X-ray study of the structural phase transition in $Sn_xGe_{1-x}Te$

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The structural phase transition in the ferroelectric semiconductor alloy series $Sn_xGe_{1-x}Te$ has been investigated using high-precision x-ray techniques. The spontaneous strain occurring at the cubic-rhombohedral transition has been measured as a function of temperature for $0.53 < x < 0.87$ and a changeover from second-order to first-order transitions is found for $x \lesssim 0.72$. The behavior in the vicinity of the tricritical point can be analyzed in terms of Landau theory and the composition dependence of the free-energy expansion coefficients has been calculated up to sixth order, the quartic coefficient becoming negative at $x \approx 0.72$. The influence of the electronic structure on the ferroelectric instability is considered and it is argued that when the band gap is small enough, simultaneous instabilities can occur in the electronic structure and the crystal structure, with the cubic semiconductor phase transforming to a rhombohedral semimetallic form. It is suggested that, as the band gap decreases going from SnTe to GeTe, the coupling between these two instabilities grows, leading to the observed line of first-order transitions.

I. INTRODUCTION

The IV-VI compounds and their alloys have been the focus of much theoretical and experimental effort over the last few years, mainly with regard to their interesting electronic properties. The system $Pb_{1-x}Sn_xTe$ is the best documented of these materials as it has important applications, in infrared detection and as a laser material, arising from the L-point band inversion at around $x \approx 0.35$.[1] The material considered in the present study, the pseudobinary alloy series $Sn_xGe_{1-x}Te$, has received much less attention but is nevertheless important from the point of view of understanding structural instabilities in narrow-band-gap materials; in particular it provides the opportunity to investigate the cubic (NaCl structure)–rhombohedral (As structure) phase transition, until now thought to be of second order (continuous), over the whole compositional range from GeTe [$T_0 \approx 690$ K (Ref. 2)] to SnTe [$T_0 \approx 100$ K (Ref. 3)] and over a very wide range of temperatures.

Previous crystallographic studies[4-6] have uncovered the gross features of the subsolidus phase diagram of $Sn_xGe_{1-x}Te$. However, the detailed structural behavior remains unclear especially the temperature variation of the order parameter {the spontaneous displacement of the Sn (Ge)–Te sublattices along [111]} and the thermodynamic order of the phase transition. The present x-ray study is directed towards these two problems and is complementary to the recent ultrasonic[7] and calorimetric[8] studies on $Sn_xGe_{1-x}Te$ alloys. New findings from the present work, on the precise nature of the phase transition, are discussed in relation to these studies and to current theories for narrow-gap materials.

II. EXPERIMENTAL DETAILS

The crystals of $Sn_xGe_{1-x}Te$ were grown in the RCA Laboratories, Zürich, by the Bridgman method as outlined in Ref. 7, and had, in common with other reported materials from this system, a slight excess of Te producing hole concentrations of around 1.5×10^{21} cm^{-3}.[9] Sn content was measured (to ±1 mol%) by determination of the lattice spacing from high angle reflections on Debye-Scherrer photographs, using the normal Nelson-Riley extrapolation to correct for sample off-centering and camera radius errors. A linear-regression fit to the lattice parameter (composition) data of Bierly *et al.*[5] was used as the composition scale. In addition, absolute chemical determinations of composition were made on four crystals of different Sn content, the measured lattice parameters being in good agreement with those of Bierly *et al.*

Multicomponent crystals grown by the Bridgman method tend to have a composition gradient along the length of the growing boule. In this case the composition gradient was less than 0.5-mol% Sn mm^{-1}, so over the dimensions of the samples used for the x-ray experiments (~0.1 mm) the composition variation was negligible. However, the composition gradient within each as-grown boule could be used to advantage as a systematic means of choosing samples with closely spaced values of x when it was required to study a particular composition range in detail. Some care was taken to check that significant compositional fluctuations were not occurring within the x-ray samples. To this end, linewidths of the highest angle x-ray reflections from samples across the compositional range studied ($0.9 > x > 0.5$) were

monitored with no measurable increase in broadening. It should be mentioned here that crystals with $0.1 < x < 0.4$ tended to have very broad x-ray reflections when cooled slowly into the rhombohedral phase. However, the cubic-phase reflections were always sharp and it was found that fast quenching from the cubic phase produced a sharp, rhombohedral x-ray pattern. This unusual behavior can be ascribed to a microtwinning mechanism and is only observed outside the composition range of interest in the present study.

The temperature dependence of the lattice parameters (a_p and α_p, the pseudocubic lattice spacing and rhombohedral angle, respectively) was measured using a very precise single-crystal continuous-recording technique[10] in which sequential back-reflection oscillation photographs of the twin-related (640) and ($\bar{6}40$) reflections are taken with Cu $K\alpha$ radiation while the crystal temperature is being varied. The low-temperature method is described in detail in Ref. 11, but it is worth mentioning here that the sequential way in which the data are recorded on a single film, combined with temperature control of better than 0.25 K, allows one to make precise relative measurements of the lattice parameters (to > 1 in 10^4), facilitating the observation of small discontinuities such as may occur at a first-order phase transition.

III. RESULTS AND DISCUSSION

Figure 1 shows the difference of the rhombohedral angle from 90°, $\Delta\alpha$ ($\equiv 90° - \alpha_p$) as a function of temperature for several samples of $Sn_xGe_{1-x}Te$. It is seen that for the Sn-rich samples ($x \geq 0.73$) the transition to the cubic phase is continuous within the experimental resolution. This is consistent with the observation of a second-order transition in pure SnTe by Iizumi *et al.*[3] and is in agreement with the findings of Rehwald *et al.*[7] for $0.75 < x < 0.91$. However, as the Sn content is decreased beyond about $x < 0.72$, a small discontinuity appears in the $\Delta\alpha$ curve and this continues to grow as the Sn content is further decreased. Again, this is consistent with the first-order transition observed by Zhukova *et al.*[12] in pure GeTe but is the first concrete evidence of discontinuous behavior in the alloys. Thermal hysteresis of as much as 14 K was measured for the crystal with $x = 0.53$; this reduces to zero as $x \to 0.72$, as expected. Hence it appears that a crossover from continuous to discontinuous behavior occurs at around $x = 0.72$. At this point, the "tricritical point"[13] (TCP), three lines of ordinary critical points meet: one in the $\Delta\alpha$-T plane, which is observed here, and two lines bounding the coexistence surfaces ("wings") for $E_\pm \neq 0$ which are joined along the first-order line in the $\Delta\alpha$-T plane. The wings will not be observable in this case because of the high conductivity of the samples although they have been observed in other ferroelectrics [e.g., in KH_2PO_4 (Ref. 14)]. To analyze the behavior of $\Delta\alpha$ in the region of the TCP we turn first to Landau theory which is expected[15] to give a good quantitative description in the limit of the TCP.

A. Free-energy expansion

In terms of Landau theory, where the free energy of the system can be expanded, in this case,

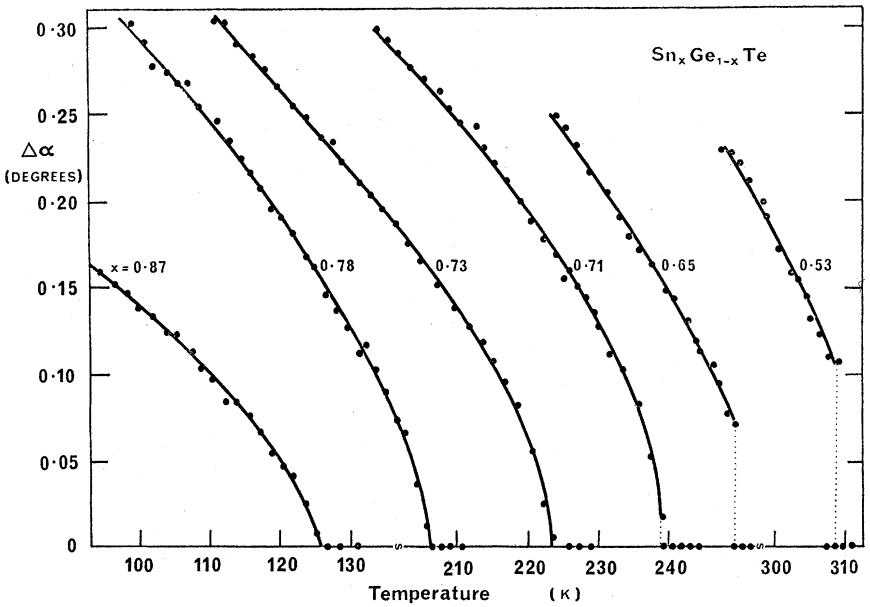

FIG. 1. Rhombohedral strain $\Delta\alpha$ as a function of temperature for several crystals of $Sn_xGe_{1-x}Te$. Data shown taken on cooling.

as a series in even powers of the order parameter

$$F = F_0 + \tfrac{1}{2}a'(T - T_C)\eta^2 + \tfrac{1}{4}b\eta^4 + \tfrac{1}{6}c\eta^6, \quad (1)$$

the TCP is given by the simultaneous conditions

$$a'(T - T_C) = 0 \text{ and } b = 0 \quad (2)$$

($b > 0$ at $T = T_C$) gives a second-order transition and $b < 0$ a first-order transition).

We note here that for $0 < x < 1$ the Landau-Lifshitz symmetry conditions[16] *permitting* a second-order transition are always obeyed and we can therefore examine the composition dependence of b in Eq. (1) for the region where the second-order transition line goes over into a line of first-order transitions.

Minimizing F now with respect to η, we obtain the stability condition for the ordered phase as

$$a'(T - T_C) + b\eta^2 + c\eta^4 = 0, \quad (3)$$

where $a', c > 0$; and T_C is the Curie temperature. Equation (3) can now be written in terms of $\Delta\alpha$:

$$a'(T - T_C) + bk'\Delta\alpha + ck'^2\Delta\alpha^2 = 0, \quad (4)$$

where

$$\Delta\alpha = k'^{-1}\eta^2, \quad (5)$$

from symmetry. Rearranging, we have

$$(b/a')k' + (c/a')k'^2\Delta\alpha = (T_C - T)/\Delta\alpha. \quad (6)$$

Figure 2 shows least-squares fits of Eq. (6) for two representative compositions, where the intercept on the vertical axis gives $(b/a')k'$ and the slope, $(c/a')k'^2$. For the crystal with $x = 0.73$, which is almost at the TCP, it can be seen that $(b/a')k'$ approaches zero, as expected. It appears from Fig. 2, and from similar plots for other compositions, that the behavior of $Sn_xGe_{1-x}Te$ conforms closely to the Landau theory at least to within a reduced temperature, $t\,[\equiv (T_C - T)/T_C)] = 0.015$. This is consistent with the observation of

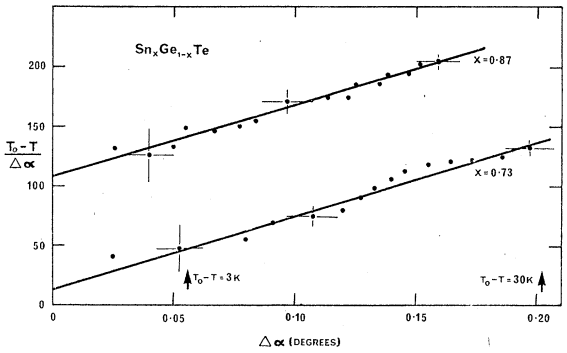

FIG. 2. Least-squares fits of Eq. (6) to data from two crystals of $Sn_xGe_{1-x}Te$ shown in Fig. 1.

mean-field behavior for pure SnTe,[17] and is also in agreement with the predictions of renormalization-group theory that mean-field results should be exact at a tricritical point in three dimensions.[18] As yet no calculations have been made for the specific case of the dipolar tricritical point (see below). Figure 2 indicates that, precisely at the tricritical point, β (in $\eta = t^{\beta}$) would be $\frac{1}{4}$, rather than $\frac{1}{2}$ at an ordinary critical point in the mean-field approximation.

Lines and Glass[19] have pointed out that free-carrier effects may be important in the critical behavior of semiconducting ferroelectrics. Away from the tricritical point, for SnTe say, it is somewhat surprising at first sight that Landau theory is still obeyed: treating the free carriers (density, $n_0 \approx 1.5 \times 10^{21}$ cm^{-3}) as a classical electron gas one would expect a static screening length, λ_s^{-1} ($\lambda_s \sim n_0^{1/6}m^{1/2}$), of the order of 2–3 Å which would effectively reduce the range of the macroscopic electric field associated with dipole ordering and thereby increase the size of the fluctuation-dominated critical region. A rough figure of $t_{\text{crit}} \approx 0.03$ is estimated from the Ginzburg criterion,[16] a critical region which is within the resolution of the present experiment. However, to obtain a more realistic figure for the screening length appropriate to dynamic processes in the semiconductor, one must replace m, the free electron mass, by m^*, the carrier effective mass in the above expression for λ_s. No figures for m^*, in $Sn_xGe_{1-x}Te$ alloys are available yet but it is well known that in narrow-gap semiconductors such as the ones considered here, m^* can reach values lower than $0.01m$. Taking this value for m^*, a dynamic screening length of 20–30 Å would result, which is considerably greater than the zero-temperature coherence length[16] of normal ferroelectrics. In this case, therefore, the effect of the large concentration of carriers on the critical region would be minimal.

B. Calculation of coefficients a', b, and c

From Eq. (1) the thermodynamic behavior of $Sn_xGe_{1-x}Te$ can be calculated. For instance, on the second-order side ($x \geq 0.72$) the discontinuity in the specific heat is given by

$$\Delta C_p = -T_C \frac{\partial^2 F}{\partial T^2} = \frac{a'^2}{2b}, \quad (7)$$

and on the first-order side ($x < 0.72$) the discontintuity in the order parameter is given by

$$(\Delta\eta)_{T_0} = -3b/4c, \quad (8)$$

which is the positive solution to Eq. (3) evaluated at $T = T_0$, the transition temperature.

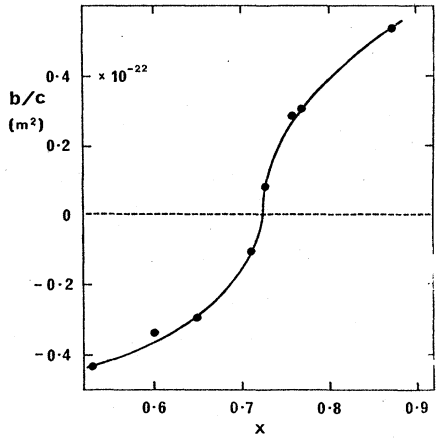

FIG. 3. Ratio of fourth-order to sixth-order free-energy coefficients as a function of composition x in $Sn_xGe_{1-x}Te$.

From Eqs. (4)–(8), and using the specific-heat data of Hatta *et al.*,[8] it is possible to calculate the composition dependence of a', b, and c with the usual assumption that these quantities are temperature independent. In Eq. (5), k'^{-1} varies from 6.0×10^{21} deg m^{-2}, for SnTe,[3] to 2.6×10^{21} deg m^{-2}, for GeTe.[20] In view of the other assumptions made above and a lack of knowledge of the coupling constant k'^{-1} for the intermediate alloys, the SnTe value of k'^{-1} was used in the calculation.

Figure 3 shows the ratio b/c as a function of composition showing that, with the assumption that c is finite and positive, b goes through zero around $x=0.72$. The positive values of b/c were derived from the ratio of the slope to the intercept taken from plots similar to those shown in Fig. 2 and the negative values were calculated from Eqs. (5) and (8). Finally, Fig. 4 shows all three coefficients plotted as a function of composition. Note that the values of a' and b calculated by Hatta *et al.*[17] are wholly consistent with the present results. Also, it is interesting to note that both a' and c decrease fairly rapidly as x decreases from 1. This probably occurs because a larger ion (Sn) is being replaced by a smaller species (Ge) which allows the lattice to strain at less cost in elastic energy. Very similar behavior for a' was observed[21] in the perovskite $KTa_{1-x}Nb_xO_3$ when Ta is replaced by Nb.

C. Microscopic picture

In wide-band-gap ferroelectrics such as $BaTiO_3$ the discontinuous behavior of the order parameter at the first-order ferroelectric-paraelectric transition can be understood in terms of an electrostrictive coupling between the displacement of the ferroelectrically active ion and the elastic strain of the crystal.[22] In lattice dynamical terms this can be thought of as anharmonic coupling between the soft TO mode and the acoustical modes of the crystal. It has been shown[23] that if sufficiently high hydrostatic pressure is applied to $BaTiO_3$ the first-order transition goes over to being second order and a similar phenomenon occurs in the perovskite solid solutions $PbZr_xTi_{1-x}O_3$ as x is decreased from 1 to 0.94.[24] One of the mechanisms[25] by which the TCP can be brought about in perovskite ferroelectrics is a reduction of the electrostrictive coupling, at high pressures or by alloying, and the applicability of this argument to $Sn_xGe_{1-x}Te$ is now investigated. IV-VI compounds

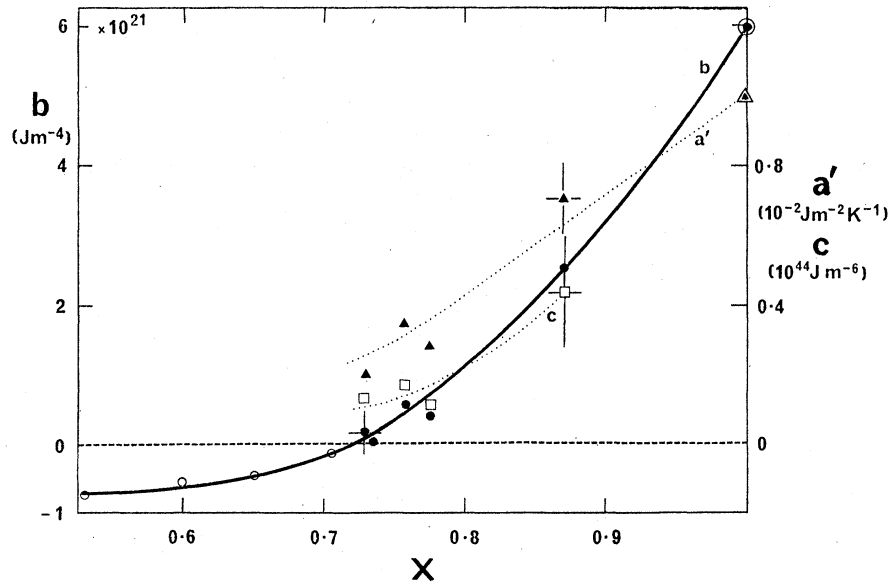

FIG. 4. a' (▲), b (●), and c (□) as a function of composition x for several crystals of $Sn_xGe_{1-x}Te$. ○: b, assuming c remains constant for $x<0.73$. ⊙, ▲ from Hatta *et al.* (Ref. 17).

have long been recognized as diatomic ferroelectrics[26] with similar lattice dynamical behavior to that of perovskites such as $BaTiO_3$. However, in the case of $Sn_xGe_{1-x}Te$, the above mechanism cannot lead to a TCP as the coupling coefficient, k'^{-1}, between strain and the square of the order parameter actually decreases as the transition becomes more first-order-like. Furthermore, application of hydrostatic pressures up to 40 kbar (see Ref. 27) does not seem to reduce the discontinuity in $\Delta\alpha$ significantly.

To understand the occurrence of the TCP in $Sn_xGe_{1-x}Te$ it is necessary to take into account the electronic structure and this is done by considering the microscopic Hamiltonian for a narrow-band-gap ferroelectric[28]:

$$H = H_{\rm ph} + H_{\rm el} + H_{\text{el-ph}} , \tag{9}$$

where

$$H_{\rm ph} = \frac{1}{2}\sum_i (P_i^\dagger P_i + \omega_i^2 Q_i^\dagger Q_i) + \frac{1}{4!N}\sum_{ijkl} \Delta(\vec{q}_i + \vec{q}_i + \vec{q}_k + \vec{q}_l)\Phi(\vec{q}_i, \vec{q}_j, \vec{q}_k, \vec{q}_l) \times Q_i Q_j Q_k Q_l \tag{10}$$

is the phonon contribution including fourth-order anharmonic coupling,

$$H_{\rm el} = \sum_{\vec{k}} (\epsilon_{v\vec{k}} c_{v\vec{k}}^\dagger c_{v\vec{k}} + \epsilon_{c\vec{k}} c_{c\vec{k}}^\dagger c_{c\vec{k}}) \tag{11}$$

is the noninteracting electronic contribution in the two-band approximation with c and v referring to the conduction and valence bands, respectively, and

$$H_{\text{el-ph}} = \frac{1}{\sqrt{MNa}} \sum_{\lambda \vec{k}'\vec{k}} \Xi\,(\vec{k}', \vec{k}) c_{c\vec{k}'}^\dagger c_{v\vec{k}} Q_\lambda \tag{12}$$

is the electron-phonon ("vibronic") contribution describing interband transitions coupled to a single phonon.

Using various forms of the above model Hamiltonian, the soft-mode behavior,[28] stability conditions for a ferroelectric distortion[29,30] and influence of free carriers on the transition[31] have been successfully calculated. Specifically, a second-order structural transition is predicted[30] when

$$2\,\Xi_{vc}^2 > \omega^2 \Delta_{\rm eff} , \tag{13}$$

where Ξ_{vc} is the interband, vibronic matrix element which mixes the valence and conduction bands (with effective gap $\Delta_{\rm eff}$) via the distortion caused by the transverse optical phonon of frequency, ω. In passing it can be seen that the inequality (13) is more easily satisfied for GeTe [$\Delta_{\rm eff} \approx 0.1$ eV (Refs. 32 and 33)] than for SnTe [$\Delta_{\rm eff} \approx 0.3$ eV (Ref. 1)] explaining the greater stability of the ferroelectric phase in GeTe.

D. Effect of interband interactions

As mentioned above, it would not seem that increased coupling of the optical and acoustical modes is responsible for the onset of the first-order transition in the GeTe-rich alloys. A solution to this problem is suggested by the work of Volkov *et al.*[34] who consider the effect of including purely electronic interband interactions in Eq. (11), of the type $(\hbar/m)\vec{k}\cdot\vec{p}$, where $\vec{k}$ is a small perturbation of the electron wave vector measured from the minimum of the conduction band at $\vec{k}_0$ (in this case the L point of the Brillouin zone) and $\vec{p}$ is the electron momentum operator at the bottom of the conduction band. Their argument is developed here to include the specific case of the $Sn_xGe_{1-x}Te$ alloys. Using a standard perturbation expansion to second order in k we have the following expression for the shifted valence band energy:

$$E_{\vec{k}}^v = E_{\vec{k}_0}^v + \frac{\hbar}{m}\vec{k}\cdot\langle u_0^v|\vec{p}|u_0^v\rangle + \frac{\hbar^2 k^2}{2m} + \frac{\hbar^2}{m^2}\frac{|\vec{k}\cdot\langle u_0^c|\vec{p}|u_0^v\rangle|^2}{E_{\vec{k}_0}^v - E_{\vec{k}_0}^c} . \tag{14}$$

In the centrosymmetric case (cubic phase of $Sn_xGe_{1-x}Te$) the term linear in $\vec{k}$ is forbidden by symmetry. However, at the ferroelectric instability, the center of symmetry is lost and the linear term is now allowed leading to a shift of the relative positions of the conduction- and valence-band extrema in k space. Furthermore, this will also allow the possibility of overlap of the extrema forming a semimetallic band structure. There is some evidence[35] that this indeed occurs at the structural transition in these materials, both SnTe and GeTe becoming superconductors below 1 K.[36] Moreover, in GeTe a strongly temperature-dependent carrier concentration has been observed[37] above T_0 which becomes temperature independent below T_0, consistent with a semiconductor-semimetal transition. The tendency to form band overlap will depend strongly on the effective cubic-phase band gap, the denominator of the second-order term in Eq. (14), and will be much more likely when $\Delta_{\rm eff}$ is small. As mentioned above, $\Delta_{\rm eff}$ decreases considerably going from SnTe to GeTe and furthermore decreases with increasing temperature in those IV-VI compounds with inverted band structure.[1] It is therefore expected that the tendency for the occurrence of the semiconductor-semimetal transition will become stronger both as x decreases and as the transition temperature increases. This also seems to be true in practice as the conductivity anomaly is found to be much stronger in GeTe (Ref. 2) than

in SnTe (Ref. 38). To summarize then, we have the possibility of simultaneous instabilities in both the crystal and electronic structures in $Sn_xGe_{1-x}Te$; it has been claimed[34] that when the coupling between the two instabilities becomes sufficiently strong the transition will cross over from second to first order. At present, it is not possible to solve exactly the equations for the coupled lattice-electronic instabilities. Could this be done there are still many parameters which have not been determined and so a quantitative prediction of the tricritical point is not yet feasible. However, it seems that the model Hamiltonian discussed above, including $\vec{k}\cdot\vec{p}$-type interactions, can adequately describe the qualitative behavior of $Sn_xGe_{1-x}Te$ observed in this study.

IV. CONCLUSIONS

Very precise x-ray measurements of the spontaneous lattice strain around the paraelectric-ferroelectric transition in $Sn_xGe_{1-x}Te$ alloys have revealed, for the first time, a crossover from continuous to discontinuous transitions as x decreases below 0.72. The tricritical behavior is analyzed in terms of Landau theory and the free-energy expansion coefficients have been calculated up to sixth order in good agreement with previous calculations on pure SnTe. Within the experimental resolution, no deviations from mean-field behavior can be observed, even away from the TCP. Direct measurements of the order parameter will be necessary before a conclusive statement can be made on this point. The present findings can be used to interpret the unusual specific-heat behavior observed recently[8] in various crystals of $Sn_xGe_{1-x}Te$ ($0.62 < x < 0.91$) where a Landau-like discontinuity in C_p, for x close to 1, goes over into a curve with what appears to be power-law behavior for $x \approx 0.79$. This behavior is just what is expected at the approach to a TCP; accurate measurements are in progress[39] to measure the specific-heat exponent α (in $C_p \sim t^{-\alpha}$) for a crystal with x closer to the tricritical value [$\alpha = \frac{1}{2}$ as calculated from Eq. (7) at the TCP].

The occurrence of the TCP in $Sn_xGe_{1-x}Te$ has been discussed qualitatively in terms of the simultaneous onset of instabilities in the crystal structure and the electronic band structure when the cubic-phase L-point band gap becomes sufficiently small. Evidence has been described which shows that the band gap tends to close with increasing temperature and decreasing Sn content, and experimentally it is just these variations that lead to the TCP. In this connection the present study points to the need for more systematic electrical measurements in the region of the phase transition, particularly in the $Sn_xGe_{1-x}Te$ alloys as x decreases from 1. The measurements could then be correlated with the structural information presented here to provide a fuller understanding of the transport behavior. Also, this present work, combined with the findings of other recent studies on the TCP in various ferroelectrics,[19] suggests that tricritical behavior may be a very general phenomenon in ferroelectric systems. Most of these display first-order transitions but, because of the fine balance of forces which led to ferroelectric distortions in the first place, the discontinuities are not large and can often be removed by relatively small physical perturbations of the relevant coupling mechanism within the crystal. This approach would enable many more studies of critical phenomena in ferroelectrics to be carried out. In the case of semiconducting ferroelectrics, such as those considered here, it is also of interest to investigate more closely the influence of the semiconducting behavior on the critical exponents particularly where the carrier density is high. Renormalization-group calculations (reviewed in Ref. 19) have been carried out for the isotropic case, which should be relevant to the high-symmetry materials (e.g., perovskites and IV-VI compounds), and it has been found that, approaching the transition from above, a crossover may occur from short-range critical behavior to long-range dipolar critical behavior with a set of exponents very different from the mean-field ones. Alternatively, in the uniaxial case, there is no such crossover and the exponents would be essentially mean-field-like with logarithmic corrections (e.g., $\eta \sim t^{1/2} |\ln t^{1/3}$). It appears that the behavior of the $Sn_xGe_{1-x}Te$ ferroelectrics would support the latter, uniaxial model, except that the resolution is not good enough to say anything about the logarithmic corrections. The question now arises as to how the screening described above affects the dipolar interactions. We have seen that the dynamic screening length is probably too long to allow critical fluctuations to be observed in these materials, but even so the possibility remains that the very-long-range dipolar interactions are affected in such a way that the presence of the carriers drives the system to a different (isotropic) fixed point. The results to date, from the present system and from pure SnTe, do not give any indication that this is happening but it would be interesting to look for the effect in more highly nonstoichiometric compositions of $Sn_xGe_{1-x}Te$ (for x close to 1) where the carrier density is greater and the screening length correspondingly shorter than in the present crystals. Finally, if the description of coupled in-

stabilities in IV-VI compounds presented here is correct, then the series $Pb_{1-x}Sn_xTe$ warrants further investigation in the region $x \gtrsim 0.2$ where the cubic-rhombohedral transition can occur.[3] As mentioned in Sec. I, a band inversion is present in this system for $x \approx 0.35$ and in accordance with the above reasoning it is expected that, around this composition, the interband interaction will be considerable. The thermodynamic order of the transition for $0.2 < x < 0.4$ has not yet been determined but an electronic instability may set in at the structural transition marked, if the interband interaction is sufficiently strong, by a discontinuous change in the lattice parameters.

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