

## Anomalous neutron scattering and ferroelectric soft modes

K S VISWANATHAN

Department of Physics, Kerala University, Kariavattom, Trivandrum 695017

MS received 2 February 1977

**Abstract.** It is suggested that anomalous neutron scattering could prove a powerful experimental tool in studying ferroelectric phase transition, the sublattice displacements of the soft modes as well as their symmetry characteristics.

**Keywords.** Neutron scattering; ferroelectric modes.

It has been shown in an earlier paper (Ramaseshan and Viswanathan 1970) that anomalous neutron scattering studies in crystals could provide a powerful method for evaluating the amplitudes of lattice waves in crystals that contain at least one anomalous scatterer in the unit cell. Strong anomalous dispersion effects occur in neutron scattering by crystals containing anomalous scatterers like  $^{113}\text{Cd}$ ,  $^{151}\text{Eu}$ ,  $^{149}\text{Sm}$  and  $^{157}\text{Sd}$ . In these nuclei, the nuclear resonance energies are low and lie in the thermal neutron range. In anomalous scattering of neutrons, the scattering factor is complex and has the form

$$f = f_0 + f' + if'' \quad (1)$$

where  $f_0$  is the normal scattering factor for wavelengths far removed from the resonance region while  $f'$  and  $f''$  are dependent on the wavelength of the incident neutron. Secondly, the real part  $f'$  of the correction could be five to ten times larger than the scattering length (Ramaseshan 1966, Singh and Ramaseshan 1968). In the following, we shall use the usual notation of lattice dynamics (Maradudin *et al* 1963). Let  $e_a(k_i|k_j)$  denote the amplitude of the lattice wave passing through the atoms of the type  $k_i$  in the unit cell of the normal mode  $Q(k_j)$  corresponding to the wave vector  $k$  and the branch  $j$  of the dispersion equation. In anomalous scattering, the intensity corresponding to the Bragg scattering by vectors  $K$  and  $-K$  are different. Let  $I_0$  and  $I_0^*$  denote the zeroth order scattering corresponding to the reciprocal lattice vectors  $K$  and  $-K$  respectively, and let  $I_1$  and  $I_1^*$  denote the intensity associated with the reciprocal lattice vectors  $(K_1 + 2\pi k)$  and  $(-K_1 - 2\pi k)$ . Then it is shown in Ramaseshan and Viswanathan (1970) that the differences  $\Delta I_1 = (I_1 - I_1^*)$  could give useful information to evaluate the quantities  $S_{k_1, k_2}$  given by

$$S_{k_1, k_2} = \frac{\hbar}{N \sqrt{M_{k_1} M_{k_2}}} R \left[ K \cdot e \left( k_2 \middle| k \right) K \cdot e \left( k_1 \middle| k \right) \right] \times \frac{[n(kj) + 1]}{2\omega_j(k)} \quad (2)$$

These quantities involve the polarization vector  $e(k_i | j^k)$  of the lattice waves passing through the different atoms in the unit cell. In fact, for a crystal with two atoms in the unit cell of which at least one is an anomalous scatterer, it was shown in Ramaseshan and Viswanathan (1970) that

$$\frac{\Delta I_1}{\Delta I_0} = S_{12} \left( \frac{\sin K_1 \cdot M}{\sin K_0 \cdot M} \right).$$

It was shown that by studying the peaks corresponding to the same  $k$  but to different values of the incident vector  $K_i$  of the momentum transfer vector such that  $K_i + 2\pi k =$  reciprocal lattice vector, one can evaluate the quantities  $e_\alpha(k_i | j^k)$  relating to the lattice waves.

Since the number of normal modes in a crystal is very large, the above method has not found much application in evaluating the amplitudes of the lattice waves in crystals and has remained a theoretical possibility. If however there exist certain normal modes having special or important physical characteristics, the method can be applied to study the amplitudes of these lattice waves. Such a situation in fact occurs in ferroelectric or antiferroelectric materials. These substances exhibit a phase transition on cooling, during which its structure changes from a high symmetry phase to a low symmetry one. The phase transition is accompanied by a spontaneous polarization at the critical transition temperature, and further one of the lattice modes becomes soft at  $T = T_c$ . The phase transition is also accompanied by a sublattice displacement of the soft mode. For ferroelectric substances, the soft mode corresponds to the vector  $k = 0$  whereas for antiferroelectric substances, it corresponds to  $k = K/2$  where  $K$  is a reciprocal lattice vector. Since the soft modes play a *crucial* role in ferroelectric phase transition and are *few* in number, anomalous scattering studies can be used to evaluate the amplitudes of these lattice modes.

Now a very large number of ferroelectric or anti-ferroelectric materials are compounds of Cd, Eu, Sm and Gd, which have isotopes that scatter anomalously. Examples of ferroelectric compounds of these nuclei are:  $\text{CdHfO}_3$ ,  $\text{Cd}(\text{Fe}_{1/2} \text{Nb}_{1/2})\text{O}_3$ ,  $\text{Cd}(\text{Sc}_{1/2} \text{Nb}_{1/2})\text{O}_3$ ,  $\text{Cd}(\text{Cr}_{1/2} \text{Nb}_{1/2})\text{O}_3$ ,  $\text{Cd}(\text{Mg}_{1/3} \text{Nb}_{1/3})\text{O}_3$ ,  $\text{Cd}_2\text{Nb}_2\text{O}_7$ ,  $\text{Cd}_2\text{Nb}_2\text{O}_6\text{S}$ ,  $\text{Cd}_2\text{CrNbO}_6$ ,  $\text{Cd}_2\text{FeNbO}_6$ ,  $\text{Sm}_2(\text{MoO}_4)_3$ ,  $\text{Eu}_2(\text{MoO}_4)_3$  and  $\beta\text{-Gd}_2(\text{MoO}_4)_3$ . Examples of anti-ferroelectric substances involving these anomalous scatterers are  $\text{CdTiO}_3$ ,  $\text{CdHfO}_3$  and  $\text{CdSc}_{1/2} \text{Nb}_{1/2} \text{O}_3$ . In fact a much larger list of the known ferroelectric and anti-ferroelectric substances has been given by Blinc and Zeks (1974) and from this list, it can be seen that a very large number of ferroelectric substances are compounds of atoms scattering anomalously. Hence the method described above can be applied to a large number of ferroelectric compounds and anomalous neutron scattering studies could provide a new and powerful method of studying the amplitudes of the soft modes, their symmetry characteristics, the sublattice displacements in these compounds, and generally the phase transition at the critical temperature of these ferroelectric compounds.

**References**

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