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NEUTRON INELASTIC SCATTERING
AT STRUCTURAL PHASE TRANSITIONS

R. A. COWLEY
Department of Physics, University of Edinburgh, Edinburgh, Scotland

Abstract. — Neutron inelastic scattering measurements in materials making structural phase transitions are reviewed. In some materials SrTiO₃ and KTaO₃ a well defined normal mode is observed whose frequency squared decreases almost linearly with temperature. In other materials appreciable damping is observed and in BaTiO₃ and KNbO₃ this damping is sufficiently large that the scattering from these modes is entirely quasi-elastic. Quasi-elastic scattering is also observed in order-disorder ferroelectrics such as NaNO₂ but in this case a well-defined almost temperature independent phonon mode is also observed. The hydrogen bonded ferroelectric DKDP gives rise to quasi-elastic scattering also but in this case its origin is less clearly understood. Recent developments including the anisotropy of the dispersion curves, critical effects and eigenvector determination are briefly discussed.

Neutron inelastic scattering measurements provide one of the most detailed ways of studying the microscopic properties which give rise to structural phase transitions. The scattering is governed by the laws of conservation of energy and wavevector and since thermal neutrons have energies and wavevectors which are compatible with those of the normal modes of vibration of the atoms in crystals, the frequencies and wavevectors of these modes may be readily measured. These techniques have now been applied to the study of several phase transitions and in this review we shall not attempt a comprehensive cover of the whole field but will briefly discuss the aspects of the phenomenon which are of most importance.

The intensity of the one-phonon part of the scattering with a frequency transfer, \( \omega \), and wavevector transfer, \( \mathbf{Q} \), is proportional to

\[
S(Q, \omega) = (n(\omega) + 1) \left| F(Q) \right|^2 \sigma(q) \Delta(Q - q),
\]

where \( n(\omega) \) is the Bose occupation number, \( \Delta(Q - q) \) is a delta function expressing that \( Q - q = \tau \), a reciprocal lattice vector, while \( F(Q) \) is the structure factor of the mode with wavevector \( q \) and branch \( j \).

\[
F(Q) = \sum_k b_k \mathbf{Q} \cdot \mathbf{U}(K | q) \times \exp(-W(K)) \exp(i\mathbf{r} \cdot \mathbf{R}(K))
\]

where \( b_k \) is the coherent neutron scattering length, \( \mathbf{U}(K | q) \) the displacement in the normal mode, \( W(K) \) the Debye-Waller factor and \( \mathbf{R}(K) \) the position in the unit cell of the atom of type \( K \). The one-phonon response function is given for a harmonic crystal by

\[
\sigma(q) = \pi\delta(\omega^2 - \omega(q)^2),
\]

where \( \omega(q) \) is the harmonic frequency of the normal mode. By using neutron scattering it is possible to measure \( S(Q, \omega) \) and hence to deduce the form of both the normal mode eigenvectors \( \mathbf{U}(K | q) \) and the response function \( \sigma(q) \).

In a crystal which undergoes a structural phase transition Cochran [1] suggested that the frequency of a normal mode decreased to zero as the phase transition was approached:

\[
\omega(q) = K(T - T_c).
\]

For a ferroelectric phase transition \( q = 0 \) but for a structural phase transition in which the unit cell size increases \( q \) corresponds to a zone boundary or possibly some other wavevector normal mode. Eq. (3) was shown to be applicable for the near ferroelectric phase transition in SrTiO₃ [2] and KTaO₃ [3]. More recently the frequency of the zone-boundary normal mode responsible for the phase transition in SrTiO₃ at 105 °K has been studied over a very wide temperature range as shown in figure 1 [4]. It may be seen from this that eq. (3) is a very reasonable first approximation.

Résumé. — Nous passons en revue les mesures par diffusion inélastique de neutrons dans les matériaux qui ont des transitions de phase structurales. Dans certains matériaux comme SrTiO₃ et KTaO₃ on observe un mode normal bien défini, dont le carré de la fréquence décroît presque linéairement avec la température. Dans d'autres matériaux on observe un amortissement appreciable et dans BaTiO₃ et KTaO₃ cet amortissement est suffisamment large pour que la diffusion de ces modes soit entièrement quasi-élastique. La diffusion quasi-élastique est aussi observée dans les ferroélectriques du type ordre désordre comme NaNO₂ mais dans ce cas un mode de phonon et pratiquement indépendant de la température est ainsi observé. Le ferroélectrique à liaison hydrogène DKDP donne aussi lieu à une diffusion quasi-élastique mais dans ce cas on comprend moins bien son origine. Nous discutons brièvement des récents développements qui contiennent l'anisotropie des courbes de dispersion, les effets critiques et la détermination des vecteurs propres.
In other materials it has been found that the normal mode is not well defined but that it is necessary to take account of the damping of the normal mode to describe the response of the crystal. Under these conditions a classically damped simple harmonic oscillator model is frequently a reasonable first approximation when eq. (2) is replaced by

\[ \sigma(q) = \frac{\omega \gamma}{(\omega^2 - \omega(q))^2 + \omega^2 \gamma^2}. \]  

This expression has been used with at least qualitative success, as shown, for example, in figure 2, to describe the scattering from the \( \Gamma_{25} \) mode responsible for the phase transition in KMnF₃ [5].

\[ T = \frac{\gamma}{\omega(q)} \]

while the total scattered intensity for a given \( q \) is proportional to \( 1/\omega(q)^2 \). Quasi-elastic scattering of this type has been observed in BaTiO₃ by Yamada et al. [6] and in KNbO₃ by Nunes et al. [7].

One of the surprising results which has been found in these perovskite materials is the behaviour of the normal modes with wavevector \( q \) in the neighbourhood of a mode \( q_0 \), which is responsible for a phase transition. In figure 3 we show \( \omega(q) \) for several different directions away from \( q_0 \) for the ferroelectric modes in SrTiO₃ [8] and BaTiO₃ [10], [5]. In the case of BaTiO₃ the dispersion curve is very anisotropic with very low frequency and overdamped modes when the polarisation vector is along the [100] direction. Little anisotropy is observed in SrTiO₃. Around the \( \Gamma_{25} \) modes both crystals show anisotropy when \( q - q_0 \) is along [100] but it is more marked for KMnF₃. These anisotropies are related to the streaks observed in the X-ray scattering of these materials [11], but at present their origin is not understood microscopically. Since both KMnF₃ and BaTiO₃ show larger anisotropies than SrTiO₃ and the modes are also more heavily damped in these materials, the anisotropy may arise in part from anharmonic interactions.

The results of figure 2 show that the normal mode may be fairly well defined well above the transition temperature but as the temperature is reduced the scattering becomes entirely quasi-elastic and the mode is overdamped. In some materials the damping constant \( \gamma \), is sufficiently large that only quasi-elastic scattering has been observed. The width of this scattering then gives a measure of the lifetime of the fluctuations.

\[ \omega(q) \]

FIG. 1. — The square of the frequency of the \( \Gamma_{25} \) soft mode frequency as a function of temperature in SrTiO₃. The dotted line is a straight line \( \omega(T - T_c) \) and other lines more complex theories as described in [4].

FIG. 2. — Neutron scattering from the \( \Gamma_{25} \) phonon in KMn₀.₈Co₀.₂F₃ as a function of temperature as compared with a best fit simple harmonic oscillator model.

FIG. 3. — The dispersion curves \( \omega(q) \) for various branches of the dispersion relations around the soft modes of SrTiO₃ at 90 °K and of BaTiO₃ [9] at 423 °K and for the \( R \) point soft mode in SrTiO₃ [8] and KMnF₃ [10], [5] at 295 °K.
A rather different picture has been obtained from studies of order-disorder ferroelectric materials such as NaNO$_3$ [12]. Above the ferroelectric phase transition in this material the NO$_3$ groups may align with the N ion along either the + b or −b direction, but below the transition temperature they align along one or other of these directions. The normal modes of vibration are then found to have frequencies which are relatively independent of temperature but in addition there is quasi-elastic scattering associated with the fluctuations in the positions of the NO$_3$ groups. The former oscillations have frequencies of $5 \times 10^{12}$ Hz while the hopping from one equilibrium position to the other occurs on a time scale of $10^9$Hz. These two types of motions are quite uncoupled from one another and give rise to different features in the scattering. In practice the transition in NaNO$_3$ is complicated because there is a sinusoidal ferroelectric phase which exists for a few degrees above $T_c$. In figure 4 we show the intensity of the quasi-elastic scattering in the paraelectric phase, sinusoidal phase, and ferroelectric phase showing that it increases in magnitude as the temperature is decreased towards $T_c$ particularly in the region of wavevectors near the periodicity of the sinusoidal phase.

Experiments have also been conducted on two materials of the KDP class. These materials are DKDP [13], [14] and DADP [15] and show a ferroelectric phase transition and an antiferroelectric phase transition respectively. In both cases only quasi-elastic scattering has been observed and its intensity has been measured as a function of temperature and wavevector as shown in figure 5. The intensity is observed to increase as the phase/phase transition is approached and furthermore to have a shape as a function of wavevector which is characteristic of a ferroelectric phase transition. It is however still uncertain whether this quasi-elastic scattering arises from an overdamped normal mode as in BaTiO$_3$, or from order-disorder scattering as in NaNO$_3$, or an overdamped tunneling mode as suggested by tunneling theories of these materials.

We have shown that the response functions $\sigma(q)$ may have quite different structures dependent upon the physical system. Recently more detailed work has been started on studying the form of $\sigma(q)$ in detail close to the phase transition. Experiments by Feder et al. [16] have shown that the shape in SrTiO$_3$ is in detail quite different from that discussed above and that these discrepancies are believed to arise from the failure of our simple models in the critical region. We can expect a large amount of detailed information about the shape of the response functions to be forthcoming in the near future.

The Brookhaven group has also shown that there are strong interferences between the scattering from acoustic modes and the ferroelectric modes. The interferences give rise to characteristic asymmetries in the scattered distributions. We can expect more detailed information of this type.

In addition to the form of the response function neutron scattering can also give information about the
normal mode eigenvectors. If the scattered intensity is measured as a function of wavevector transfer \( Q \) for the same wavevectors \( q \) the eigenvectors \( U(K | q) \) can be obtained by a similar process to that used in finding crystal structures [17]. Measurements of this type have been made of the modes involved in many different phase transitions as described for example for DKDP and DADP in this conference [18].

References

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