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Raman and x-ray spectra of single-crystal Bi-Sb alloys

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Raman and x-ray spectra have been recorded for single-crystal Bi-Sb alloys over most of the compositional range. The long-wavelength optical-phonon frequencies of pure Bi and Sb are changed only slightly by alloying. At least one new Raman mode appears in the mixed crystals which cannot be explained by a model of random atom occupancy of lattice sites. X-ray diffractometer studies rule out most, but not all arrangements of long-range order in the alloys. A broadening and splitting of x-ray peaks is observed and is interpreted as indicating macroscopic inhomogeneities either of crystal composition or crystal domain orientation.

I. INTRODUCTION

The vibrational modes in a large number of alloy systems have been studied through Raman and infrared spectra in recent years.[1] In alkali-halide systems, a single long-wavelength mode is usually observed, while zinc-blende-type mixed crystals typically show a two-mode type of behavior. In Ge-Si alloys, a third mode appears.[2-6] This mode-number progression is believed to be related to crystal binding, from the strong long-range electrostatic force in ionic crystals to the nonionic predominantly nearest-neighbor force in Ge-Si.

Bi-Sb alloys have received attention in the past because of the appearance of semiconductivity for Sb concentrations of approximately 10–20%. As in Ge-Si, bonding in Bi-Sb crystals is nonionic. However, in the diamond structure of Ge and Si the optical modes are degenerate at $k = 0$, so that each element exhibits a single frequency, while assymmetry in the crystals of As, Sb, and Bi splits the degeneracy, giving rise to *two* optical frequencies in each elemental crystal. Here the point-group symmetry is D_{3d} with three optical lattice modes, type A_{1g} and E_g, all Raman active and infrared inactive, where the two E_g modes are degenerate for zone-center phonons.[7-9] In these crystals, atoms are located on planes of alternate spacing perpendicular to the trigonal axis. For phonons propogating along that axis, the A_{1g} mode represents a pure longitudinal motion (LO) of the atom planes and the E_g mode is a pure transverse motion (TO) of the planes.[8] It is worth noting also that analysis of neutron-diffraction data for Bi indicates the importance of long-range forces in the crystal.[8,9]

The Raman spectra of As, Sb, and Bi have already been reported.[10] Remarkably, they show that the ratio of frequencies A_{1g} to E_g in each of the three elements has almost exactly the same value, namely, 1.32 (which is suspiciously close to $\frac{4}{3}$ for a crystal with trigonal symmetry). There is no theoretical basis for this result, which may or may not be accidental.

It was of interest to compare the mode behavior in Bi-Sb alloys with the types already known, and also to observe the effect of alloying on the A_{1g}/E_g frequency ratios. The mode behavior should resemble that for Ge-Si, except that two sets of modes are to be expected. Further, it has been suggested that the third mode in Ge-Si alloys may be due to clustering of atom types, long-range ordering, or macroscopic inhomogeneities,[4-6] all typical subjects for x-ray studies (which apparently have not yet been made on Ge-Si).

The present work is perhaps the first to report both Raman and x-ray measurements on the same crystal alloy system.

II. EXPERIMENTAL RESULTS

All samples were single crystal, and all spectra were taken on surfaces cleaved perpendicular to the trigonal axis. A backscattering geometry[10] was employed for Raman measurements, with an incident illumination intensity of 0.5 W at 4880 Å from an argon laser. Similar spectra were also recorded with 0.1 W at 6328 Å from a He-Ne laser.

Figures 1 and 2 show the Raman spectra at 300 °K. Measurements also were taken at 80 °K, and a comparison of Stokes–anti-Stokes intensity ratios at the two temperatures verified that the observed peaks represent one-phonon processes. Resolution was limited mainly by peak broadening and the close spacing of the peaks, so that additional peaks may very well be hidden in the spectra.

Figure 3 shows a plot of the frequencies of identifiable peaks as a function of alloy composition. In pure Bi or Sb, the upper frequency is the A_{1g} mode and the lower is the E_g mode. The mode frequencies in pure Sb decrease slowly and monotonically with the addition of Bi, while the mode frequencies of pure Bi increase slowly with the addition of Sb. This differs from the Ge-Si system, where the characteristic frequency of either element decreases upon addition of the other. As discussed later on, the difference can be ascribed simply to the relative values of the crystal forces involved.

In Bi-Sb alloys, the modes at ~150 and ~115 cm^{-1} evidently are Sb-Sb vibrations of the A_{1g} and E_g types, respectively, while the modes at ~100 and ~75 cm^{-1} represent corresponding Bi-Bi vibrations.

It may be noted that the frequency ratio $A_{1g}/E_g \approx 1.32$ for either Sb or Bi persists in the alloys.

An additional peak at 125 cm^{-1} is evident in spectra of the mixed crystals. By analogy with the Ge-Si systems in which three modes are observed, one might expect three modes each for A_{1g} and E_g types for a total of six, or two in addition to the four A_{1g} and E_g Sb-Sb and Bi-Bi vibrations. If one of these extra two modes is the peak at 125 cm^{-1}, the other may very well be hidden at lower frequencies among the broadened closely spaced peaks.

Little is known theoretically about the nature of vibrations in alloys in the range of 50–50 composition. To explain the appearance of new modes in mixed crystals, various ideas have been forwarded, such as clustering of atom types, macroscopic inhomogeneties, and long-range order,[4–6] all of which are subjects for x-ray investigation. The only published x-ray work on Bi-Sb alloys was done on powder samples.[11]

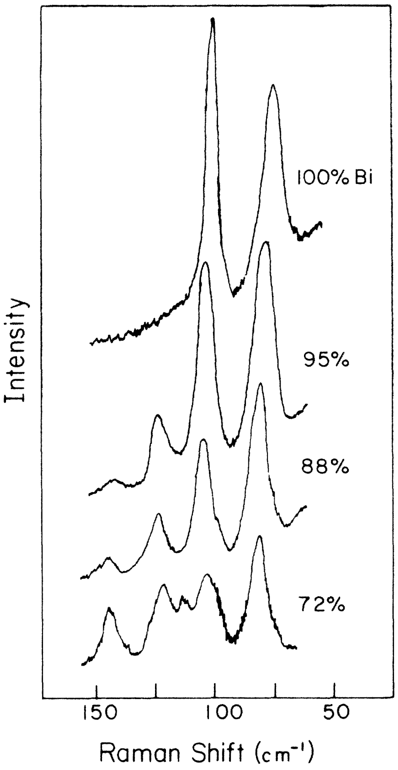

FIG. 1. Raman spectra of Bi-Sb alloys. Instrumental resolution is 3.3 cm^{-1}.

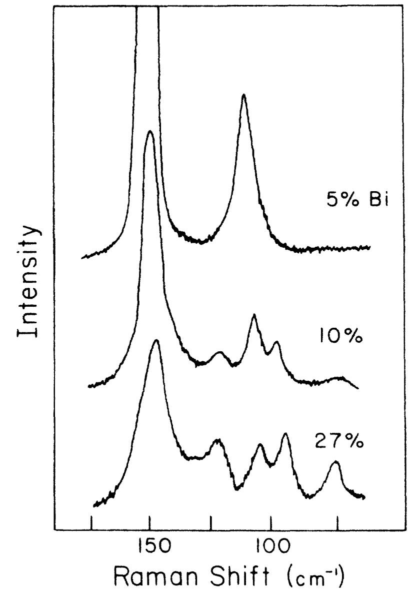

FIG. 2. Raman spectra of Bi-Sb alloys.

We have made x-ray diffraction studies on the cleavage planes of our single crystals. X-ray spectra were recorded on a diffractometer equipped with electronics for a logarithmic intensity output. This display mode was chosed to emphasize any small peaks that might appear. The copper source produced two x-ray lines, $K\alpha$ and $K\beta$, and although a nickel filter was used to attenuate the latter, the logarithmic intensity display made the $K\beta$ peaks appear relatively large. Accordingly, each diffraction order registered a

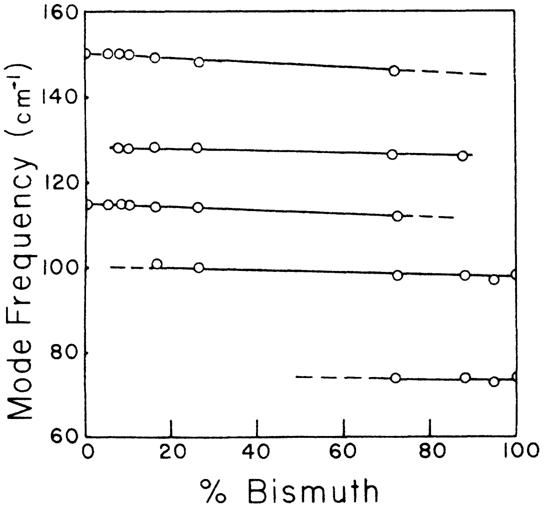

FIG. 3. Optical-mode frequencies vs alloy composition.

major peak due to $K\alpha$, together with a $K\beta$ satellite twin.

The spectra of Fig. 4 show four orders of diffraction from $(00n)$ planes, where $n = 3$, 6, 9, and 12 as expected for this structure. Normally speaking, long-range order in the mixed crystals should produce new peaks in the spectrum. Figure 4 shows no evidence of this, despite the fact that the logarithmic intensity scale emphasizes small peaks. However, the results do not rule out the possibility of long-range order; we defer further discussion of this point to Sec. III.

In Fig. 4 there is indication of peak broadening at the higher-diffraction orders. Figure 5 shows the result of a careful study of the fourth-order peak. In particular, the recording for the 72% Bi crystal reveals a splitting of that band into at least four peaks. Our interpretation of this effect is that it results from macroscopic inhomogeneities either of alloy composition or crystal domain orientation. A variation in alloy composition, for example, means a change in unit-cell dimensions,[11] resulting in an angular shift for the peak; variations in domain orientation would have a similar result. In either case, Fig. 5 shows a splitting into resolvable peaks rather than a uniform line broadening, so that the statistical distribution of inhomogeneities would have to fall into several discrete values, as opposed to a Gaussian-like random distribution around some average value.

If compositional inhomogeneity is assumed, then the total width of the peak in the 72% Bi alloy represents a variation of 0.2 Å in the c-axis unit-cell dimension, approximately 2% of the cell's length. According to the data of Cucka and Barrett,[11] the alloy composition must change by 34% to provide the 0.2-Å change in cell dimension, i.e., composition varies by ±17% from the average value.

To our knowledge, the effect illustrated in Fig. 5 has not previously been reported for any alloy. Being easily overlooked unless higher-diffraction orders are carefully studied, it may not at all be unique to Bi-Sb.

III. DISCUSSION

To describe lattice modes in mixed crystals, a so-called random-atom-displacement model has been proposed.[12] In this model, each lattice site in an $A_x B_{1-x}$ alloy is occupied by A atoms with probability x and by B atoms with probability $1-x$. Combining this idea with the Born–Von Karman

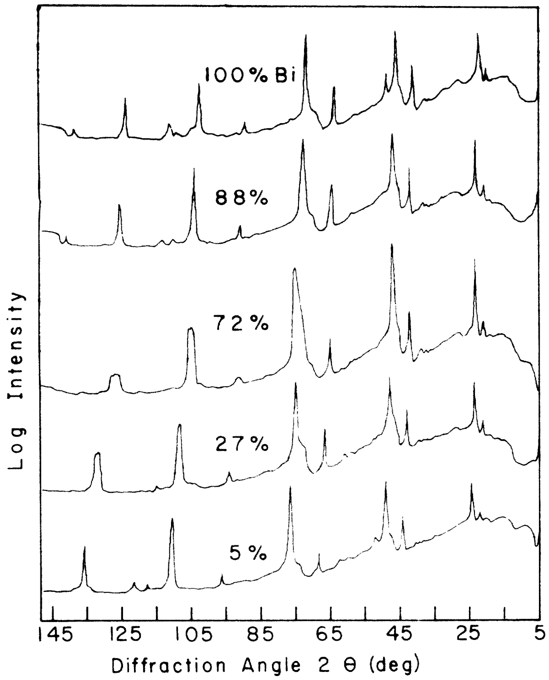

FIG. 4. X-ray diffractometer spectra of Bi-Sb alloys. The trigonal axes of the crystals are along $\theta = 0$. Four diffraction orders are shown. In each order, the main peak is due to copper $K\alpha$ radiation and the satellite twin to $K\beta$ radiation. The logarithmic intensity scale emphasizes the relatively weak satellites.

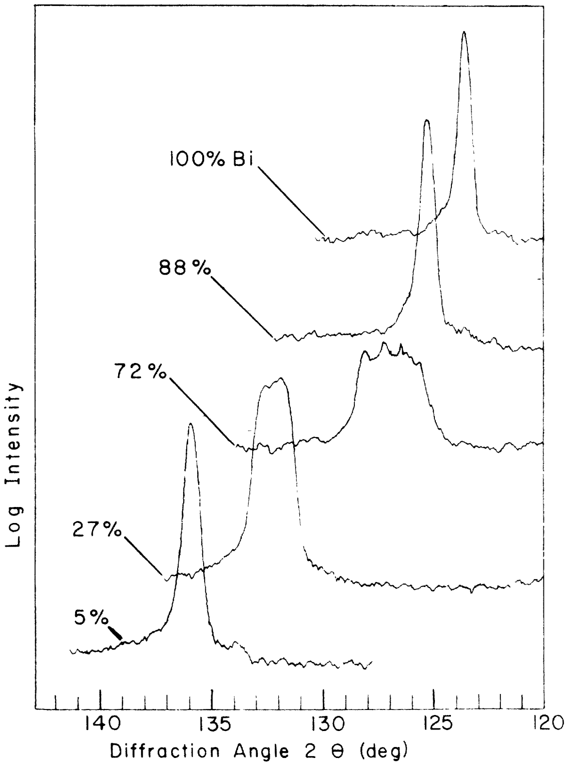

FIG. 5. Fourth-order x-ray diffraction of Bi-Sb alloys. Unfiltered $K\beta$ radiation was used here, since the $K\alpha$ diffraction peak occurred beyond the angular range of the instrument.

analysis of the Bi structure by Varnell *et al.*,[8] we find that the curves in Fig. 3 at ~150 and ~100 cm^{-1}, which represent A_{1g}-type Sb-Sb and Bi-Bi vibrations, can be fitted nicely using only a simple parameter besides those used for the pure elements, namely, a Bi-Sb force constant. (We are speaking here of the long-wavelength limit.) The same model does equally well for the E_g-type Sb-Sb and Bi-Bi modes at ~115 and ~75 cm^{-1}, again with a single new parameter. For either set, the required value of the Sb-Bi force constant falls between those for Sb-Sb and Bi-Bi. If a value smaller than either the Sb-Sb or Bi-Bi values is chosen, the curves of frequency versus composition will have the properties of the Ge-Si system, where the characteristic frequency of each element is lowered by the introduction of the other.

The model, despite its dependence on Sb-Bi force constants, predicts that only Sb-Sb and Bi-Bi vibrational modes can have a nonvanishing Raman intensity, i.e., a total of four A_{1g} and E_g Raman peaks. Random-atom displacement in an otherwise perfect lattice does not explain the fifth peak observed at ~125 cm^{-1} in Bi-Sb alloys, or the third peak in Ge-Si.

In the perfect lattice, atoms lie on pairs of planes, or planes of alternate spacing, perpendicular to the trigonal axis. Each hexagonal unit cell is intersected by six planes. The hexagonal arrangement of atoms within each plane repeats every third plane, so the set of six planes through a cell can be labeled *ab-ca-bc*.

It is instructive to consider several types of complete ordering in a 50-50 alloy, specifically where atoms in any one plane are either *all* Sb or *all* Bi. Such planes will be denoted by Sb or Bi. The arrangement SbSb-BiBi-SbSb··· can be discarded, since it leads to a unit cell of twice as many planes and twice the length, contrary to the x-ray data of Fig. 4. The arrangement SbBi-BiSb-SbBi··· likewise can be ruled out. However, the ordering SbBi-SbBi-SbBi··· would give a diffraction spectrum of exactly the type observed, characteristic also of pure Bi or Sb or of a random-atom-displacement lattice. Moreover, the structure factor calculated for the totally ordered arrangement is identical to that of the random-atom case for (00*n*) planes.[13] (For other sets of planes there will be some difference in structure factors.)

From the example given, we conclude that the absence of new peaks in the mixed crystal x-ray spectra of Fig. 4 rules out most, but not all the possibilities of long-range order.

The following hypothetical case is suggestive. In a 72% Bi alloy, assume that 35% of the volume consists of crystal domains of 50% Bi composition in which there is complete ordering of the type described above, and that 65% of the volume is taken by domains of 84% Bi composition in which there is no long-range order. The two domain types differ by 34% in composition, corresponding to a 0.2-Å difference in unit-cell dimension, with the result that each diffraction order splits into two peaks separated by the full width shown in Fig. 5. Aside from the portion between the split peaks, the simplified example is entirely consistent with all features of the x-ray spectrum while the occurrence of long-range order in domains that occupy about $\frac{1}{3}$ of the crystal is sufficient to explain the appearance of additional Raman modes.

IV. SUMMARY

Optical lattice modes in Bi-Sb alloys are analogous to those in Ge-Si alloys in most of the basic features. As in Ge-Si, explanation of all observed modes requires more than a model based on random-atom occupancy of lattice sites. X-ray spectra rule out most, but not all arrangements of long-range order. Analysis of at least one arrangement reveals the experimental difficulty of proving the absence of *all* long-range order by means of x-rays. The broadening and splitting of x-ray peaks in the mixed crystals indicates macroscopic inhomogeneities in composition or in crystal-domain orientation.

The connection between the order-disorder properties of the lattice as revealed by x-rays and the optical modes revealed by Raman scattering has not yet been established. Future experiments will include prolonged temperature-annealing of the crystals and diffractometer studies on planes other than (00*n*).

ACKNOWLEDGMENTS

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