

CONF-770722-2

HIGH PRESSURE STUDIES OF SOFT MODE TRANSITIONS IN SOLIDS\*

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ABSTRACT

An overview of the soft mode concept and of high pressure studies of soft mode transitions in solids is given. Typical results on displacive ferroelectric (SbSI) antiferrodistortive [ $\text{Gd}_2(\text{MoO}_4)_3$  and  $\text{BaMnF}_4$ ] transitions as well as on coupled proton-phonon soft mode transitions ( $\text{KH}_2\text{PO}_4$ ) are used to demonstrate that hydrostatic pressure can strongly modify the balance of forces responsible for soft mode behavior. Emphasis is placed on the physical implications of the results and on the general trends of the available data on the different classes of soft mode transitions, for it is such trends that have led to a greater understanding of the nature of the forces involved.

\* Work supported by the U.S. Energy Research and Development Administration under Contract AT(29-1)789.

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## I. INTRODUCTION

Ever since it was introduced in 1960 to describe certain displacive ferroelectric transitions,<sup>1,2</sup> the concept of soft phonon modes has greatly enhanced our understanding of the static and dynamic properties of many structural phase transitions in solids. By a soft mode we simply mean a normal mode of vibration whose frequency decreases (and thus the lattice literally softens with respect to this mode) and approaches zero as the transition point is approached. From a lattice dynamical point of view, the limit of stability of a crystal lattice is approached as the frequency of any one mode decreases and approaches zero, for then, once the atoms are displaced in the course of the particular vibration, there is no restoring force to bring them back, and they assume new equilibrium positions determined by the symmetry (eigenvector) of this soft mode.

The soft mode concept was first developed to describe continuous or second-order phase transitions.<sup>1</sup> For such transitions, symmetry considerations require that only one normal mode of a certain polarization and wavevector be involved.<sup>1</sup> The frequency of this mode vanishes precisely at the transition and there is a one-to-one correspondence between the symmetry properties of the eigenvector of the soft mode and the static ionic displacements accompanying the transition. The eigenvector describes the pattern of atomic displacement associated with the phonon relative to the equilibrium lattice sites. The crystal structure of the new phase is determined by the superposition of this pattern of atomic displacements on the structure of the old phase. For first-order phase transitions, on the other hand, there are generally no symmetry requirements, and the description of such transitions in terms of soft modes, if at all valid, is quite involved. However, there are many known cases where, while the transition is first order, it appears nearly second-order from a lattice dynamical viewpoint (i.e. there is

substantial pre-transition mode softening), and for such cases the considerations obtained from treatments of second-order transitions apply.

In addition to its frequency and eigenvector, the soft mode (or any phonon for that matter) must also be characterized by its wavelength (or wavevector  $q$ , where  $q = 2\pi/\lambda$ ). The wavelength determines how the atomic displacements in one unit cell relate to those in adjacent unit cells. In ferroelectric crystals, identical ions in adjacent unit cells undergo identical displacements but with negative and positive ions undergoing opposite displacements and thereby producing a macroscopic polarization. The soft mode leading to such a circumstance is thus necessarily a long wavelength (or Brillouin zone center,  $q = 0$ ) transverse optic (TO), infrared-active phonon (Fig. 1a). In antiferroelectric crystals, on the other hand, identical ions in adjacent unit cells undergo opposite displacements and there is no net polarization. The characteristic wavelength of a phonon leading to such displacements is thus typically twice the lattice parameter  $a$ , and the wavevector of the soft mode is then  $q = 2\pi/2a$ , i.e., a Brillouin zone boundary phonon (Fig. 1b). More generally, the soft mode can be either an optic or acoustic phonon and of either long or short wavelength. Furthermore, in more complicated cases the soft mode can be a coupled mode involving the coupling of two or more fundamental excitations. Examples of these various possibilities are known,<sup>3,4</sup> and we shall discuss a few examples in this paper.

It is generally accepted that the decrease in the frequency of the soft mode ( $\omega_s$ ) as the transition temperature ( $T_c$ ) is approached is caused by the cancellation between competing lattice forces. One might suspect that pressure can significantly affect the balance between such forces and thereby strongly influence, or even induce, soft mode behavior. This has indeed turned out to be the case<sup>5</sup> and there now exists a substantial body of literature illustrating that high pressure studies have been important — sometimes essential, to the understanding of the phenomena involved.

In the space available for this review it is not possible to give anything like a detailed account of the pressure results on materials which exhibit soft mode behavior. Rather, we shall enumerate the various classes of soft mode transitions that have been investigated under hydrostatic pressure, illustrate some of the important features by a few specific results, and comment on the physical implications of these results. The reader is referred to the cited references for details. The following paper in this Conference Proceedings (by Peercy) presents specific pressure results on soft modes in some ferroelectrics.

For the present purpose we have, somewhat arbitrarily, divided the soft mode transitions investigated at high pressure into the following classes:

- 1 - Displacive ferroelectric soft mode transitions
- 2 - Displacive antiferrodistortive soft mode transitions
- 3 - Coupled proton-phonon soft mode transitions
- 4 - Other soft mode transitions.

In the fourth class we include several interesting, but generally unrelated, soft mode transitions where high pressure studies have led to important results. Following some brief theoretical considerations we shall deal with each of the above classes.

## II. THEORETICAL CONSIDERATIONS

Inherent in the soft mode picture of phase transitions is the premise that the crystal is unstable in the harmonic approximation with respect to the soft mode.<sup>1</sup> Specifically, the square of the harmonic frequency,  $\omega_0^2$ , is presumed to be sufficiently negative (i.e.,  $\omega_0$  is imaginary) that this mode cannot be stabilized by zero-point anharmonicities alone. Thermal fluctuations then renormalize  $\omega_0$  and make it real at finite temperature, thereby stabilizing the lattice. The transition temperature is the temperature where the

renormalization is complete. Formally, the anharmonic crystal potential can be written as a series expansion in the displacements (or normal mode coordinates), and perturbation or self-consistent treatments are then used to solve for the normal modes. Considering only quartic anharmonicities for the purposes of the discussion to follow, self-consistent treatments<sup>6</sup> yield for the renormalized frequency of mode  $j$  with wavevector  $q$

$$\omega_T^2(jq) = \omega_0^2(jq) + \sum_{\mu k} g_{j\mu}^{(4)}(qk) \frac{1}{2\omega(\mu k)} \coth \frac{\omega(\mu k)}{2k_B T}, \quad (1)$$

where  $g_{j\mu}^{(4)}$  are effective fourth-order coupling constants and the summation is over all modes  $\mu$  and wavevectors  $k$ . At suitably high temperature the second term on the right-hand side of Eq. 1 can be expected to vary linearly with  $T$  so that

$$\omega_T^2(jq) = \omega_0^2(jq) + \alpha T, \quad (2)$$

where  $\alpha$  is a positive constant. Experimentally, the soft-mode frequency  $\omega_s$  is found to vary with temperature as

$$\omega_s^2 \equiv \omega_T^2(j'q') = K(T - T_0), \quad (3)$$

where  $K$  is a positive constant and  $T_0$  is the (second-order) transition temperature. Comparing Eqs. 2 and 3 we then note that  $T_0 = -\omega_0^2/K$ .

In ferroelectric crystals the temperature dependence of  $\omega_s$  (Eq. 3) is responsible for the observed Curie-Weiss temperature dependence of the static dielectric constant,  $\epsilon$ , and the divergence of  $\epsilon$  at the transition, namely

$$\epsilon = C/(T - T_0), \quad (4)$$

where  $C$  is a constant. This is because  $\epsilon$  and  $\omega_s$  are related by the Lyddane-Sachs-Teller relationship which, for example for a diatomic crystal, has the form

$$\frac{\epsilon}{\epsilon_{\infty}} = \frac{\omega_{LO}^2}{\omega_{TO}^2} \equiv \frac{\omega_{LO}^2}{\omega_s^2}, \quad (5)$$

where  $\epsilon_{\infty}$  is the high (optical) frequency dielectric constant and  $\omega_{LO}$  and  $\omega_{TO}$  are the long wavelength longitudinal and transverse optic frequencies of the polar phonon.  $\epsilon_{\infty}$  and  $\omega_{LO}$  exhibit very weak temperature dependence so that to a very good approximation

$$\epsilon(T)\omega_s^2(T) = \text{constant} \quad (6)$$

When dealing with a soft mode,  $\omega_o(j'q')$  is purely imaginary and stabilization to  $\omega_T(jq)$  is provided by the  $\alpha T$  term (neglecting any small stabilization provided by zero-point fluctuations). Even so, it should be strongly emphasized that the interesting and unusual features of the soft mode are not so much a consequence of the large anharmonicities as they are a result of the extremely small (or imaginary) harmonic frequencies. This point has been emphasized earlier.<sup>1,7</sup> Furthermore, there is evidence suggesting that the changes in the harmonic interactions dominate the pressure effects. Thus, although the anharmonic interactions will change with pressure, it will suffice for the purposes of qualitative arguments to consider only the harmonic interactions.

What causes  $\omega_o(jq)$  to be small or imaginary and what determines its pressure dependence? Some answers are provided in the following Sections.

### III. DISPLACIVE FERROELECTRIC SOFT MODE TRANSITIONS

Conceptually displacive ferroelectric transitions are the simplest and best understood soft mode transitions. As indicated earlier, in this case the soft mode is a zone center TO phonon, and its harmonic frequency [dropping the (jq) notation] can be expressed as<sup>1</sup>



$$\mu \omega_0^2 = R - \frac{(Ze^*)^2}{v} [C(0)] \quad , \quad (7a)$$

$$\propto (\text{S.R. interaction}) - (\text{L.R. interaction}) \quad (7b)$$

where  $\mu$  is the appropriate reduced mass,  $(Ze^*)$  is the effective ionic charge,  $v$  is the unit cell volume,  $C(0)$  is the electrostatic force constant for the  $q = 0$  mode and  $R$  is the sum of the appropriate short-range force constants. Thus it is seen that  $\omega_0^2$  is given by the difference between a short-range (S.R.) interaction and a long-range (L.R.) interaction, and the negative value of  $\omega_0^2$  (for ferroelectrics with finite transition temperatures) results from the over-cancellation of the positive S.R. interactions by the L.R. interactions.

With pressure the interionic distance  $r$  is decreased and this increases the S.R. forces ( $\sim r^{-n}$ , where  $n \approx 10$ ) much more rapidly than the L.R. forces ( $\sim r^{-3}$ ) leading to an increase in  $\omega_0^2$  which in turn leads to a decrease in  $T_c$ . This effect can be most readily seen from Eq. 3. A larger  $\omega_s$  at constant  $T$  necessitates a lower  $T_c$ . Alternatively, as  $\omega_0^2$  becomes less negative, we do not need to go to as high a temperature ( $\equiv T_c$ ) to stabilize  $\omega_s$  and make it real. Ultimately, at sufficiently high pressure,  $\omega_0$  can be expected to become real. In such a circumstance the crystal will be stable with respect to this mode at all temperatures, i.e., the transition vanishes.

These theoretical predictions are confirmed by the available experimental evidence. The decrease in  $T_c$  with pressure has been observed experimentally for many displacive ferroelectrics<sup>5,8</sup> and the ultimate vanishing of ferroelectricity has been observed in perovskite ferroelectrics<sup>5</sup> and SbSI.<sup>9</sup> The SbSI results will serve to illustrate the main features of the pressure effects.

Antimony sulpho-iodide, SbSI, is a widely studied ferroelectric. The crystal is orthorhombic both above (space group  $D_{2h}^{16}$  - Pnam) and below (space group  $C_{2v}^9$  - Pn22<sub>1</sub>) the ferroelectric transition temperature  $T_c \approx 290$  K.

The structure, shown in Fig. 2a, consists of doubly-linked chains extending along the ferroelectric c-axis. The transition is driven by the softening of a long wavelength TO phonon<sup>10</sup> whose eigenvector is depicted in Fig. 2b and consists of opposite displacements of the Sb and S ions relative to the I ions.

Figure 3 shows the temperature dependence of the c-axis dielectric constant  $\epsilon_c$  at different pressures.<sup>9</sup> The transition temperature,  $T_c$ ,<sup>11</sup> defined by the peak in  $\epsilon_c(T)$ , decreases rapidly with increasing pressure and ultimately the low temperature ferroelectric phase vanishes. At 7.80 kbar there is a clearly defined transition at  $\sim 6$  K, but the transition completely vanishes at slightly higher pressure as shown by the 9.1-kbar isobar.

In the high temperature paraelectric phase the  $\epsilon_c(T)$  data in Fig. 3 obey at each pressure the Curie-Weiss law, Eq. 4, as is illustrated by the linear  $\epsilon_c^{-1}(T)$  responses in Fig. 4. The data in Fig. 4 also represent the  $\omega_s^2(T)$  response at each pressure, as can be readily deduced from Eq. 6. Representing this linear  $\omega_s^2$  response by Eq. 2, we see that the extrapolation of the straight lines back to  $T = 0$  K yields the harmonic frequency,  $\omega_0$ , squared. Examination of the results in Fig. 4 shows that for pressures  $\lesssim 7.2$  kbar  $\omega_0$  is imaginary. It increases with pressure and ultimately becomes real and finite (see the 8.5-kbar isobar). This implies that the lattice then becomes stable with respect to this mode at all temperatures, i.e. the ferroelectric phase vanishes, as we have mentioned.

Figure 5 shows the pressure dependence of  $T_c$ . The initial slope  $dT_c/dP = -39.6 \pm 0.6$  K/kbar, appears to be the largest pressure effect for any ferroelectric.<sup>12</sup> The initial shift of  $T_c$  is linear but becomes somewhat nonlinear at high pressure. This nonlinearity is most likely a result of the nonlinear pressure dependences of the lattice parameters (or unit cell volume) of SbSI. Note that the slope

$dT_c/dP$  is finite as  $T_c \rightarrow 0$  K. This behavior is similar to that observed for the perovskites<sup>5</sup> and can be readily understood in terms of the soft mode picture.

An important feature of the results in Fig. 5 is that the value of  $dT_c/dP$  is about the same when  $T_c \approx 290$  K (the 1 bar value) as it is when  $T_c \leq 10$  K. Since the magnitude of the anharmonic contributions must have decreased drastically between 290 K and  $\sim 10$  K, the experimental evidence indicates that  $dT_c/dP$  is dominated by changes in the harmonic interactions, i.e. by changes in  $\omega_0$ , as suggested earlier.

Another feature of the SbSI data that is worth noting is the pressure-induced change in the character of the transition (compare the 1-bar and 2.0-kbar isobars in Fig. 3). The transition is first order at 1 bar but appears second order at  $\geq 2$  kbar. This change, which is observed in most dielectric constant measurements,<sup>9,13</sup> actually occurs between 1 and 2 kbar and is now definitely known to be associated with the occurrence of a Curie critical point (a tricritical point) at  $\sim 1.4$  kbar and  $\sim 235$  K.<sup>14</sup> This is the point where the transition changes from first (at low pressure) to second order. There has been much recent interest in tricritical points and other multicritical points, and ferroelectrics at high pressure are uniquely suited for exploring such critical points. In addition to SbSI pressure-induced tricritical points occur or are expected to occur in ferroelectrics such as  $\text{KH}_2\text{PO}_4$ <sup>15</sup> and the perovskites.<sup>16,17</sup> The tricritical points in  $\text{KH}_2\text{PO}_4$  and SbSI are discussed in the papers by V. H. Schmidt<sup>18</sup> and P. S. Peercy,<sup>19</sup> respectively, in the Proceedings of this Conference.

One of the manifestations of a tricritical point in a ferroelectric is that slope ratio of the inverse susceptibility (or dielectric constant) in the ferroelectric phase to that in the paraelectric phase should change from 2 for a second-order transition to 4 at the tricritical point.<sup>9,14</sup> Recent, yet

unpublished, data by the author on an SbSI sample from the same batch of material as used by Peercy in his Raman scattering work<sup>14</sup> confirm this expected change. The results are shown in Fig. 6. A more detailed account and interpretation of these results will be published elsewhere.

Finally we note that there are many crystals which have a  $q = 0$  TO phonon which softens with decreasing temperature (i.e. a ferroelectric soft mode) but for which the softening is not complete down to the lowest temperatures, and thus the crystals remain stable with respect to this mode. Such crystals have become known as incipient ferroelectrics. Several such crystals have been investigated at high pressure, and the results exhibit the expected relatively large increase in soft mode frequency and decrease in the extrapolated transition temperature  $T_0$  (see Eq. 3) with increasing pressure. Examples include  $\text{SrTiO}_3$ ,<sup>12,20</sup>  $\text{KTaO}_3$ ,<sup>20,21</sup>  $\text{TiO}_2$ ,<sup>22</sup>  $\text{PbF}_2$ ,<sup>23</sup>  $\text{KMnF}_3$ <sup>24</sup> and  $\text{Sn}_{1-x}\text{GeTe}$  alloys.<sup>25</sup> The reader is referred to the cited papers for details.

#### IV. DISPLACIVE ANTIFERRODISTORTIVE SOFT MODE TRANSITIONS

Whereas for ferroelectric transitions the physical origin of the soft mode behavior has been understood in terms of a cancellation of the positive short-range forces by the negative Coulomb forces, the origin of the soft mode behavior in so-called antiferrodistortive transitions has not been known. However, some recent results<sup>8,26,27</sup> based on high pressure data and lattice dynamical calculations have shed considerable light on this question. By antiferrodistortive transitions we refer to those transitions driven by soft zone boundary (or short wavelength) optic phonons. Displacive antiferroelectric transitions are a sub-set of these.

There are now many known examples of displacive antiferrodistortive transitions and most of these have been studied at high pressure. In all cases the transition

temperature increases with pressure.<sup>26</sup> This is in marked contrast with the behavior of the soft mode ferroelectrics where  $T_c$  always decreases with pressure. We illustrate the behavior of the antiferrodistortive transitions by two examples:  $Gd_2(MoO_4)_3$  and  $BaMnF_4$ .

Gadolinium molybdate,  $Gd_2(MoO_4)_3$ , and its rare-earth isomorphs crystallize in a tetragonal structure (space group  $D_{2d}^3 - P_4\bar{2}_1m$ ) at high temperature and transform on cooling to an orthorhombic phase (space group  $C_{2v}^8 - Pba2$ ). The transition is driven by a soft zone-boundary optic phonon at the  $M(\frac{1}{2}, \frac{1}{2}, 0)$  point of the Brillouin zone whose frequency obeys Eq. 3.<sup>28</sup> The ionic displacements associated with this mode consist primarily of counter rotations of adjacent  $MoO_4$  tetrahedra. The orthorhombic phase is actually ferroelectric,<sup>29</sup> but this ferroelectricity is accidental being a manifestation of anharmonic coupling between the soft mode displacements and zone-center optic and acoustic mode displacements.<sup>28</sup> The ferroelectricity, but not the transition, disappears when the crystal is clamped.<sup>29</sup>

Figure 7 shows the temperature dependence of the static dielectric constant of  $Gd_2(MoO_4)_3$  in the vicinity of the transition temperature measured along the orthorhombic c-axis. The transition is first order and its temperature  $T_c$  exhibits a large increase with pressure, the initial slope being  $dT_c/dP = 33.5$  K/kbar. This is in close agreement with that reported by Shirokov et al.<sup>30</sup> The inset shows that  $T_c(P)$  is somewhat nonlinear over the 6-kbar range of the data.

Barium manganese fluoride,  $BaMnF_4$ , is orthorhombic (space group  $C_{2v}^{12} - A2_1am$ ) at room temperature, the structure consisting of layered sheets of linked  $MnF_6$  octahedra with the Ba ions located between the layers.<sup>31</sup> On cooling it undergoes an apparently second-order structural transition at 247 K.<sup>31</sup> The structure of the low temperature phase is still unresolved. Raman scattering results indicated that the transition is driven by a soft zone boundary optical phonon,<sup>32</sup> but more

recent inelastic neutron scattering data<sup>33</sup> indicated that the wavelength of the mode is actually incommensurate with the lattice. Despite this complication, the soft mode is a short wavelength optic phonon which most likely involves rotations of adjacent  $\text{MnF}_6$  octahedra.

Figure 8 shows several isobars of the static dielectric constant in the vicinity of  $T_c$  measured along the orthorhombic a-axis and the shift of  $T_c$  with pressure.<sup>31</sup> The qualitative similarity of these results to those on  $\text{Gd}_2(\text{MoO}_4)_3$  in Fig. 7 is evident.

Table I summarizes results on a variety of antiferrodistortive transitions including the best understood and studied cases  $\text{SrTiO}_3$  and  $\text{KMnF}_3$ . For contrast, results on a variety of soft mode ferroelectric transitions are given. The Table emphasizes what was mentioned earlier: in all cases where the transition is driven by a soft zone center (z.c.) TO mode (i.e. a ferroelectric mode)  $T_c$  decreases with pressure, whereas in all cases where the transition is driven by a soft zone boundary (z.b.) or short wavelength mode  $T_c$  increases with pressure. This contrast is most striking in crystals like  $\text{SrTiO}_3$ ,  $\text{PbZrO}_3$  and  $\text{PbHfO}_3$  which have both kinds of soft modes in the same crystal and where the associated transition temperatures exhibit opposite pressure effects. This appears to be a general result for ferroelectric and antiferrodistortive soft mode transitions to which we know of no exception at present. What are the lattice dynamical implications of these results?

As can be deduced from Eq. 3, the increase of  $T_c$  with pressure for the soft z.b. phonon transitions results from the softening of the soft mode frequency with pressure. The clue for the explanation of this result was suggested by the results of some lattice dynamical calculations on  $\text{SrTiO}_3$ .<sup>34,35</sup> These results show that for the z.b. modes at the  $(\frac{1}{2} \frac{1}{2} \frac{1}{2})R$  and  $(\frac{1}{2} \frac{1}{2} 0)M$  points of the Brillouin zone the short-range interaction is negative (i.e. attractive) whereas

the electrostatic interaction is positive. These results and their implications do not appear to have been appreciated until recently.<sup>8,26,27</sup> They indicate that, for the modes in question, the balance of forces leading to an imaginary harmonic frequency, and therefore soft mode behavior, is due to the over-cancellation of the positive electrostatic interactions by the negative short-range interactions. This situation is opposite to that in ferroelectrics. In other words, for the z.b. soft modes the roles of the short-range and electrostatic interactions are reversed from what they are for the ferroelectric case. It has been suggested that this reversal in the roles of forces is a general phenomenon applicable to all the crystals in Table I.<sup>26</sup> This generalization then provides a ready explanation for the increase of  $T_c$  with pressure for the soft z.b. phonon transition. By analogy to Eq. 7b we write

$$\mu\omega_0^2 \propto [(\text{Electrostatic interaction}) - (\text{S.R. interaction})] \quad (8)$$

Since pressure increases the magnitude of the short-range forces more rapidly than the magnitude of the electrostatic forces,  $\omega_0^2$  becomes more negative and a higher temperature is needed to provide the necessary stabilization of the high temperature phase by anharmonic interactions, i.e. a higher  $T_c$ .

An interesting observation based on the above discussion is that with increasingly higher pressure, and as the ions get closer and closer, the short-range interaction could not be expected to continue to be attractive. Ultimately they should become repulsive. If this were the case, then a reversal in the sign of  $dT_c/dP$  might be expected at sufficiently high pressure. Such a reversal has been recently observed<sup>31</sup> in  $\text{BaMnF}_4$  at  $\sim 10$  kbar. This observation might reflect the expected reversal in the sign of the short-range interactions.

## V. COUPLED PHONON-PROTON SOFT MODE TRANSITIONS

Potassium dihydrogen phosphate ( $\text{KH}_2\text{PO}_4$  or KDP) and its isomorphs are an important class of soft mode hydrogen-bonded ferroelectrics in which the protons play an essential role in determining the transition and related physical properties. This role is most evidenced by the unusually large effects on both the static and dynamic properties observed on deuteration.<sup>36</sup> For example the Curie temperature  $T_c$  of KDP increases from 122 K to  $\sim 230$  K on replacing the two protons by deuterons. Pressure studies on these materials have turned out to be crucial to the understanding of the nature of soft mode and the transition. Among the important pressure results are: (i) the vanishing of the ferroelectricity at high pressure,<sup>37</sup> (ii) the demonstration that the soft mode, which is overdamped at all temperatures at 1 bar, can be made underdamped at high pressure.<sup>38,39</sup> This resolved a long-standing question as to whether the mode is a collective, propagating excitation or a single particle-like diffusive excitation, and (iii) the demonstration that the proton motion remains coupled to an optic phonon in the low temperature phase.<sup>40</sup> Items (ii) and (iii) are considered in Peercy's paper.<sup>19</sup> Here we comment briefly on the pressure dependence of  $T_c$  and the vanishing of the ordered state. Specifically, we consider KDP.

In the high temperature phase KDP is tetragonal, the structure consisting of tetrahedral  $\text{PO}_4$  groups connected by a network of  $\text{O-H}\cdots\text{O}$  hydrogen bonds which lie very nearly in the basal plane with proton motion predominantly perpendicular to the  $c$ -axis. The polarization in the ferroelectric state is determined by the displacements of the  $\text{K-PO}_4$  groups along the  $c$ -axis. The presently accepted lattice dynamical picture for the transition is as follows.<sup>41</sup> In the high temperature phase the protons tunnel between two minima of a double-well potential along the  $\text{O-H}\cdots\text{O}$  bonds with the proton motion coupled to the  $\text{K-PO}_4$  TO phonon with polarization along



the c-axis. At the transition the protons order preferentially in the potential minima and consequently  $K-PO_4$  displacements become frozen in. The picture is then one of a coupled proton-phonon motion. A detailed approximate treatment of this coupled motion was given by Kobayashi,<sup>41</sup> who on solving the coupled system Hamiltonian for the coupled proton tunneling-optic mode frequencies and requiring that the lower frequency branch  $\omega_-$  vanish at  $T_0$ , obtained the following expression for  $T_0$

$$4\Omega/\tilde{J} = \tanh(\Omega/kT_0) \quad , \quad (9)$$

where  $\Omega$  is the proton tunneling frequency and  $\tilde{J}$  accounts for the dipolar interaction among protons and for the proton-lattice coupling. This equation has solutions and therefore a finite  $T_0$ , only when  $(4\Omega/\tilde{J}) < 1$ . The physical picture represented by Eq. 9 is as follows:  $T_0$  is determined by the competition between two fields, (i) a dipolar field represented by  $\tilde{J}$  which tends to order the protons and induce ferroelectricity, and (ii) a transverse tunneling field represented by  $\Omega$  which tends to disorder the protons and stabilize the high temperature phase. At 1 bar the dipolar field dominates, so that  $(4\Omega/\tilde{J}) < 1$ , and there is a finite  $T_0$ .

It is expected,<sup>37,42</sup> and has been confirmed experimentally,<sup>40,42</sup> that  $\Omega$  increases and  $\tilde{J}$  decreases with pressure. This enhances the disordering tendency of the tunneling field with respect to the ordering tendency of the dipolar field and leads to a lowering of  $T_0$ . At sufficiently high pressure the ratio  $(4\Omega/\tilde{J})$  should become  $\geq 1$  so that no ordering is possible and the transition vanishes.

These predictions are confirmed by experiments as can be seen for KDP in Fig. 9. In fact the  $T_c(P)$  data in this figure are well-fitted by Eq. 9 (solid curve).<sup>43</sup> The fit is quite good and Eq. 9 correctly predicts the observed result that  $(dT_c/dP) \rightarrow -\infty$  as  $T_c \rightarrow 0$  K. Figure 9 also shows results for two partially deuterated crystals. The data for the 35% deuterated crystal are qualitatively

similar to those for KDP, although we were not able to completely suppress  $T_c$  for this crystal because of the limited pressure range of the apparatus used. The data on the 82% deuterated sample extend to only 25 kbar, and  $T_c(P)$  is linear over this range. It would be of considerable interest to extend the pressure measurements on this and on completely deuterated crystals to much higher pressure and observe how  $T_c$  vanishes. This is important for the following reason. For  $KD_2PO_4$  it is generally agreed that  $\Omega \approx 0$ , so that Eq. 9 reduces to  $4kT_c = \tilde{J}$ , which is the Ising model result. In this case we would expect that  $T_c \rightarrow 0$  K with a finite slope  $dT_c/dP$ , unlike the response of KDP and the lightly deuterated crystals.

Finally we mention briefly the case of the antiferroelectric members of the KDP class of hydrogen-bonded crystals exemplified by ammonium dihydrogen phosphate ( $NH_4H_2PO_4$  or ADP) and its isomorphs. The high temperature phase of these crystals is isomorphous with KDP, and the crystals exhibit deuteration effects on  $T_c$  similar to those for KDP; however, the ordering of the protons in the hydrogen bonds at  $T_c$  is such as to result in antiferroelectric low temperature phases.<sup>37</sup> The effect of pressure on  $T_c$  of ADP has been reported<sup>37</sup> and is qualitatively similar to that for KDP:  $T_c$  decreases with pressure and ultimately vanishes with  $dT_c/dP \rightarrow -\infty$ . Thus, for these hydrogen-bonded crystals  $T_c$  decreases with pressure for both the ferroelectric and antiferroelectric transitions. This is in marked contrast to the behavior of the displacive soft mode transitions described in Secs. III and IV where  $T_c$  decreases with pressure for ferroelectric transitions and increases for antiferroelectric transitions. This difference in behavior emphasizes the fact that it is the proton motion in the hydrogen bond that plays the key role in KDP-type crystals.<sup>37</sup>

## VI. OTHER SOFT MODE TRANSITIONS

In this Section we merely want to draw attention to a few interesting, though unrelated, soft mode transitions for which pressure studies have proven to be very useful. Specifically we mention the transitions in  $\text{TeO}_2$ , the rare-earth pentaphosphates and the  $\beta$ -tungsten superconductors.

Paratellurite,  $\text{TeO}_2$ , undergoes a pressure-induced second-order transition at  $\sim 9$  kbar and 295 K from the tetragonal structure ( $D_4^h - P4_12_12$ ) to an orthorhombic structure ( $D_2^h - P2_12_12_1$ ).<sup>44,45</sup> This was the first known example of a pure strain-induced transition. The transition is driven by a soft shear acoustic mode propagating along a  $\langle 110 \rangle$  crystal direction and polarized along a  $\langle \bar{1}10 \rangle$ . The velocity associated with this mode softens slightly with decreasing temperature, but the transition cannot be induced by temperature alone; pressure is thus essential for studying this transition. A phenomenological theory for the transition has been developed,<sup>46</sup> but the microscopic origin of the instability leading to the transition remains unknown.

The rare earth pentaphosphates  $\text{RE}_5\text{O}_{14}$  (where RE is one of the rare earth ions Nd, La or Tb) crystallize in an orthorhombic structure (point group  $D_{2h}$ ) at high temperature and transform on cooling to a monoclinic structure (point group  $C_{2h}$ ).<sup>19</sup> The monoclinic phase is ferroelastic, i.e. its domains can be oriented by the application of a mechanical stress. The transition is accompanied by a soft long wavelength Raman-active (nonpolar) optical phonon which interacts strongly near  $T_c$  with an acoustic phonon governed by the elastic constant  $C_{55}$ . It is  $C_{55}$  which vanishes at  $T_c$  thereby precipitating the transition. The effects of pressure on the Raman spectra and  $T_c$  of some members of this group have been investigated by Peercy.<sup>19</sup> It is found that  $T_c$  increases with pressure, a behavior that may be typical of ferroelastic transitions, but it is not at present understood from a

lattice dynamical viewpoint. More work is needed to better understand these materials.

The cubic  $\beta$ -tungsten (or A-15) are best known for their high temperature superconductivity. Also important is the fact that several members of this family exhibit, on cooling, a phase transition from cubic to tetragonal ( $D_{4h}^9 - P4_2/mmc$ ) at a temperature  $T_L$  somewhat higher than the superconducting transition temperature  $T_c$ . The structural transition is associated with a soft shear acoustic mode propagating along  $\langle 110 \rangle$  and polarized along  $\langle 1\bar{1}0 \rangle$ .<sup>47</sup> There has been some evidence linking this lattice instability and the high superconducting  $T_c$ .<sup>47</sup>

Pressure studies have yielded some important results on  $V_3Si$  and  $Nb_3Sn$ , the two most investigated members of A-15 family.<sup>48,49</sup> It has been found that for  $V_3Si$ ,  $T_L$  decreases with pressure whereas  $T_c$  increases.<sup>48</sup> The opposite is true for  $Nb_3Sn$ .<sup>49</sup> These opposite pressure effects on  $T_L$  and  $T_c$  in the two isomorphous compounds have been interpreted in terms of a pressure-induced electron transfer from the s to the d bands.<sup>49</sup> A more detailed discussion of these results and other pressure effects on these compounds is given in the paper by Chu.<sup>50</sup>

## VII. CONCLUDING REMARKS

In this paper we have given a brief overview of the soft mode concept and of high pressure studies of soft mode transitions in solids. It was mentioned that the decrease of the frequency of the soft mode as the transition is approached is caused by a balance between competing forces, and that this balance can be strongly influenced by hydrostatic pressure. The effects of pressure on soft mode behavior in different classes of soft mode transitions were discussed briefly with emphasis on the physical implications of the results. Comparisons of pressure effects among the different classes reveal general trends which have led to a better understanding of the nature of the competing forces involved.

The results presented and the literature cited emphasize the important -- often essential, role of high pressure research in the study of soft mode transitions. Such research has not only yielded exciting new phenomena that occur at high pressure, but it has also improved our understanding of the response of materials at atmospheric pressure. There can be no doubt that such research will always be important in the study of phase transitions.

#### ACKNOWLEDGMENT

It is a pleasure to acknowledge the expert experimental assistance of B. E. Hammons.

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Table I. Pressure dependence of the transition temperature  $T_c$  for a variety of crystals which exhibit displacive structural phase transitions. z.b. and z.c. stand for Brillouin zone boundary and zone center, respectively. (Table taken from Ref. 26)

Crystal	Symmetry of Hi Temp Phase	Soft Mode (Sym.)	$T_c^a$ (°K)	$dT_c/dP$ (°K/kbar)
BaMnF <sub>4</sub>	Ortho.-C <sub>2v</sub> <sup>12</sup>	z.b.	47.3	3.3
Gd <sub>2</sub> (MoO <sub>4</sub> ) <sub>3</sub>	Tetrag.-D <sub>2d</sub> <sup>3</sup>	z.b.	430	33.5
(NH <sub>4</sub> ) <sub>2</sub> Cd <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	Cub. -T <sup>4</sup>	z.b.	92	3.3
-----				
SrTiO <sub>3</sub>	Cub.-O <sub>h</sub> <sup>1</sup>	z.b. (R <sub>25</sub> )	110	1.7
"		z.c. (Γ <sub>15</sub> )	36	-14.0
KMnF <sub>3</sub>	Cub.-O <sub>h</sub> <sup>1</sup>	z.b. (R <sub>25</sub> )	186	3.0
CsPbCl <sub>3</sub>	Cub.-O <sub>h</sub>	z.b. (M <sub>3</sub> )	320	7.6
"		z.b. (R <sub>25</sub> ) <sup>b</sup>	315	5.2
"		z.b. (R <sub>25</sub> ) <sup>b</sup>	311	5.4
PbZrO <sub>3</sub>	Cub.-O <sub>h</sub> <sup>1</sup>	z.b.	507	4.5
"		z.c. (Γ <sub>15</sub> )	475	-16.0
PbHfO <sub>3</sub>	Cub.-O <sub>h</sub> <sup>1</sup>	z.b.	434	5.9
"		z.c. (Γ <sub>15</sub> )	378	-10.0
-----				
BaTiO <sub>3</sub>	Cub.-O <sub>h</sub> <sup>1</sup>	z.c. (Γ <sub>15</sub> )	393	-5.2
PbTiO <sub>3</sub>	Cub.-O <sub>h</sub> <sup>1</sup>	z.c. (Γ <sub>15</sub> )	765	-8.4
-----				
SbSI	Ortho.-D <sub>2h</sub> <sup>16</sup>	z.c.	292	-37.0
Pb <sub>5</sub> Ge <sub>3</sub> O <sub>11</sub>	Hexag.-C <sub>3h</sub> <sup>1</sup>	z.c.	450	-6.7

a -  $T_c$  is either the actual transition temperature of the Curie-Weiss temperature deduced from the static susceptibility.

b - These modes derive from the R<sub>25</sub> mode of the cubic phase.

FIGURE CAPTIONS

- Fig. 1 Schematic representation of the ionic displacements associated with a ferroelectric (FE) mode and an antiferroelectric (AFE) mode in a diatomic linear chain.
- Fig. 2 (a) Structure of SbSI.  
(b) Eigenvector of the ferroelectric soft mode showing the Sb and S displacements relative to I.
- Fig. 3 Temperature dependence of the static dielectric constant of SbSI at different pressures showing the vanishing of the ferroelectric state.
- Fig. 4 Temperature dependence of the inverse static dielectric constant (or the square of the soft mode frequency) in the high temperature paraelectric phase of SbSI at different pressures.
- Fig. 5 Pressure dependence of the ferroelectric transition temperature of SbSI.
- Fig. 6 Pressure dependence of the inverse static dielectric constant of SbI at different temperatures showing the variation of the slope ratio of the inverse dielectric constant in the ferroelectric phase to that in the paraelectric phase on approaching the tricritical point at  $\sim 1.4$  kbar and  $\sim 235$  K.
- Fig. 7 Isobars of the temperature dependence of the dielectric constant of  $\text{Gd}_2(\text{MoO}_4)_3$  along the tetragonal c-axis showing the effect of pressure on the antiferrodistortive transition temperature.
- Fig. 8 (a) Isobars of the dielectric constant of  $\text{BaMnF}_4$  vs. temperature.  
(b) Pressure dependence of the antiferrodistortive transition temperature.
- Fig. 9 Pressure dependence of the ferroelectric transition temperature of  $\text{KH}_2\text{PO}_4$  and two partially deuterated crystals.

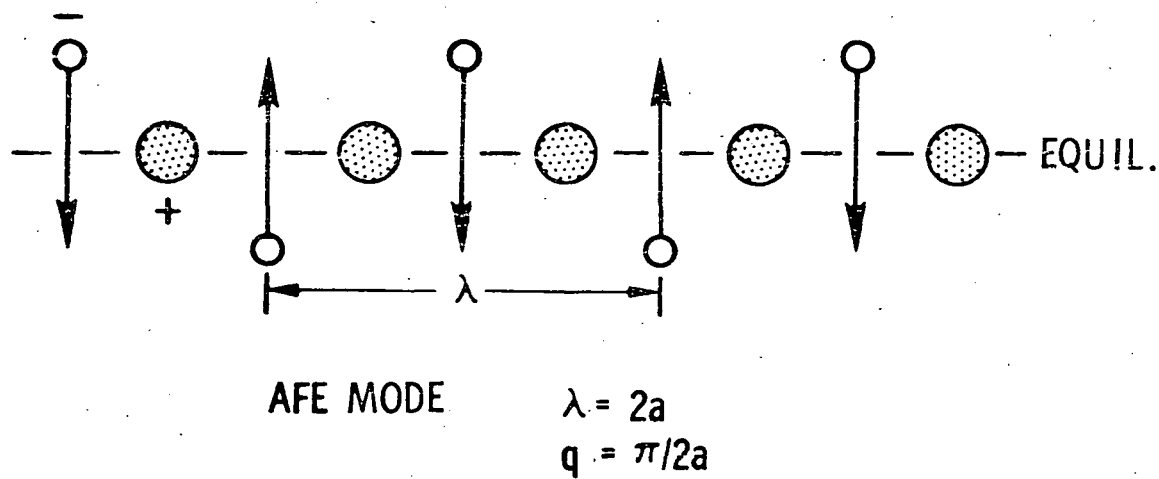
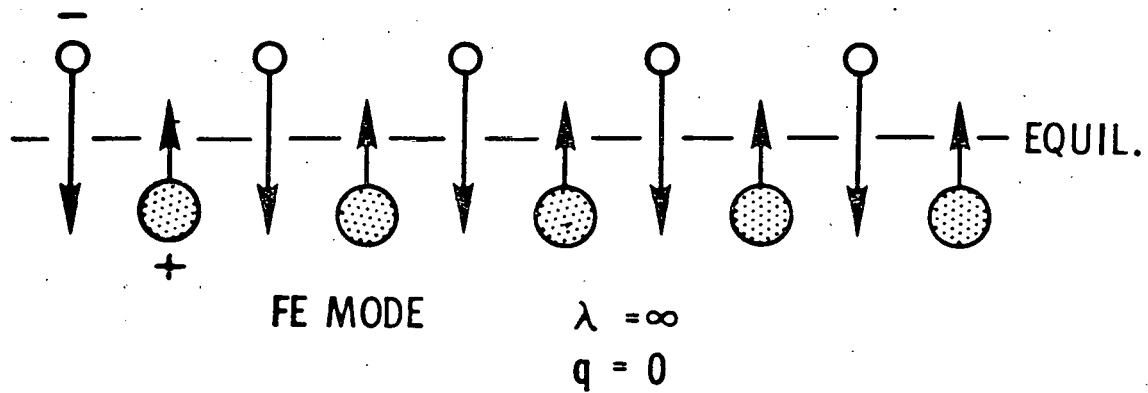
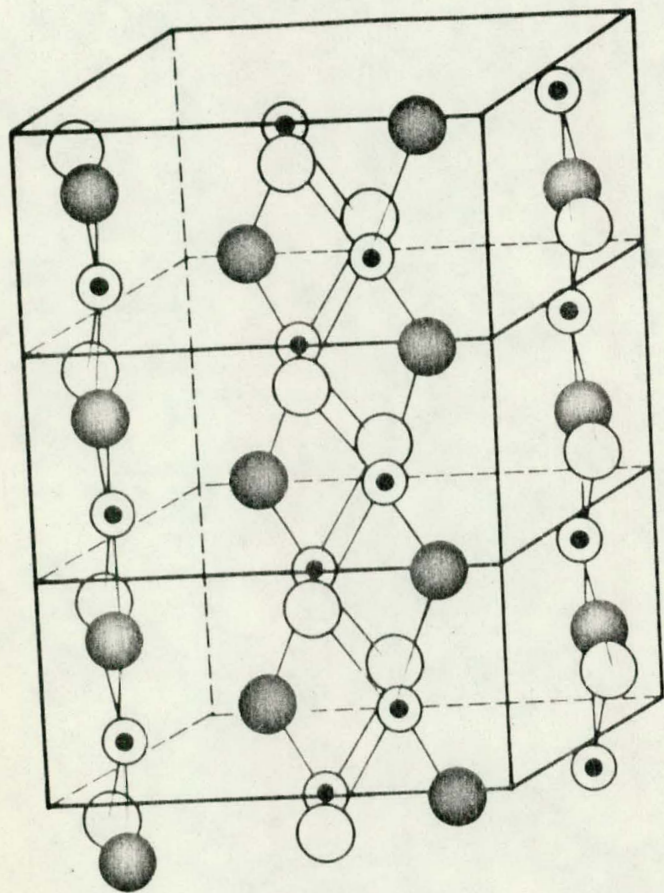


Fig. 1  
Samara

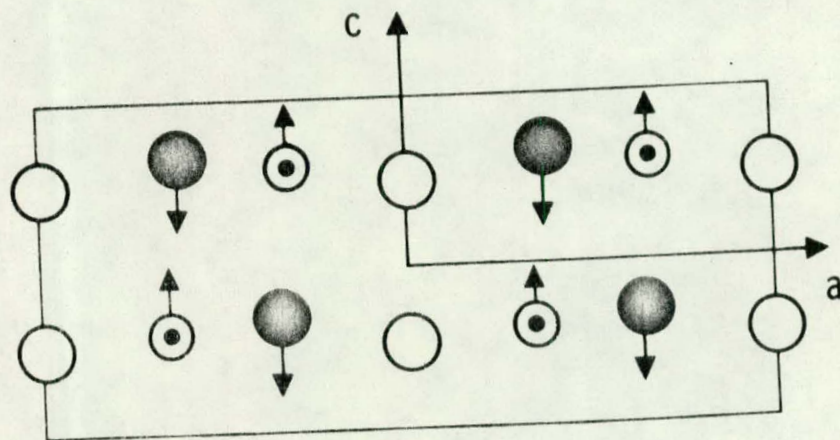
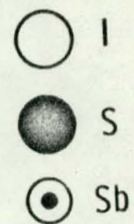


(a)

SbSI  
 PE:  $D_{2h}^{16}$  (Pnam)

FE:  $C_{2v}^9$  (Pna2<sub>1</sub>)

$C_2^2$  (P2<sub>1</sub>)



(b)

Fig. 2  
 Samara

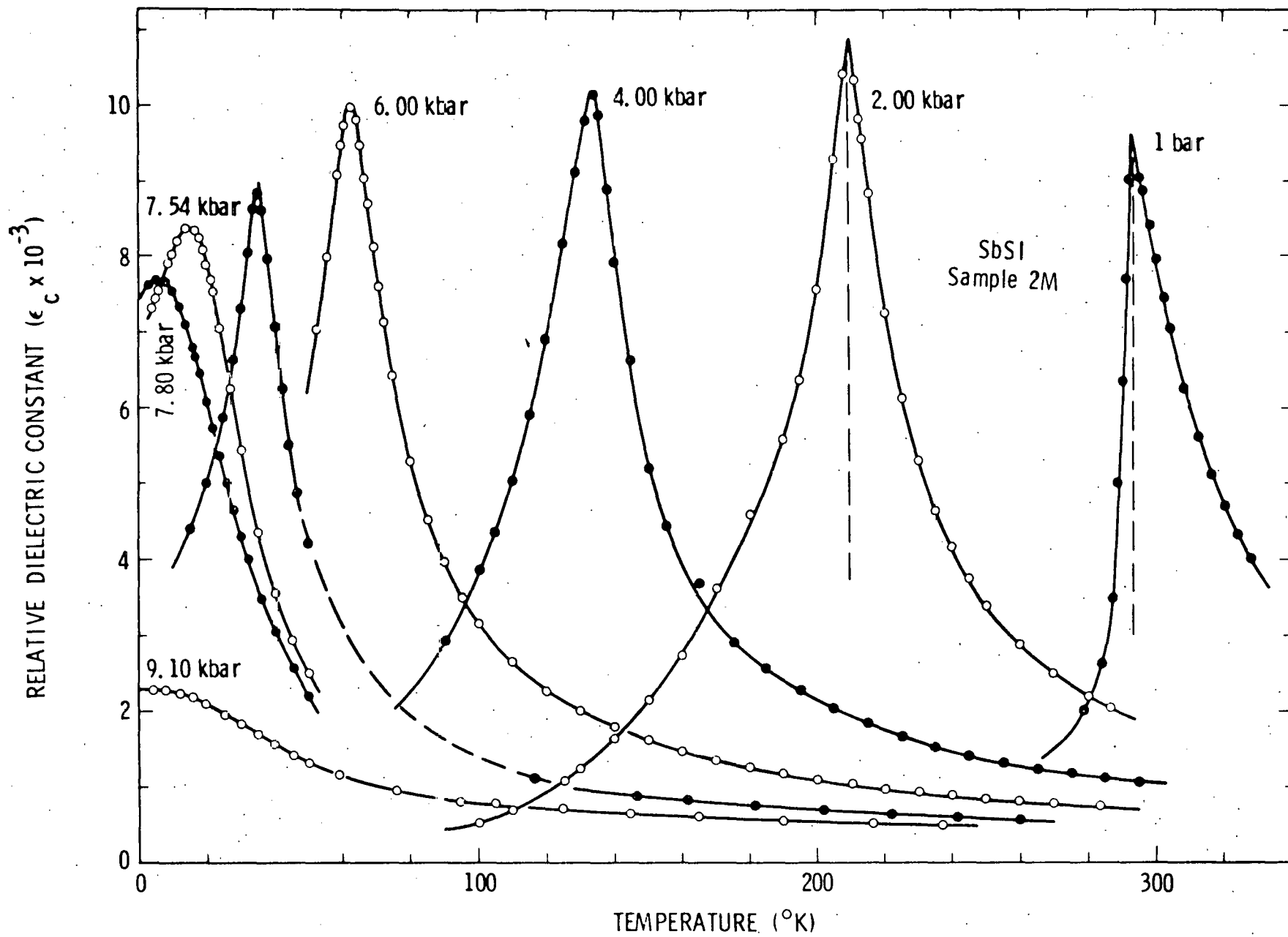


Fig. 3  
Samara

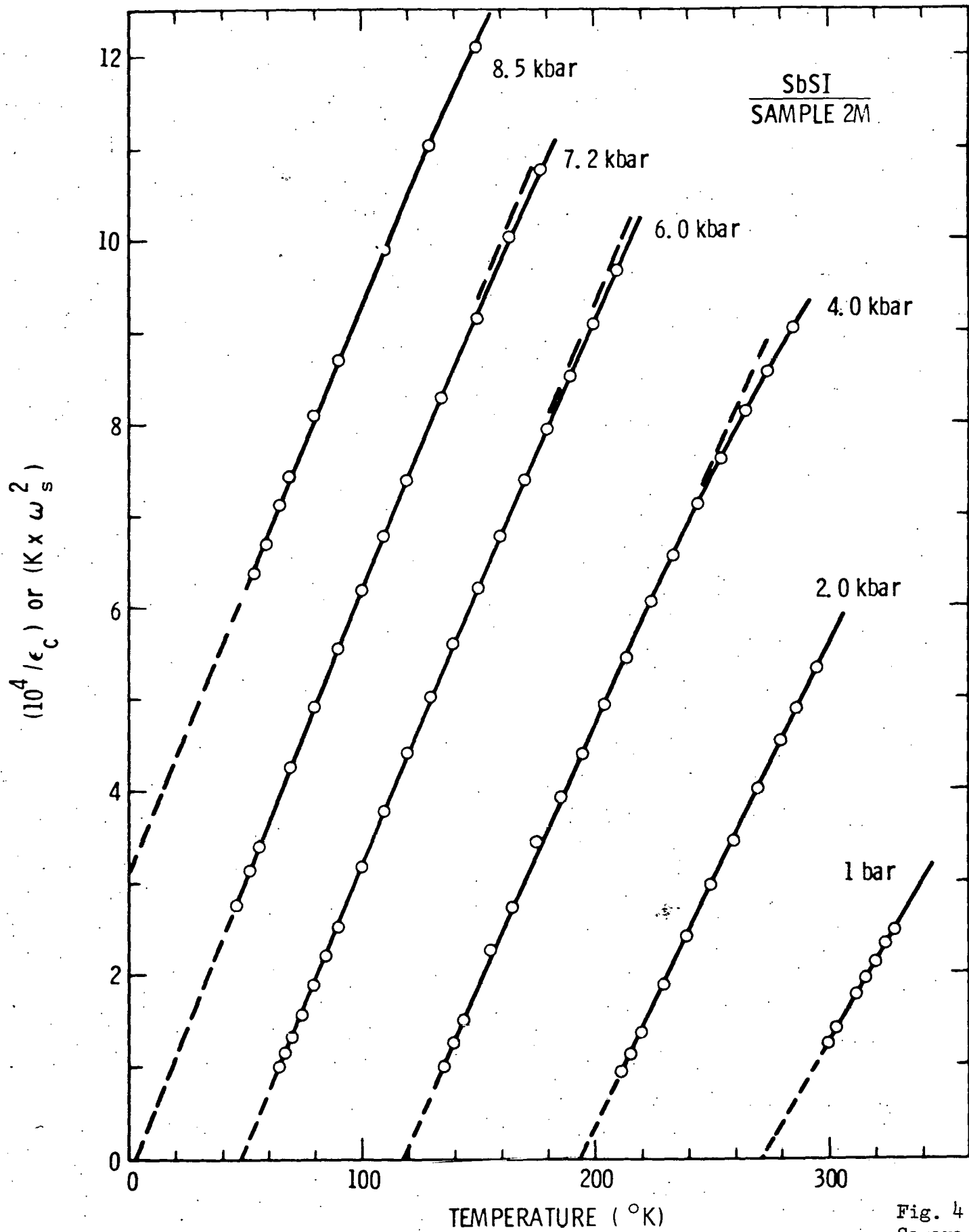


Fig. 4  
Samara

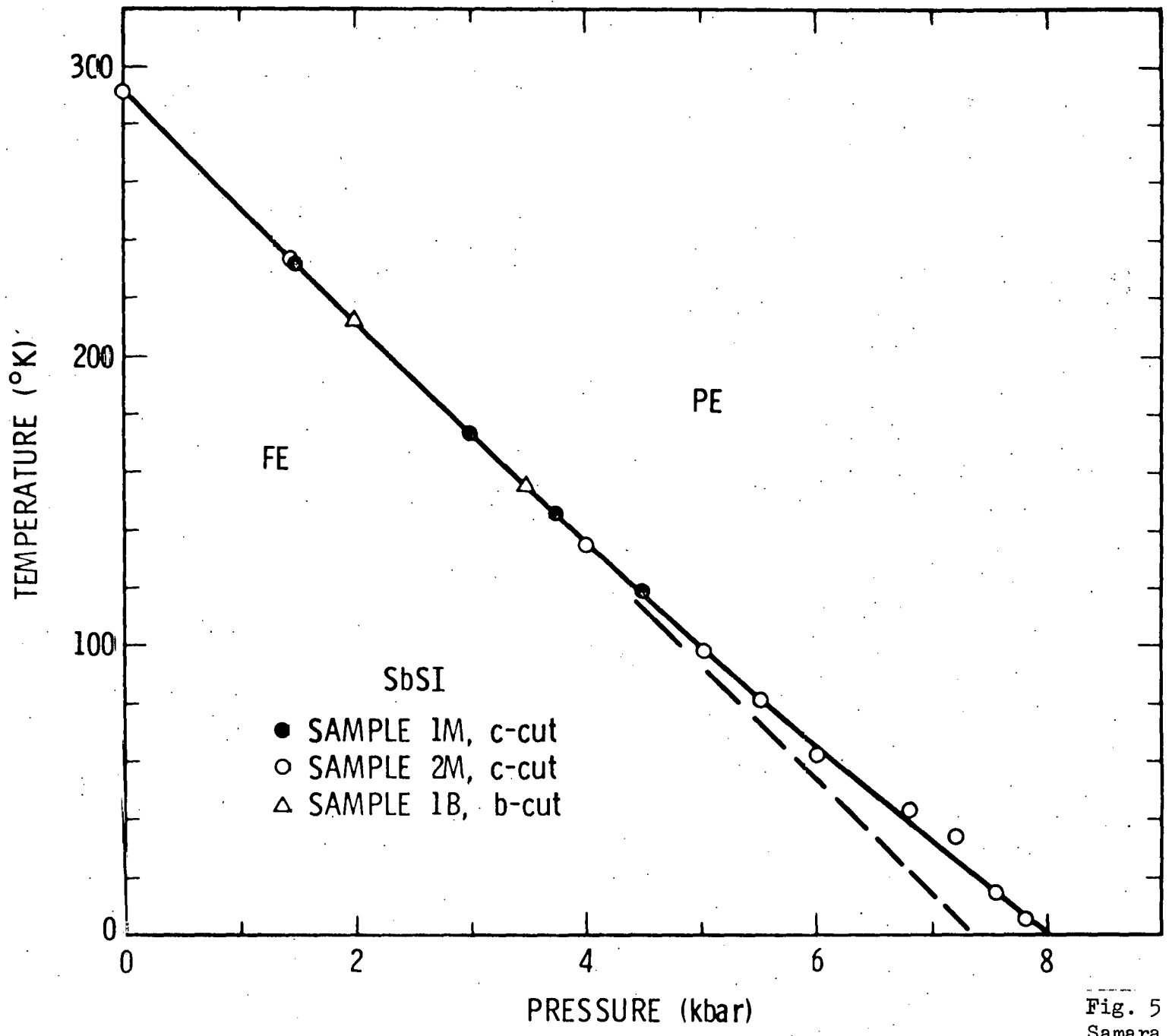


Fig. 5  
Samara

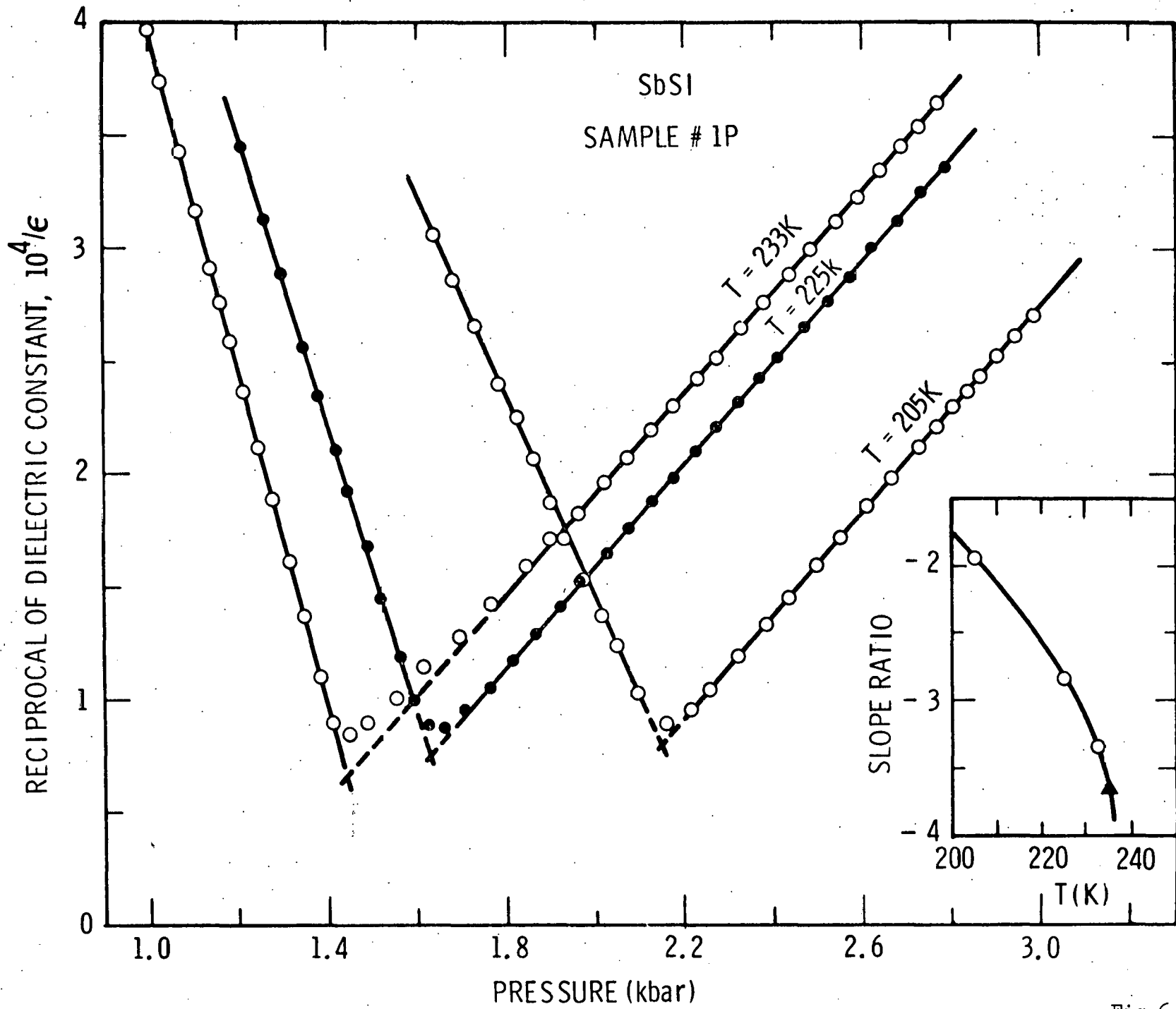


Fig.6  
Samara



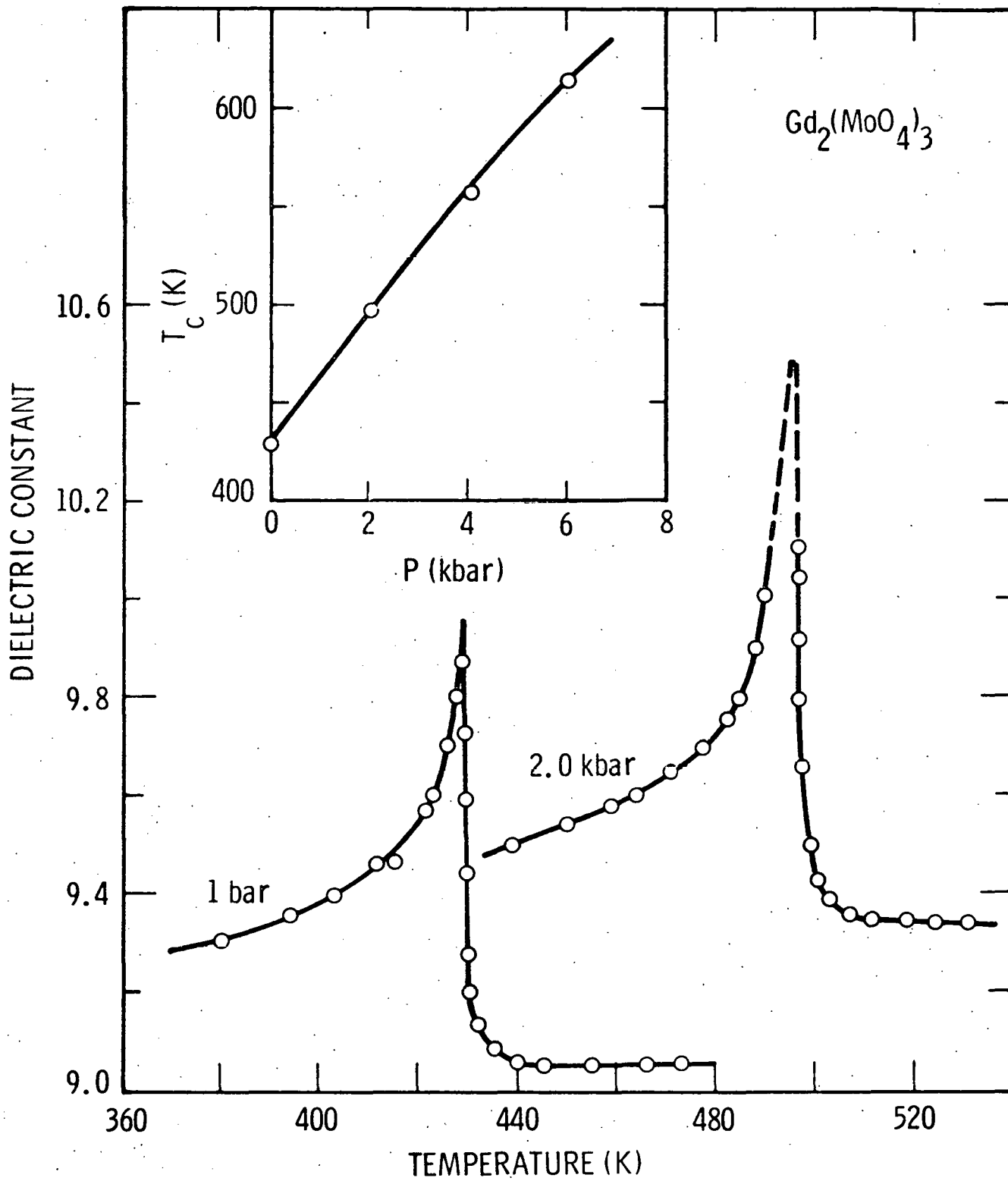


Fig. 7  
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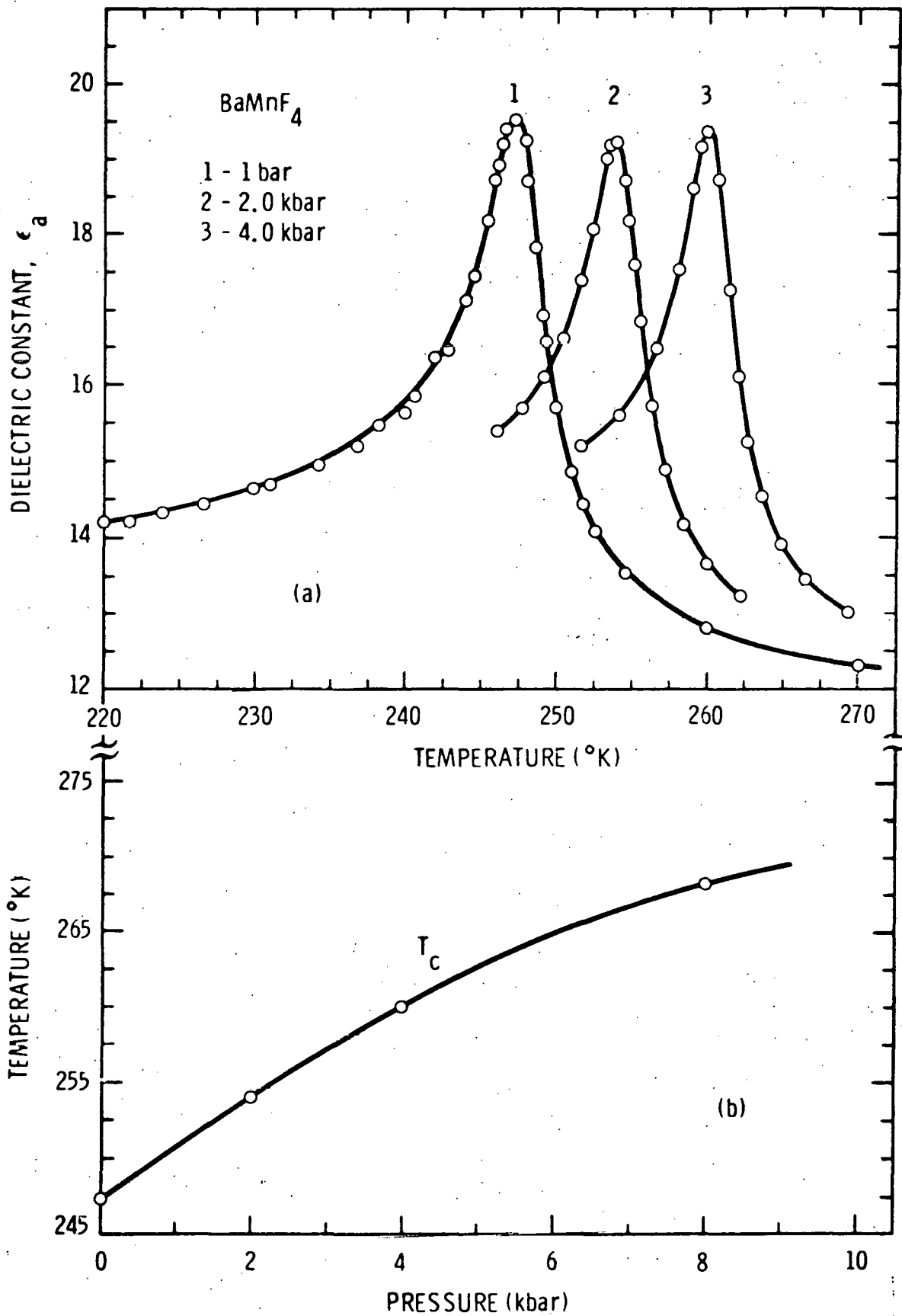


Fig. 8  
Samara

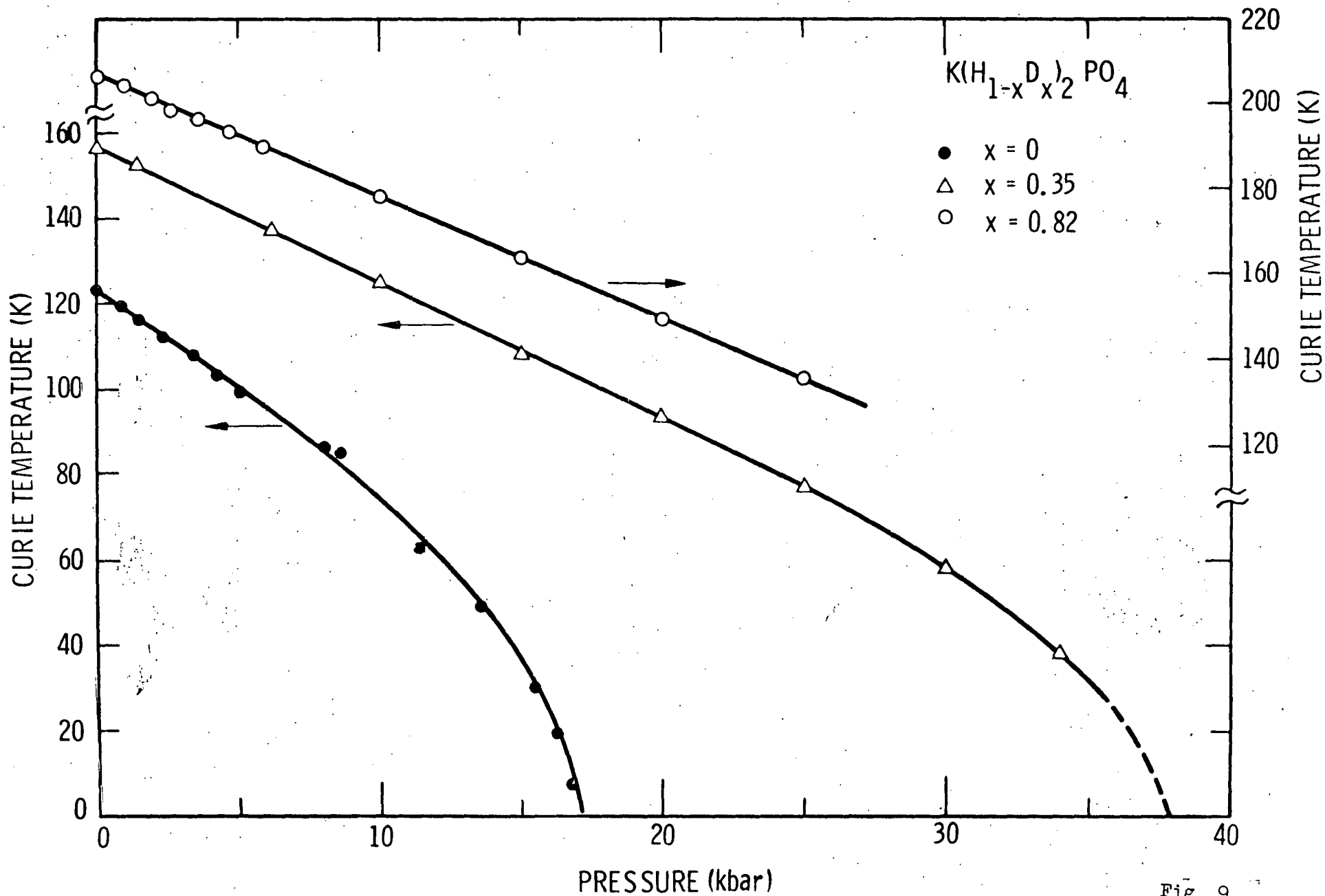


Fig. 9  
Samara