Ferroelectric Transition in $Pb_{1-x}Ge_xTe$: Extended X-Ray-Absorption Fine-Structure Investigation of the Ge and Pb Sites

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Extended x-ray-absorption fine-structure measurements have been made on the Ge and Pb edges of ferroelectric $Pb_{1-x}Ge_xTe$ disordered alloys. Our results show that Ge atoms are displaced approximately 0.8 Å from the cell center both below and above the transition, implying that the ferroelectric transition involves long-range ordering of the dipoles. We have also measured the displacement of the Pb sublattice relative to the Te sublattice, thus showing evidence for a simultaneously order-disorder and displacive transition.

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In this Letter, we report the first direct measurements showing that off-center site occupation in semiconductor alloys may drive a ferroelectric phase transition. We observe these effects in $Pb_{1-x}Ge_xTe$ alloys, but believe that the effect may be a general one for alloys in which a substitutional atom has a size significantly different from that of the host atom it replaces. The measurements described here strongly suggest that the local bond-length distortion in alloys plays an important role in structural phase transitions. We propose a new order-disorder model of the transition and confirm a previous tentative explanation of anomalies in electrical resistivity and specific heat of $Pb_{1-x}Ge_xTe$ alloys.

$Pb_{1-x}Ge_xTe$ alloys have a large atomic-size mismatch between the Ge^{2+} ions and the Pb^{2+} ions they replace, where the ionic radii of Ge and Pb are 0.73 and 1.2 Å, respectively. Interestingly, although PbTe itself is not ferroelectric, the addition of even 0.05% Ge to PbTe induces the structural transition.[1] The high-temperature phase of the alloy has the cubic rocksalt structure (the same as PbTe), and distorts ferroelectrically to the trigonal structure at the transition temperature T_c, which depends on x. X-ray diffraction,[1,2] Raman scattering,[3,4] and ultrasonic sound-propagation[5] results indicate that the transition is second order, displacive in character, and is associated with the softening of a transverse-optic phonon mode along the trigonal c axis, similar to GeTe.[6,7]

However, the $Pb_{1-x}Ge_xTe$ alloy system has several interesting anomalous experimental results. First, T_c is a strongly nonlinear function of x, rising from 0 to 230 K from $x=0.005$ to 0.10.[1,8-11] Second, the electrical resistivity for small x exhibits a logarithmic increase with a decrease of temperature near and below T_c.[8,12-14] Third, an enhancement of resistivity an order of magnitude higher than that in $Pb_{1-x}Sn_xTe$ is seen at T_c.[15] Finally, a Schottky-type specific heat observed at low temperatures suggests a two-level system.[13]

None of these anomalies can be adequately explained by the existence of the soft mode alone, and are obviously due to the replacement of Pb by Ge. Since the Ge ions are about 0.47 Å smaller than Pb ions, it is not even clear *a priori* that Ge is on a Pb site. Because these alloys are disordered, x-ray diffraction results are difficult to interpret and the local microscopic structures of the alloys are poorly understood.

A technique capable of determining the local structural order in disordered alloys is extended x-ray-absorption fine structure (EXAFS). With use of EXAFS, it is possible to determine the near-neighbor bond lengths, types of nearest neighbors, and information about the vibrational amplitudes of atoms, all about the "average" Ge ion. In contrast, other common structural techniques such as x-ray or neutron scattering are limited in that they cannot easily probe the environment about each constituent in a disordered alloy separately. An additional advantage of EXAFS is that single-crystal samples are not necessary, reducing uncertainties due to the crystal quality.

Polycrystalline $Pb_{1-x}Ge_xTe$ alloys, with $x=0.01$ to 0.10, were prepared by quenching a stoichiometric melt of GeTe of 99.999+% purity and PbTe of 99.9999+% purity in sealed quartz ampoules at 4×10^{-6} Torr. These ingots were annealed at 600 °C in the same ampoules for about 250 h and rapidly quenched in water. Alloys with $x=0.18$ and 0.30 were made from stoichiometric melt of Ge, Pb, and Te of purities 99.999+%, 99.9999+%, and 99.9999+%, respectively, in quartz ampoules, the inside ampoules, the inside surfaces of which were pyrolized with carbon to avoid reaction of lead with silica.[16] These alloys were annealed for 360 h. The $x=0.18$ alloy was annealed in ingot form, but the alloy with $x=0.30$ was crushed to powder of size less than 74 μm and the powder was annealed. Control samples were used to monitor the progress of solid solubility of alloys with $x=0.18$ and 0.30 at various annealing times by measurement of the lattice parameters by x-ray diffraction. Complete solid solubility was assumed obtained when the lattice parameters were the same as those of $Pb_{1-x}Ge_xTe$ within limits of accuracy of the

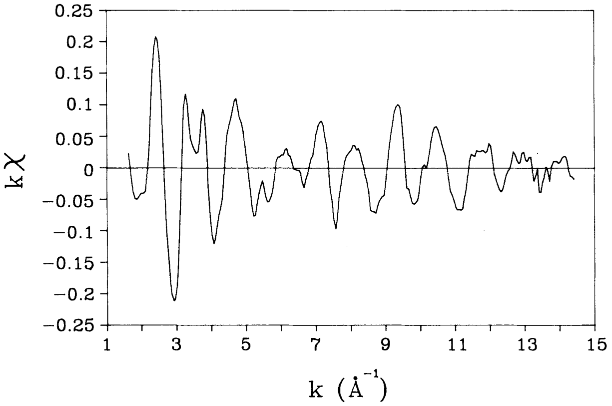

FIG. 1. Normalized k-weighted EXAFS oscillations, $k\chi$, for $\mathrm{Ge_{0.18}Pb_{0.82}Te}$ at 13 K.

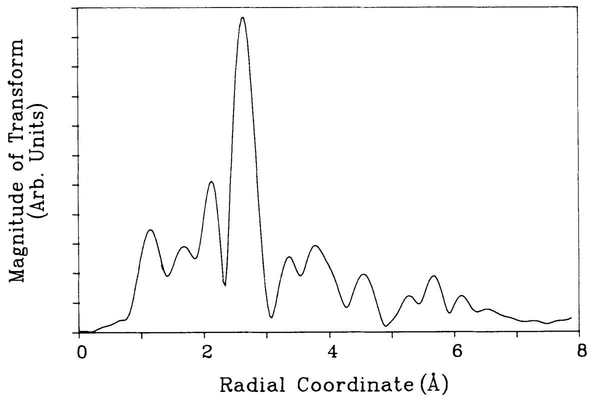

FIG. 2. Magnitude of Fourier transform of $k\chi$ of Fig. 1.

lattice-parameter measurements (±0.002 Å).[1] Complete solubility for the alloy with $x=0.3$ could not be attained. Although no diffraction lines for a second phase were observed, the lattice parameter indicated a single-phase alloy of $x=0.26$. Our results are not expected to change significantly as a result of the presence of small amount of a Ge-rich phase.

EXAFS measurements were made on these alloys at the Ge K edge at the Stanford Synchrotron Radiation Laboratory (SSRL) and National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory with the X11 beamline. At SSRL, room-temperature EXAFS data were taken in the transmission mode on alloys with $x>0.10$ and in transmission and fluorescence mode on the rest of the alloys. At NSLS, EXAFS measurements were made at four different temperatures from $T=13$ to 300 K on alloys with $x+0.05$ through 0.30. The cubic and trigonal phases of all these alloys, except $\mathrm{Ge_{0.3}Pb_{0.7}Te}$ (with $T_c \simeq 370$ K), can be accessed by these temperatures.[1] Room-temperature EXAFS measurements on the Zn K edge of ZnTe and several low temperatures and room-temperature measurements on the Ge K edge of GeTe were also made for use as standards for the data analysis.

A typical EXAFS scan is shown in Fig. 1. A striking feature of this spectrum is that the amplitude of oscillations drops almost to zero at electron wave number $k=5.9$ Å^{-1}. Although the backscattering amplitude of Te is small at this value of k, the data show the clear signature of beats between two different distances, corresponding to a distance difference of 0.8 Å. A Fourier transform of this spectrum is shown in Fig. 2. Note that at these short distances, there is no possibility of contamination by extra multiple-scattering peaks.

Further quantitative analysis demands a nonlinear least-squares fit of the data,[17] with the following model emerging. If the Ge ions occupied the normal substitutional Pb site, we would measure a single first-shell distance of about 3.2 Å with six Te neighbors. Instead, we find a clear signature of three Te atoms at 2.86±0.03 Å and three Te atoms at 3.65±0.10 Å in the high-temperature phase. Further, within our uncertainties, these bond lengths are independent of temperature and Ge concentration, both below and above the ferroelectric transition. The most straightforward interpretation of this is that even in the cubic phase the Ge ions are moving off center toward {111} corners of the unit cube by 0.7 to 0.8 Å.

Earlier experiments have provided no direct experimental evidence of these off-center ions. For example, x-ray diffraction measurements have concentrated on the *symmetry* change through the transition. The randomly off-center ions in the high-temperature phase preserve the cubic symmetry of the lattice. The off-center Ge atoms *do* alter the structure factor, but only (subtly) modify peak intensities. Similarly, Raman measurements have focused on the soft-phonon modes. Both of

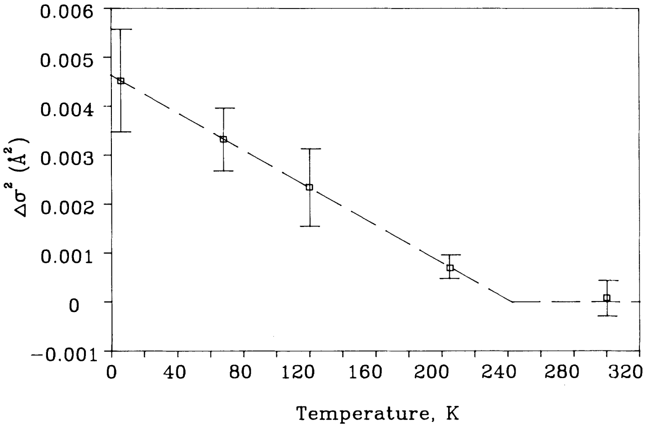

FIG. 3. Mean square spread in bond lengths, $\Delta\sigma^2$, about the Pb ion in $\mathrm{Ge_{0.1}Pb_{0.9}Te}$ as a function of temperature, as compared with pure PbTe measured at the same temperatures. This quantity is proportional to the square of the sublattice shift.

these techniques should, in principle, be able to observe the off-center ions if the right experiments are performed.

In the trigonal phase, the Pb atom is no longer at the center of the unit cell because of the relative shift of Pb and Te sublattices along the trigonal c axis. The magnitude of the shift, often used as the order parameter of the transition, increases with decreasing temperature and increasing Ge concentration. The sublattice shift may be determined directly from EXAFS measurements of the Pb edge, because the shift causes a splitting of the Pb—Te bond lengths. The distance shift is too small to be resolvable in the EXAFS, but it *is* manifested as a contribution to the EXAFS Debye-Waller factor. In order to compensate for the thermal contribution to the Debye-Waller factor, we compare Pb-edge alloy data to pure PbTe, measured at the same temperature. Figure 3 shows the sublattice shift for the $x=0.10$ alloy as a function of temperature as determined with EXAFS.

The shift of the Pb atoms relative to the Te sublattice implies that the relative displacement of the Ge ion from the Pb site *decreases* with lower temperature or higher Ge concentration. For example, in measurements made at 10 K, we find that in the 18% Ge alloys (with $T_c=300$ K), the Ge ions move 0.55 ± 0.05 Å relative to the Pb site, while in the 1% Ge alloy (with $T_c=30$ K), the Ge ions move 0.75 ± 0.05 Å.

These results obviously contradict the standard model of a displacive ferroelectric transition, where the Ge ions would undergo some change of local environment through the transition. The realization that the Ge ions are always off center rather suggests an order-disorder model of transition of Ge ions, where interaction (either direct or phonon mediated) between off-center Ge dipoles actually drives the transition. The strong dependence of T_c on composition is explained by the decrease in average Ge-Ge distance as the Ge concentration is increased.

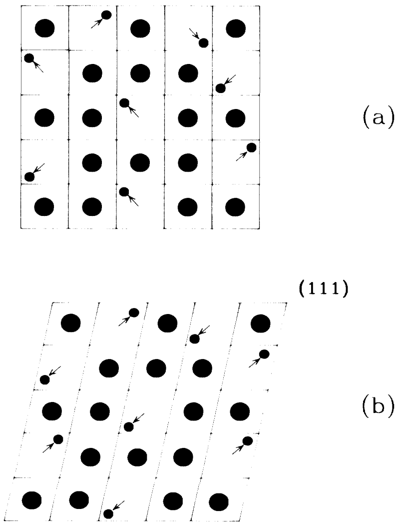

FIG. 4. Two-dimensional schematic of the proposed alignment of off-centered Ge ions in (a) high-temperature cubic phase, and (b) low-temperature trigonal phase. Large circle, Pb; small circle, Ge. The Te ions sit at the intersection of the lines.

Our EXAFS results are consistent with one theoretical explanation of the experimental "anomalies" of $Pb_{1-x}Ge_xTe$. A proposed model for the resistivity anomaly of Ref. 13 is based on the premise of off-center ions. Because of the atomic-size mismatch, it has been previously suggested that the Ge^{2+} ions may be displaced from the regular Pb site.[18,19] In the cubic phase the atoms would be displaced in any one of the eight equivalent {111} directions, while in the distorted phase, the displacements would be restricted to the trigonal axis. Figure 4 shows a two-dimensional schematic of the proposed orientation of Ge ions in the alloy in the cubic and trigonal phases. The dependence of T_c and dielectric constants on x have been explained in the context of this model by Katayama and Murase.[19] Yaraneri *et al.*[13] and Katayama, Maekawa, and Fukuyama,[20] on the basis of the work by Cochrane *et al.*,[21] have proposed a quasi-Kondo two-state mechanism for the low-temperature resistivity and specific-heat anomalies. Features of the Yaraneri model are that (a) the ions must be off center in either of the two directions determined by the trigonal axis, and (b) the displacement of the ions must be large compared with the atomic p wave functions of Ge. Our results that Ge ions are displaced by 0.55 to 0.8 Å are totally consistent with the Yaraneri model.

In summary, we have made the first direct structural measurements of ion in a disordered alloy distorting to an off-center position both below and above a ferroelectric transition. These results are consistent with other experimental measurements of the alloy, including low-temperature resistivity and heat-capacity anomalies. We have also directly measured the shift of the Pb sublattice relative to the Te sublattice, showing the displacive character of the transition. Thus, our EXAFS measurements imply that the transition has both a displacive character, as the Pb sublattice shifts relative to the Te sublattice, and an order-disorder character, as the off-center Ge dipoles align. The presence of the Ge ions is crucial, because alignment of the off-center ions appears to precipitate the transition. We believe that this effect may be a general one for alloys in which a substitutional atom has a size significantly different from that of the host atom it replaces.

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