experimental studies, especially in the case of structural work. As experimental techniques become more efficient and data more reliable, it is apparent that more information could potentially be extracted from detailed measurements than is customary at present. For example, diffuse scattering can provide information on the pair-displacement correlations, and ultimately the pair-correlation function, and the temperature factors can help to establish whether soft modes are present and which atoms are involved.

Recognizing that a need exists for parallel theoretical studies of structural phase transitions, we aim in the present work to calculate crystallographic properties [namely, mean-square displacements (MSD's) and coherent scattering distributions] for a model system possessing a second-order soft-mode structural phase transition. The work follows on from calculations on a one-dimensional system (a chain) of coupled anharmonically vibrating atoms. MSD's, one-particle probability densities, effective one-particle potentials and fourth-order cumulants of the displacements were calculated (Mair, 1983*a*, *b*) as well as pair-displacement correlations (Johnson & Mair, 1985) and disorder diffuse scattering (Mair, 1984*a*). The present model is an extension of the system to two dimensions and so ordering can occur at a finite temperature, T_C. Unlike the one-dimensional case, which could be treated in a semi-analytical way, the two-dimensional calculations are made with the technique of molecular dynamics.

The details of the model and numerical methods have already been reported (Mair, 1986) so only an outline of these will be presented. Mair (1986) also gives results on MSD's, some of which are repeated

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here together with new MSD results. A subsequent paper (Mair, 1987) reports the temperature dependence of the pair-displacement correlations and the frequency spectrum of the order-parameter correlation function, showing the mode softening and central peak formation.

While the model system reproduces the essential features and temperature dependence of some properties of soft-mode phase-transforming crystals, it is not suitable for quantitative comparison with any real system. In particular, the model system is two-dimensional, of rather limited size, and the Hamiltonian, whilst carefully chosen in some respects, still possesses some arbitrary features. These shortcomings in the model do not detract from the paper's more general aim, which is to demonstrate the power of a model in which explicit coupling is allowed between atoms and to point out some of the limitations of uncoupled models.

Model

The vibrational potential, Φ, is written in terms of the displacements (x_{lk}, y_{lk}) of the atoms from high-temperature equilibrium positions identified by points (l, k) on a square lattice. Dividing Φ into an effective one-particle potential, $\varphi_{\rm anh}$, and a harmonic coupling component, φ_c, we define

$$\varphi_{\rm anh} = \sum_{lk} (m\omega_0^2/2)[(|x_{lk}| - d)^2 + (|y_{lk}| - d)^2]. \quad (1)$$

Although $\varphi_{\rm anh}$ is anharmonic, with four equivalent minima in the $\langle 11 \rangle$ and symmetry-related directions, it has quadratic walls.

$$\begin{aligned}\varphi_c = \sum_{lk} \{&(m\omega_C^2/2)[(x_{lk} - x_{l+1\,k})^2 + (y_{lk} - y_{l\,k+1})^2 \\ &+ (x_{lk} - x_{l\,k+1})^2 + (y_{lk} - y_{l+l\,k})^2] \\ &+ (m\omega_D^2/2)[(x_{lk} - y_{l+1\,k})^2 + (y_{lk} - x_{l+1\,k})^2 \\ &+ (x_{lk} - y_{l\,k+1})^2 + (y_{lk} - x_{l\,k+1})^2]\} \end{aligned} \quad (2)$$

$$\Phi = \varphi_{\rm anh} + \varphi_c. \quad (3)$$

With a choice of temperature-independent numerical values for the parameters $m\omega_0^2 = 4{\cdot}0$, $d = 0{\cdot}1$, $m\omega_D^2 = 1{\cdot}0$, $m\omega_C^2 = -0{\cdot}1$ [model 1*B* of Mair (1986)], the potential has two deep minima in the directions $\langle 1, -1 \rangle$ and $\langle -1, 1 \rangle$. For temperatures $T < T_C$, the atoms order themselves antiferrodistortively near these minima. Fig. 1 shows the high- and low-temperature unit cells and (schematically) the two deep minima near each high-temperature site. Note that there are two atoms in the unit cell, both of the same mass.

The potential (1) has a cusp-shaped potential barrier, which might be regarded as an undesirable shape. Calculations have therefore been carried out for a modified $\varphi_{\rm anh}$ in which this cusping is rounded off by the replacement of $(|x| - d)^2$ by

$$ax^6/d^4 + bx^4/d^2 + cd^2 \quad \text{for } |x| < d/4$$

and analogously for the y component of $\varphi_{\rm anh}$. The choice of $a = 426{\cdot}667$, $b = -64$ and $c = 0{\cdot}708333$ ensures that $\varphi_{\rm anh}$ is smooth everywhere.

All calculations are for a square crystal of N^2 atoms where $N = 40$, except for the model with the rounded potential barrier, for which case $N = 20$. The molecular dynamics computations were performed on a Cyber 205, extensive use being made of vector processing.

The order parameter, given by the time-averaged value of S_x, where

$$S_x = N^{-2} \sum_{lk} (-1)^{l+k} x_{lk} \quad (4)$$

is zero for $T \geq T_C$ and follows the expected Ising-like behaviour for $T < T_C$ (Mair, 1986). S_x is the x component of the space-averaged shift in position of an atom from its high- to its low-temperature mean position. S_y, defined analogously to (4), is equal to $-S_x$, after averaging both components of S over time.

The MSD's are calculated with respect to the high-temperature (HT) equilibrium positions of the atoms. However, a diffraction experiment provides MSD's referred to the low-temperature (LT) atomic mean positions if $T < T_C$. In order to obtain MSD's referred to these new origins it may readily be shown that

$$\langle x^2 \rangle_{\rm LT} = \langle x^2 \rangle_{\rm HT} - S_x^2 \quad (5)$$

and analogously for the $\langle y^2 \rangle$.

In the single-scattering approximation the coherent scattered intensity I is given by

$$I(\mathbf{h}) = \sum_{ij} f_i(\mathbf{h}) f_j(\mathbf{h}) \exp[2\pi i \mathbf{h}.(\mathbf{r}_i - \mathbf{r}_j)]. \quad (6)$$

In our calculations the scattering factors f_i, f_j are chosen arbitrarily as the electron-scattering factors for silicon. Note that these electron-scattering factors are approximately proportional to the X-ray ones over the low-angle range of reciprocal space

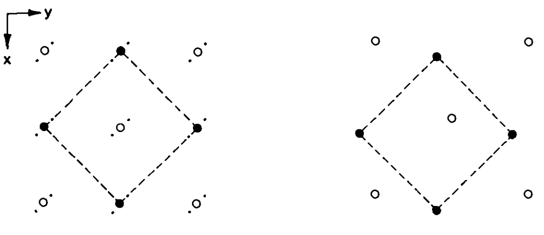


Fig. 1. The high- (left diagram) and low-temperature structures for the model. Open and closed circles represent the two atoms in the unit cell. The pairs of points are discussed in the text. The symmetries are *cmm* $(T > T_C)$ and *pm* $(T < T_C)$.

considered. The $\mathbf{r}_i$, $\mathbf{r}_j$ are the final instantaneous positions of the 1600 atoms after a suitable number of time-steps in the molecular-dynamics runs. The numerical evaluation of the intensity was accomplished by the use of discrete Fourier transforms. In practice, to reduce the effects of noise in the intensity distributions, the final intensity $\langle I \rangle$ was taken as the mean intensity for six separate sets of positions, corresponding to widely separated time steps.

Results

1. *Mean-square displacements*

The MSD's are presented in Fig. 2. The results for the rounded potential barrier, as shown by the crosses in the figure, deviate only slightly from the full curve for the unmodified barrier. The largest deviations, as might be expected, are near T_C (where $T_C = 0{\cdot}029$ in the scaled temperature units) and are probably a result of the slight lowering by rounding of the potential barrier. We may conclude that the cusp shape for the barrier is of little consequence, at least for the MSD. A more severe change in the potential barrier was investigated by Mair (1986). This produced similar but larger deviations.

The MSD, when referred to the high-temperature equilibrium positions, *i.e.* $\langle x^2 \rangle_{\rm HT}$, is quite smooth for this second-order phase transition, T_C occurring at the point of inflexion. *It is only through referring the MSD's for* $T < T_C$ *to the new origins corresponding to the low-temperature structure* (*i.e.* by introducing $\langle x^2 \rangle_{\rm LT}$) *that the MSD can exhibit a cusp at* T_C.

Fig. 2 shows the same trends as experimental results for MSD's of soft-mode systems, at least for $T > T_C$ where most detailed measurements have been made. [*E.g.* $CsPbCl_3$ and $CsPbBr_3$ (Sakata, Harada, Cooper & Rouse, 1980) and K_2SnCl_6 (Mair, 1984*b*). See also the results of Nelmes, Kuhs, Howard, Tibballs & Ryan (1985) for a narrow temperature range near T_C for the mildly first-order phase transitions in KH_2PO_4 and KD_2PO_4.] Of special interest are the results of Lander & Brown (1985) for the average MSD of atoms in $AuCu_3$ at temperatures in the vicinity of the order-disorder transition. Although in this case the ordering depends upon specific site occupancies, rather than small atomic displacements, the experiment gave a smooth average MSD through T_C.

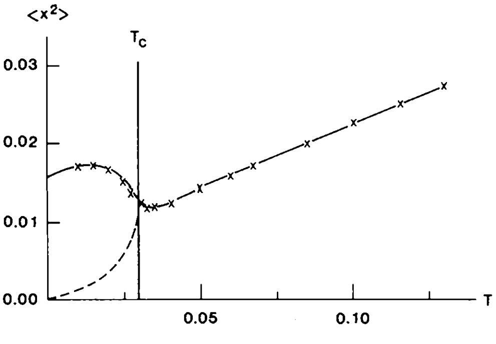


Fig. 2. The MSD as a function of scaled temperature. The full line is $\langle x^2 \rangle_{\rm HT}$, the crosses giving values for the model with the rounded potential barrier. The broken line is $\langle x^2 \rangle_{\rm LT}$ of equation (5). To the scale of the diagram, no difference occurs in $\langle x^2 \rangle_{\rm LT}$ for the modified potential barrier. The MSD's are in dimensionless units, the displacements being expressed as fractions of the lattice constant.

Note that for an atom undergoing harmonic motion, the MSD is a straight line through the origin [see Mair (1986), where a case is given in which one component of an atom's motion is harmonic]. Note also that the straight line for $T \gg T_C$, which is also observed in the experimental results for $CsPbCl_3$, $CsPbBr_3$ (Sakata *et al.*, 1980) and K_2SnCl_6 (Mair, 1984*b*), is a consequence of the quadratic walls of $\varphi_{\rm anh}$ and the harmonic nature of φ_c. A quartic potential for $\varphi_{\rm anh}$ therefore gives an incorrect high-temperature behaviour for the MSD [as obtained by Schneider & Stoll (1980)].

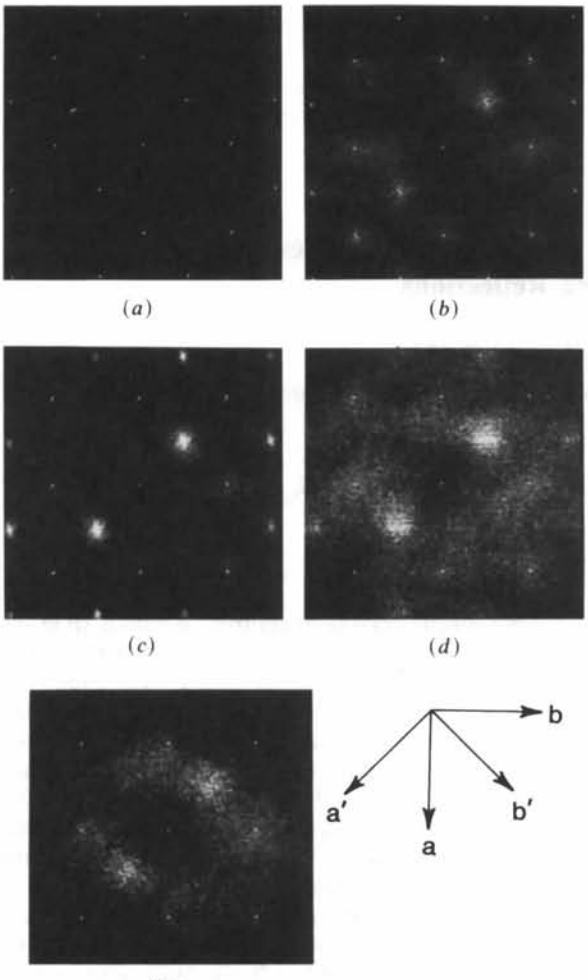
2. *Coherent scattered intensities*

The Bragg and diffuse scattering for a series of five temperatures (two below T_C and three above) are presented in Fig. 3 for the model defined by equations (1) to (3). The a and b axes are directed along the x and y axes of Fig. 1, alternative primed axes being introduced for convenience of interpretation.

The symmetry of all the diffraction patterns is *cmm*. For $T > T_C$, Bragg peaks occur at $h' + k' = 2n$, corresponding to the face-centred structure of the high-temperature cell. For $T < T_C$, the occurrence of superlattice peaks means that Bragg peaks occur at all reciprocal-lattice points except for $h' = 4n$ with $k' = 2m + 1$ ($|h'|, |k'| = 0, 1$ and $0, 3$ in the figure). These are special absences resulting from the two atoms in the unit cell having the same scattering factors. At $T = 0{\cdot}01$ additional absences occur at $h' = 2n + 2$, $k' = 4n$ ($|h'|, |k'| = 2, 0$ in Fig. 3*a*). This may be understood in terms of the coordinates of the low-temperature unit cell (x', y') of $(0, 0)$ and $(p, \frac{1}{2})$. As the temperature tends to zero, the choice of parameters for the model means that p tends to $\frac{1}{4}$ [see Table 2 of Mair (1986)]. For those coordinates and indistinguishable scattering factors for both atoms in the unit cell, the additional absences occur.

For $T > T_C$, the two strongest diffuse peaks occur at $(\pm 1, 0)$ in the primed coordinate system. The positions of the peaks are consistent with the wave vector of the soft mode driving the phase transition. This transverse mode occurs at wave vector $\mathbf{q}_s = \pi / a(\mathbf{e}_1 + \mathbf{e}_2)$, where $\mathbf{e}_1$ and $\mathbf{e}_2$ are unit vectors in the x and y directions, respectively, and a is the lattice constant. The mode softening is demonstrated by Mair (1987).

The intensity of the diffuse peaks decreases and the width increases as T is raised, but the peaks are still present even at quite high temperatures (Fig. 3*e*). If we recall that the peak width is proportional to the inverse correlation length (*e.g.* Mair, 1984), this means that the atomic displacements remain correlated far above T_C. As T is lowered the correlation length increases to a large but finite value at T_C. Below T_C (Fig. 3*b*) there is still some diffuse scattering around the superlattice peak, indicating that the correlation length is still increasing. This is a reflection of the fact that the pair-displacement correlations vary smoothly through T_C (Mair, 1986, 1987), although they increase rapidly at T_C. Only at the lowest temperatures (Fig. 3*a*) does this diffuse scattering disappear.



(*a*) (*b*)

(*c*) (*d*)

(*e*)

Fig. 3. The Bragg and diffuse-scattered intensities for scaled temperatures of (*a*) 0·01, (*b*) 0·02625, (*c*) 0·03125, (*d*) 0·06 and (*e*) 0·13, where $T_C = 0{\cdot}029$. Intensity levels were calculated on a logarithmic scale, with 16 grey levels, ranging from 10^{-4} to 10^{-1} (so that $I \leq 10^{-4}$ appears black and $I \geq 10^{-1}$ appears white). The origin of reciprocal space is at the geometrical centre of each diffraction pattern.

Within the limitations imposed by the noise in the distributions and the convolution with the square aperture function representing the finite size of the crystal, it appears that the diffuse peaks are isotropic. This result is consistent with calculations on a two-dimensional nearest-neighbour Ising model, which predict that the spin–spin correlations are isotropic (Kadanoff, 1966). That system is a spin analogue of the present model.

Discussion

1. *The importance of coupling*

For a model system to exhibit *any* disorder diffuse scattering it must include coupling between the atoms. A system of uncoupled atoms cannot produce any structure in the diffuse scattering, only a smooth increase in diffuse intensity with scattering angle until the Debye–Waller factor takes over at high angles (Willis & Pryor, 1975; Cowley, 1975). It is less obvious, perhaps, that coupling has a significant effect on the MSD's. In fact, as shown below, *the correct temperature dependence for the MSD's requires a model potential with explicit coupling between the atoms.*

Uncoupled-atom approximations to the MSD for systems with a structural phase transition include the work of Itoh (1984) and a mean-field approximation to the present model (Mair, 1986). The method of Itoh is effectively a split-atom model with provision for temperature dependence of the atom separation to be related to an order parameter of the form $\tanh(C/k_BT)$, where C is a constant. With the MSD's referred to origins for the structure of the high-temperature phase, Itoh's formula reduces to

$$\langle x^2\rangle_{\rm HT} \propto k_BT + cd^2, \qquad (7)$$

where d is the separation of the split atoms at $T > T_C$ and c is a constant. Equation (7) is just a straight line and so is only correct for $T \gg T_C$.

The mean-field approximation to the MSD for the model in this paper (see Mair, 1986) gives a straight line for $T \gg T_C$ and is still qualitatively similar to Fig. 2 for $T < T_C$, but has a downward-directed cusp in $\langle x^2\rangle_{\rm HT}$ at T_C. The fully coupled model presented here shows that $\langle x^2\rangle_{\rm HT}$ is smooth at all temperatures, with a minimum just above T_C (rather than a cusp at T_C) and T_C occurring at the point of inflexion in the curve.

2. *Split-atom models*

Although they are not suitable for predicting the temperature dependence of the MSD's, split-atom models are convenient for fitting Bragg diffraction data from phase-transforming crystals. If moments of the displacement no higher than the second are required, this fitting device appears to form a reasonable practical approach. However, there is no reason to believe that Bragg intensities fitted with a split-atom model necessarily correspond to a static distribution of atoms about fractionally occupied sites. In the present model, for example, the atoms are continuously hopping across the potential barrier for $T > T_C$ and even below T_C some hopping occurs until the temperature is low enough for the ordering to be complete. Nevertheless, a split-atom model would give a reasonable fit to the corresponding Bragg scattering [see Mair (1983*b*), where a split-atom model is used to fit probability densities for a one-dimensional analogue of the present data].

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Anharmonicity of Atomic Vibrations in Magnesium by Measurement of Almost-Forbidden Reflections

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Abstract

The X-ray intensities of almost-forbidden reflections 301 and 303 in a single crystal of magnesium have been measured at 293 K. Effective monochromatization by appropriate electronics was utilized to increase the observability of these weak reflections. The data are interpreted in terms of atomic vibrations by application of a quantum-statistical one-particle formalism that allows anharmonic contributions to the atomic temperature factor. A value of $-0{\cdot}43\,(3)\ \mathrm{eV\,Å^{-3}}$ is obtained for the third-order anharmonic parameter, the negative sign being deduced from the coordination. This outcome is in accordance with earlier results concerning anharmonic vibrations.

1. Introduction

A proper consideration of symmetry requirements has an important implication in diffraction studies. For some simple crystal structures, in which all atoms are at special positions and not located at the centre of symmetry, the conventional special extinction rules may be violated. Consequently, weak 'forbidden' reflections - more properly termed almost-forbidden reflections - may occur. X-ray and neutron diffraction studies on the first and best known case - the 222 reflection in diamond structures - have demonstrated both non-sphericity of valence-charge density and anharmonicity of thermal vibrations (Roberto & Batterman, 1970; Keating & Nunes, 1971; Bilderback & Colella, 1975). Recently, almost-forbidden reflections have been observed in hexagonal close-packed zinc (Merisalo, Järvinen & Kurittu, 1978) and cadmium (Merisalo, Peljo & Soininen, 1978), and in tetragonal tin (Merisalo & Järvinen, 1978). In all these studies the data were interpreted in terms of anharmonicity of lattice vibrations. The most recent measurement on the almost-forbidden reflection 202 of white tin (Merisalo & Soininen, 1979) revealed the

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