



EVIDENCE FOR FERROELECTRICITY IN IV-VI COMPOUNDS

G. Pawley

► To cite this version:

G. Pawley. EVIDENCE FOR FERROELECTRICITY IN IV-VI COMPOUNDS. Journal de Physique Colloques, 1968, 29 (C4), pp.C4-145-C4-150. 10.1051/jphyscol:1968423 . jpa-00213627

HAL Id: jpa-00213627

<https://hal.science/jpa-00213627>

Submitted on 4 Feb 2008

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

EVIDENCE FOR FERROELECTRICITY IN IV-VI COMPOUNDS

G. S. PAWLEY

Department of Natural Philosophy — The University, Edinburgh, Scotland

Résumé. — Parce que les méthodes habituelles servant à établir le caractère ferroélectrique des cristaux ne sont pas applicables au cas de corps de haute conductivité, on doit alors introduire d'autres moyens basés sur d'autres propriétés ferroélectriques. L'analyse de la structure cristalline peut fournir un modèle montrant la possibilité de polarisation réversible, mais une preuve plus convaincante peut venir de l'étude de la dynamique du cristal. La diffusion inélastique cohérente des neutrons donne les fréquences des modes normaux du cristal et la variation en température de certains modes peut indiquer la ferroélectricité ou l'antiferroélectricité. Des exemples de ces phénomènes sont présentés pour SnTe, suggérant, de plus, que les solutions solides de SnTe avec GeTe forment un vaste domaine où existe le caractère ferroélectrique.

Abstract. — Because the usual methods for establishing ferroelectricity in crystals are not possible for crystals with high conductivities, other ways must be introduced based on other ferroelectric properties. Analysis of the crystal structure can provide a model showing the possibility of reversible polarisation, but more convincing evidence can come from the study of the dynamics of the crystal. Neutron inelastic coherent scattering yields the frequencies of the normal modes of the crystal, and the temperature dependence of certain modes can point to ferroelectricity or antiferroelectricity. Examples of both these phenomena are presented for SnTe, suggesting moreover that the solid solutions of SnTe with GeTe form a wide ferroelectric range.

1. Introduction. — The standard methods of establishing the existence of ferroelectricity in a crystalline substance have until recently been sufficient to remove any doubt in most cases [1]. Ferroelectricity is confirmed by hysteresis in the E-D (field-displacement) relationship. The crystal is polarised permanently in a certain direction, but this polarisation can be reversed by application of a large enough field, known as the coercive field. The resulting crystal structure (at least for any case of interest here) is related to the initial structure by centrosymmetric inversion. Clearly this means that the ferroelectric crystal structure must be acentric. The ferroelectric transition occurs between this acentric structure and a centric structure, that is from the ferroelectric to the paraelectric phase. Evidence for the onset of ferroelectricity can be found in the paraelectric phase by studying the temperature variation of the static dielectric constant, $\epsilon(0)$. This follows a Curie-Weiss law

$$\frac{\epsilon(0) - 1}{4\pi} = \frac{C}{T - T_c}. \quad (1)$$

Conventional evidence for ferroelectricity clearly depends on the crystal being an insulator. No crystal with substantial conductivity could show any of the dielectric phenomena above, therefore no such crystal

could be classed as ferroelectric. We wish to extend the classification so as to include those semi-conducting (or even metallic) crystals which display other properties indicative of ferroelectricity. Here we turn to Cochran's [2] theory of ferroelectricity and show, with SrTiO_3 as an example, the relationship between the dielectric phenomena and the variation of a certain mode of vibration of the crystal.

A basic relation between certain modes of vibration of a crystal and its dielectric constants has been proved by Lyddane, Sachs and Teller [3].

$$\frac{\nu_{L.O.}^2(0)}{\nu_{T.O.}^2(0)} = \frac{\epsilon(0)}{\epsilon(\infty)}. \quad (2)$$

Here $\nu_{L.O.}(0)$ and $\nu_{T.O.}(0)$ are the frequencies of the longitudinal and transverse optic modes with zero wave number, $\epsilon(0)$ and $\epsilon(\infty)$ are the static and high frequency dielectric constants. Cochran and Cowley [4] have shown that, for a structure with n optic modes

$$\prod_{i=1}^n \frac{\nu_{L.O.}^2(0)_i}{\nu_{T.O.}^2(0)_i} = \frac{\epsilon(0)}{\epsilon(\infty)}. \quad (3)$$

Cochran [2] argues that the lowest frequency transverse optic (T. O.) mode is highly temperature dependent

while all the other modes are relatively constant. Thus if the Curie-Weiss law, equation (1), is obeyed, this T. O. frequency varies as

$$\nu_{\text{T.O.}}^2(0) = K(T - T_c). \quad (4)$$

Strontium titanate has a Curie temperature of 32 °K, and we are here interested in the phenomena in the cubic paraelectric phase. The exact nature of the transition or transitions is however still uncertain. The temperature dependence of the lowest T. O. mode has been measured by Cowley [5] using the technique of neutron inelastic scattering and his measurements of the dispersion relation for the phonon branch with wave vectors along [100] are shown in figure 1.

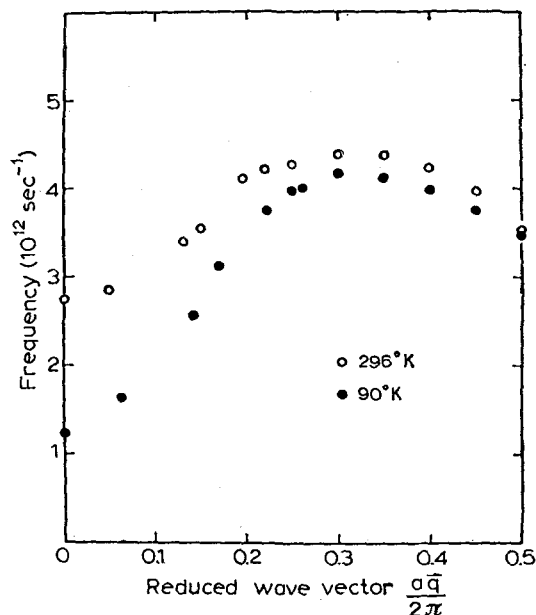


FIG. 1. — The dispersion in the lowest transverse optic branch of SrTiO_3 for wave vectors along [100] at 90 °K and 296 °K.

This contains results at two temperatures whereas figure 2 shows values of $\nu_{\text{TO}}^2(0)$ at a number of temperatures. Figure 2 also shows the variation of $\epsilon(0)^{-1}$ with temperature, as measured by Mitsui and Westphal [6], and the juxtaposition of these results emphasises the simultaneous validity of equations (1) and (4). Thus the appropriate temperature variation of the dielectric constant or the frequency of the lowest T. O. mode (the ferroelectric, soft or Cochran mode) are equivalent evidence for a ferroelectric transition.

2. Diatomic ferroelectrics. — For some years BaTiO_3 has been the simplest known ferroelectric

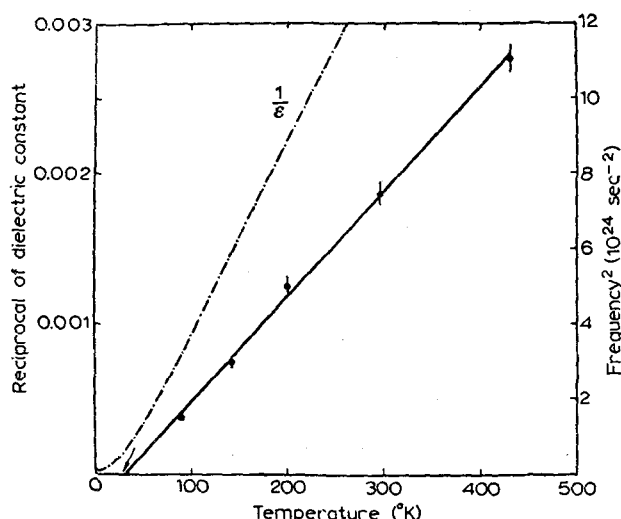


FIG. 2. — The temperature variation of the reciprocal of the static dielectric constant and the square of the frequency of the transverse optic mode of zero wave number for SrTiO_3 .

crystal, containing only five atoms in the unit cell. Cochran [7] in studying PbTe , pointed out that there is in principle no reason why a diatomic ionic crystal should not have a ferroelectric transition. Work on PbS and PbTe [8], both n-type extrinsic semiconductors with carrier concentrations of about 10^{19} cm^{-3} , led to the study of SnTe , a p-type semiconductor with a much higher carrier concentration.

All these substances have the NaCl structure, so it is instructive to compare their phonon dispersion curves with those of KBr and NaI [9]. Figure 3 shows part of the measured dispersion curves for these five crystals. This part, similar in each case, is sufficient for our present purposes. Figure 3 (a) and (b) show KBr and NaI in which we see that the T. O. branch

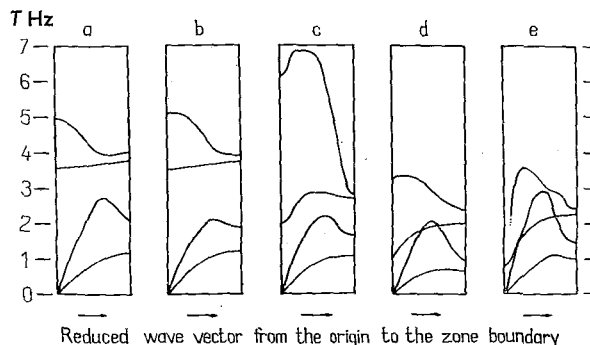


FIG. 3. — The measured phonon dispersion curves for five crystals with the NaCl structure for wave vectors along [100]. (a) KBr at 90 °K, (b) NaI at 100 °K, (c) PbS at 296 °K, (d) PbTe at 296 °K, (e) SnTe at 100 °K.

is flat in both cases. In contrast the T. O. branches for PbS, PbTe and SnTe (Fig. 3 (c), (d) and (e)) show a marked drop as the wave vector tends to zero. This effect is most noticeable in SnTe and prompted measurements at a number of temperatures [10]. The results are shown in figures 4 and 5 respectively.

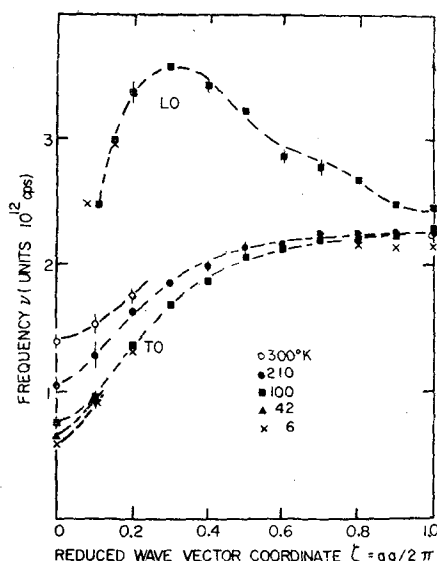


FIG. 4. — The dispersion of the optic modes of vibration with wave vectors along [100] in SnTe at various temperatures.

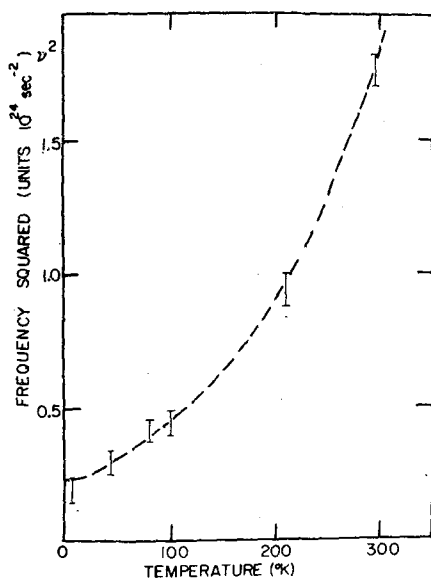


FIG. 5. — The square of the transverse optic mode frequency at zero wave number as a function of temperature, in SnTe.

The obvious similarity provides lattice dynamical evidence of an approach to a ferroelectric phase, suggesting that the crystal of SnTe used for these

measurements would not quite become unstable against the T. O. mode of vibration at absolute zero.

The phonon dispersion curve measurements are ideal for use in the study of models for the forces in crystals, and the «shell» model has proved most useful for ionic crystals [8, 9]. This model is an extension of Born's model, taking into account the electronic polarisability of the ions. This model has provided a good fit with experiment for KBr and NaI but a progressively poorer fit for PbS, PbTe and SnTe. The effect of screening by the carriers in the last three crystals is seen (Fig. 3) in the drop in the longitudinal optic (L. O.) branch frequency when the wave number is of the order of or less than the Thomas-Fermi screening length [8]. An attempt to modify the shell model to take account of the effect of screening on all the dispersion branches has met with some success [11].

3. The α -GeTe transition. — It has been established that GeTe undergoes a phase transition, thought to be second order, from a cubic phase with the NaCl structure above 670 °K to a rhombohedral phase below this temperature [12]. The lower symmetry structure is known as α -GeTe. In addition GeTe and SnTe form a continuous range of solid solutions, and at each composition there is a definite transition temperature which varies almost linearly with composition. Extrapolation to pure SnTe gives a transition temperature about 0 °K which is not inconsistent with the lattice dynamical evidence.

Arguing from the phonon dispersion curve measurements we could have predicted the crystal structure of α -GeTe. In a mode of vibration at zero wave number all the atoms of one chemical species are moving in unison, and for the optic mode both species are moving in opposition. Figure 6 shows how the amplitude of this mode of vibration in the NaCl structure on

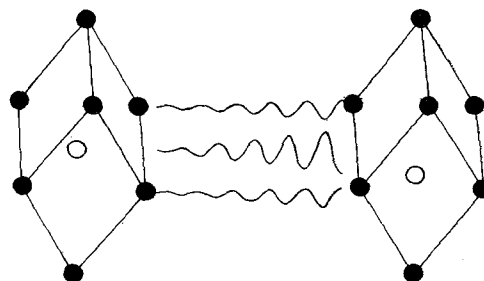


FIG. 6. — The ferroelectric mode in the GeTe transition. At left is the primitive rhombohedron of the NaCl type structure, and at right the structure of the lower phase with displacements exaggerated. ● Te, ○ Ge.

the left increases as the temperature is lowered towards the transition temperature.

The amplitude increases as the frequency falls until the crystal becomes unstable and transforms to the rhombohedral structure on the right. The central atom in this diagram is evidently germanium as its displacement would be greater than that of tellurium in this mode as germanium is the lighter atom. The germanium atom is positioned on the main body diagonal of the rhombohedron distant $u \neq 0.5$ fractional units from the tellurium. Evidently both u and $(1 - u)$ are equally probable, corresponding to the two ferroelectric structures.

Much therefore depends on the results of X-ray structure analysis. This has received much recent attention [13, 14, 15] with conflicting conclusions. Goldak et al. [13] present the most accurate set of results, namely counter measurements of ten reflections from a powder specimen (no work has yet been reported on single crystals). They fit the distorted acentric structure by least squares and obtain a high reliability factor,

$$R = \sum (I_{\text{obs}} - I_{\text{calc}}) / \sum I_{\text{obs}} \sim 0.05,$$

where I_{obs} and I_{calc} are the observed and calculated X-ray intensities. They find difficulty with the temperature factors and present an unrealistic model where the temperature factor for the heavier atom is higher than for the lighter atom. However they show that a large variation in temperature factors does not alter their estimate for u of $.474 \pm .004$. No account is taken of the known slight deficiency of germanium in the crystal structure, but their results could not possibly be explained in terms of a centrosymmetric model.

This result is supported by Zhukova & Zaslavskii [14]. They give more results than [13], again counter measurements, and find $u = 0.47$ (no error given) by a trial and error procedure. The R factor, calculated for the present article using the same 10 reflections of [13] was 0.17. This is dominated by one poor agreement, otherwise the comparison with [3] is very good. They conclude by giving $u = 0.466$, obtained by a Fourier summation shown in figure 7.

Kabalkina et al. [15] are concerned mainly with the transition to the cubic structure at 40 kbar, which they show is probably first order. Here no X-ray intensities are given, but it is concluded that $u = 0.50$. One set of intensities is given at a different pressure and are so approximate that no conclusion about the crystal structure could be based on them. We must disregard this result and accept that the structure is indeed acentric, as in figure 6.

The other results which Kabalkina et al. [15] obtain

do not rely on X-ray intensities but on more accurately measurable lattice parameters. They point out the most interesting result that the observed phase transition is similar to the transition of antimony to a cubic

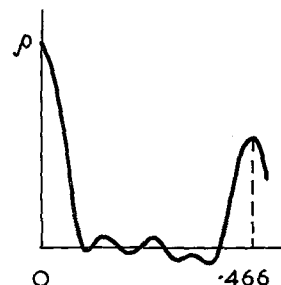
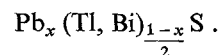


FIG. 7. — Electron density along the main diagonal of the rhombohedral GeTe unit cell, showing the acentric positioning of the atoms [14].

phase at 70 kbar. Indeed the similarities between the Group V elements and the IV-VI compounds have been appreciated for some time. It was in fact just this similarity which prompted the band structure work of Cohen, Falicov and Golin [16] who predicted the acentric α -GeTe structure, leading on to the structure analysis [13].

Having dispersed all doubt about the α -GeTe structure we can now conjecture as to the structure of



This has been shown [17], again by studying cell dimensions, to have a cubic phase and a rhombohedral phase. Figure 8 indicates the point in the solid solution range where the transition occurs. The usefulness of IV-VI compounds as piezoelectric semiconductors has

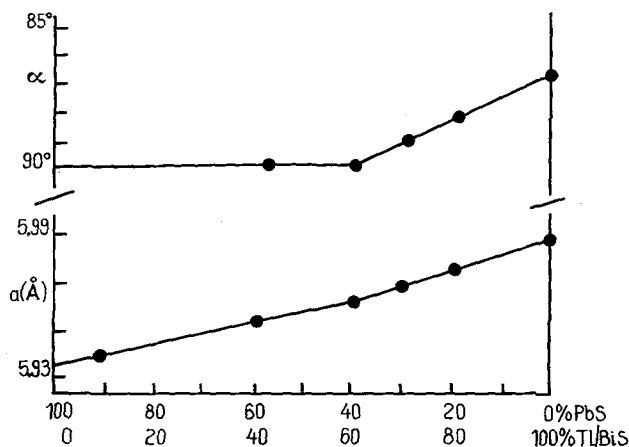


FIG. 8. — Variation of the cell parameters with composition of $\text{Pb}_x (\text{Ti}, \text{Bi})_{\frac{1-x}{2}} \text{S}$ after Malevskii [17].

been hampered by high conductivity, but as the conductivity of PbS can be considerably reduced this system has promise of applications.

One application has been suggested by Gulyaev and Karabanov [18] where a layered piezoelectric and semiconductor is required. With the modern method of doping at specific depths by bombardment this suggestion could certainly be realised.

4. Antiferroelectricity. — SnTe undergoes another type of phase transition not mentioned before in this paper. At high pressures (18 kbar [19]) the cubic phase gives way to an orthorhombic phase where the structure is similar to that of SnS and SnSe (see Wykoff [20]). The cell dimensions are roughly $2a : a/\sqrt{2} : a/\sqrt{2}$ where a is the lattice parameter for the NaCl type cube. Scrutiny of the structure suggests a mechanism for this transition. Although the rigour of group theory could be applied a diagrammatic explanation gives a deeper understanding [21].

Figure 9 shows part of an NaCl type structure with the $2a : a/\sqrt{2} : a/\sqrt{2}$ cell outlined. Looking down the z -axis at this cell we see the structure and symmetry of

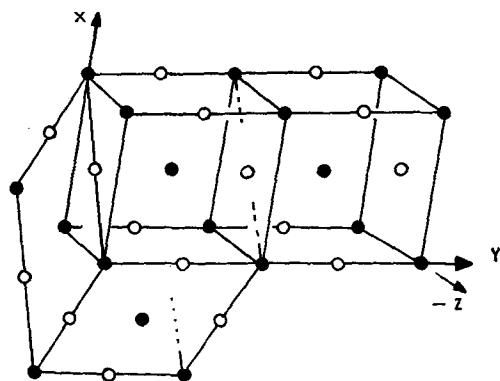


FIG. 9. — Part of an NaCl-type structure with an orthorhombic cell outlined.

figure 10 (a). Below this in figure 10 (b) is the symmetry of the SnS structure (Pbnm) which is evidently a subgroup of figure 10 (a). Figure 11 shows arrows from the undisturbed NaCl positions to the known positions in SnS, suggesting a wave of displacements within the crystal. The wave drawn in figure 11 cuts the arrows to the sulphur positions because in any mode of vibration of this sort the lighter atoms are displaced more than the heavier atoms. The wavelength of this wave is clearly $2a$, the atomic displacements are transverse and the variation takes place along the $[100]$ direction. Consequently this wave is the transverse zone boundary mode with wave vector in the $[100]$

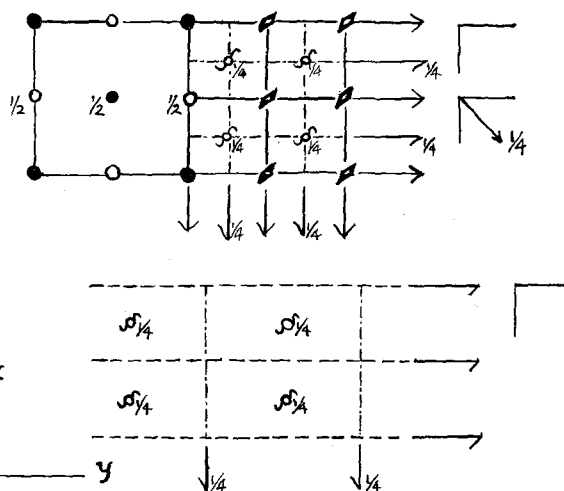


FIG. 10. — The symmetry of figure 9 as viewed down z , and the subgroup symmetry of the SnS structure.

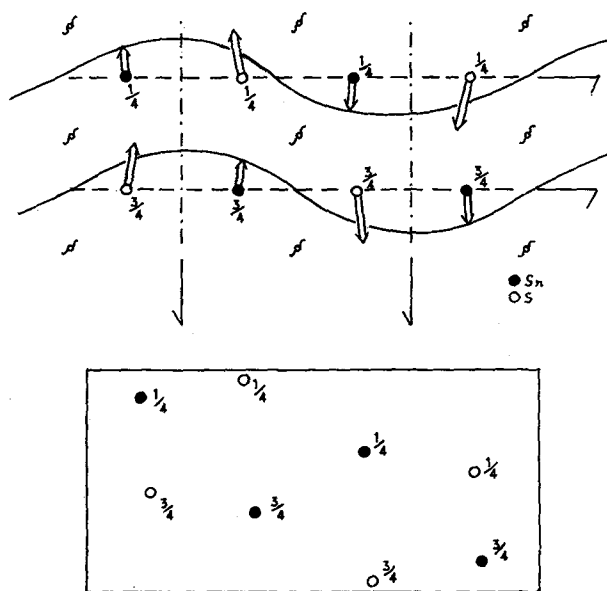


FIG. 11. — The SnS structure, suggesting wave-like displacements from an NaCl-type structure.

direction. This corresponds to a point on the right hand side of the dispersion curves of figure 3. We would therefore expect to see the frequency in the lowest branch at this point decrease as pressure is applied to the crystal. Alternatively at one pressure we would expect the frequency in the branch to drop as the wave vector tends to the zone boundary. This latter effect is noticeable only in SnTe, and although the effect is small the measurements are accurate enough for the drop to be significant.

It is clear that the SnS structure classes as antiferroelectric as the polarisation in one half of the unit cell is exactly compensated by that in the other half. It is not unrealistic to suggest therefore that the pressure induced phase transition observed in SnTe [19] is antiferroelectric, brought about by the instability of the crystal against a mode of vibration (Fig. 12) in accordance with Cochran's theory as extended to antiferroelectricity [22].

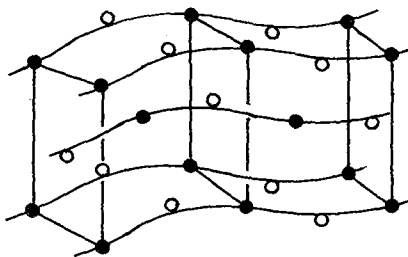


FIG. 12. — The SnTe antiferroelectric mode of vibration.

It might be argued that the displacements in SnS from which the above deductions are made are much too large to constitute a « frozen mode » ; too large, in other words, to be the amplitude of the mode of vibration at the time of transition. However SnS itself is not known to have a NaCl type structure or a phase transition. Its orthorhombic structure must be much more stable than that of SnTe so we might expect the displacements from SnS to be an exaggeration of the « frozen mode » in SnTe.

5. Conclusion. — Evidence for ferroelectricity need not rest on electrical measurements. Analysis of the crystal structures both above and below the phase transition can suggest a mode of vibration which plays an important part in the phase transition. As the crystal in the high symmetry phase is brought in temperature towards the transition, the frequency of this mode drops until the amplitude is large enough to cause transition. The ultimate test of this mechanism of transition is to measure the frequency of this mode as a function of temperature, which is done most elegantly by neutron inelastic coherent scattering.

Acknowledgements. — I wish to thank all those with whom I have been associated in the work on SnTe [10,11], and the Atomic Energy of Canada Ltd., whose equipment was used for the SnTe measurements.

References

- [1] JONA (F.) and SHIRANE (G.), *Ferroelectric Crystals*. Oxford : Pergamon, 1962.
- [2] COCHRAN (W.), *Advances in Physics*, 1960, **9**, 387.
- [3] LYDDANE (R. H.), SACHS (R. G.) and TELLER (E.), *Phys. Rev.*, 1951, **59**, 673.
- [4] COCHRAN (W.) and COWLEY (R. A.), *J. Phys. Chem. Solids*, 1962, **23**, 447.
- [5] COWLEY (R. A.), *Phys. Rev.*, 1964, **134**, A981.
- [6] MITSUI (T.) and WESTPHAL (W. B.), *Phys. Rev.*, 1961, **124**, 1354.
- [7] COCHRAN (W.), *Physics Letters*, 1964, **03**, 193.
- [8] COCHRAN (W.), COWLEY (R. A.), DOLLING (G.) and ELCOMBE (M. M.), *Proc. Roy. Soc. (London)*, 1966, **A293**, 433.
- [9] WOODS (A. D. B.), BROCKHOUSE (B. N.), COWLEY (R. A.) and COCHRAN (W.), *Phys. Rev.*, 1963, **131**, 1025.
- [10] PAWLEY (G. S.), COCHRAN (W.), COWLEY (R. A.) and DOLLING (G.), *Phys. Rev. Letters*, 1966, **17**, 753.
- [11] COWLEY (E. R.), DARBY (J. K.) and PAWLEY (G. S.), in preparation.
- [12] BIERLY (J. N.), MULDAWER (L.) and BECKMAN (O.), *Acta Met.*, 1963, **11**, 447.
- [13] GOLDAK (J.), BARRETT (C. S.), INNES (D.) and YODELIS (W.), *J. Chem. Phys.*, 1966, **44**, 3323.
- [14] ZHUKOVA (T. B.) and ZASLAVSKII (A. I.), *Kristallografiya*, 1967, **12**, 37.
- [15] KABALKINA (S. S.), VERESHCHAGIN (L. F.) and SEREBRYANAYA (N. R.), *Z. Exp. Theor. Fiz.*, 1966, **51**, 1358.
- [16] COHEN (M. H.), FALIKOV (L. M.) and GOLIN (S.), *I. B. M. Jour. Res. Develop.*, 1964, **8**, 215.
- [17] MALEVSKII (A. Yu.), *Doklady*, 1966, **169**, 1324.
- [18] GULYAEV (Yu. V.) and KARABANOV (A. Yu.), *Fiz. Tech. Poluprovodnikov*, 1967, **1**, 753.
- [19] KAFALAS (J. A.) and MARIANO (A. N.), *Science*, 1964, **143**, 952.
- [20] WYCKOFF (R. W. G.), *Crystal structures*, Vol 1. New York : Wiley, 1963.
- [21] COCHRAN (W.) and ZIA (A.), *Phys. Stat. Sol.*, 1968, **25**, 273.
- [22] COCHRAN (W.), *Advances in Physics*, 1961, **10**, 401.

BIRMAN, J. — Your conjecture about possible instability of a zone edge mode showing the SnS structure as a « distorted rocksalt, antiferroelectric » may receive some indirect support from the recent, similar, proposal by P. A. Fleury, J. F. Scott and J. N. Worlock (*Physical Review Letters*, **21**, 16, 1968) relating to the interpretation of the 110 °K phase transition in SnTiO₃ as involving zone edge mode instability.

PAWLEY, G. S. — We hope that this is so, and this transition is already under study at Chalk River, using the crystal of reference [5].