Phonon Spectra of Ge-Si Alloys

R. A. LOGAN, J. M. ROWELL, AND F. A. TRUMBORE
Bell Telephone Laboratories, Murray Hill, New Jersey
(Received 23 July 1964)

The energies of the optical and acoustical zone-boundary phonons have been measured in single-crystal alloys of germanium and silicon as functions of alloy composition. The data were obtained by observing the effect of phonon emission upon tunneling currents at low temperatures in narrow *p-n* junctions made in these alloys. The heavily doped alloys were prepared by solvent evaporation and thermal-gradient crystal-growth techniques. Comparison of the composition dependence of the phonon energies with calculations of Braunstein, Moore, and Herman indicates that the Ge-Si alloys form in an ordered diamond-type lattice where the minority atoms occur only as next-nearest neighbors rather than in clusters of similar atoms.

INTRODUCTION

WHEN current flow in a *p-n* junction occurs by band-to-band tunneling across an indirect energy gap, the current-voltage (I-V) characteristic obtained at low temperaturees (<20°K) exhibits inflections at biases corresponding to the energies of the emitted phonons or phonon combinations. Phonon energies have been observed in Ge and Si[1–4] and polaron and phonon effects have been studied in the III-V semiconductor compounds;[3,5] these measurements were made either by direct observation of the I-V characteristic or of the bias dependence of the derivative dI/dV or d^2I/dV^2 with consequent improvement in precision. The phonon energies measured by tunneling studies were in good agreement with those obtained by neutron scattering experiments[6,7] and those by optical-absorption techniques.[8] Moreover, the theoretical understanding of the lattice vibrational spectra of regular crystals such as germanium and silicon was sufficiently advanced to quantitatively describe the observed spectra.[9]

Not only does the extension of these studies to mixed crystals such as Ge-Si alloys present some experimental difficulties, but the theoretical calculations of the lattice vibrational spectra[10] depend upon the specific model assumed for the mixing in the alloy. With existing technology, it would be extremely difficult to grow homogeneous single crystals of Ge-Si alloys sufficiently large to obtain the phonon spectra from neutron-scattering studies. From optical-absorption measurements, the four fundamental phonon energies in Ge-Si were obtained by Braunstein[11] from the three characteristic absorption bands by assuming that the two longitudinal phonons were of equal energy. Since the longitudinal phonons differ appreciably in energy in both silicon and germanium, this assumption limits the precision of the measurement of the phonon energies obtained from the optical data.

Tunnel junctions have been made in degenerate *n*-type, single-crystal Ge-Si alloys using the alloy process. Four characteristic maxima in the plots of d^2I/dV^2 versus V permit unambiguous identification of the four fundamental phonon energies at each alloy composition. By using a lower temperature of measurement (~ 1°K) and a differentiation technique of greater resolution, the experimental precision has been improved over that obtained in previous studies.[4]

EXPERIMENTAL PROCEDURE

A. Crystal Growth

The preparation of heavily doped Ge-Si crystals covering the wide range of composition listed in Table I was accomplished by using several crystal growth techniques. The crystal containing 7% silicon (all percentages used in this paper are expressed as atomic percentage) was an undoped crystal obtained from Goss who used a slow solidification technique.[12] A degenerate *n*-layer about 1 mil deep was formed in this material by arsenic diffusion in a sealed quartz capsule at 850°C for 136 h. This growth technique becomes more difficult to apply to material of intermediate compositions.

The samples containing 22 and 46% silicon were antimony-doped crystals grown on seed crystals of silicon and Ge-35% Si, respectively, by using a solvent evaporation technique described previously for the growth of antimony-doped germanium and silicon single crystals.[13,14] The Ge-35% Si seed crystal was grown by the thermal gradient techniques, as discussed below. Cracking was observed in the 22% silicon crystal, grown

[1] L. Esaki and Y. Miyahara, Solid-State Electron. **1**, 13 (1960).
[2] N. Holonyak, J. Lesk, R. Hall, J. Tieman, and H. Ehrenreich, Phys. Rev. Letters **3**, 167 (1959).
[3] R. N. Hall, *Proceedings of the International Conference on Semiconductor Physics* (Academic Press Inc., New York, 1961), p. 193.
[4] A. G. Chynoweth, R. A. Logan, and D. E. Thomas, Phys. Rev. **125**, 877 (1962).
[5] R. N. Hall, J. H. Racette, and H. Ehrenreich, Phys. Rev. Letters **4**, 456 (1960).
[6] B. N. Brockhouse and P. K. Iyengar, Phys. Rev. **111**, 747 (1958).
[7] B. N. Brockhouse, Phys. Rev. Letters **2**, 1256 (1959).
[8] J. R. Haynes (private communication).
[9] W. Cochran, Phys. Rev. Letters **2**, 530 (1959); W. Cochran, Proc. Roy. Soc. (London) **A253**, 260 (1959).
[10] R. Braunstein, A. R. Moore, and F. Herman, Phys. Rev. **109**, 695 (1958).
[11] R. Braunstein, Phys. Rev. **130**, 879 (1963).
[12] F. X. Hassion, A. J. Goss, and F. A. Trumbore, J. Phys. Chem. **59**, 1118 (1955).
[13] W. G. Spitzer, F. A. Trumbore, and R. A. Logan, J. Appl. Phys. **32**, 1822 (1961).
[14] F. A. Trumbore, P. E. Freeland, and R. A. Logan, J. Electrochem. Soc. **108**, 458 (1961).

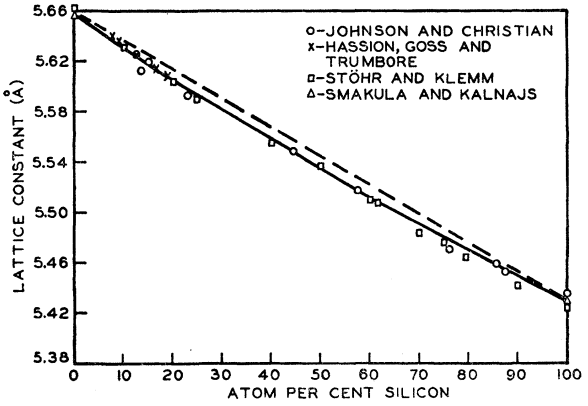

FIG. 1. Lattice parameter versus alloy composition based on literature data. (Refs. 12 and 16). The curve drawn through the experimental points differs somewhat from the curves of Stohr and Klemm (whose data have been converted to Å units from kX units) and of Johnson and Christian. Comparison of these authors lattice parameters for pure Ge and Si with the generally accepted values of Smakula and Kalnajs indicates good agreement for Ge but a fairly wide variation for Si. More weight was given to the higher lying points of Johnson and Christian since any occluded liquid phase in the growth of their samples would lead to higher Ge contents in their chemical analyses, possibly accounting for some of the scatter in their data.

on silicon, but not in the 46% silicon crystal grown on the Ge-Si seed. In the present case growth occurred as antimony evaporated from ternary Sb-Ge-Si melts. It is also possible that some growth occurred due to cooling of the saturated melt (see Ref. 13). Although small crystals were obtained, in the case of the 46% silicon crystal the sample was large enough to make Hall effect measurements. The samples containing 70 and 79% silicon were also antimony-doped crystals and were grown by using a sealed-tube thermal-gradient technique used previously for the growth of germanium and silicon.[15] In this work the crystals were grown by the transfer of excess silicon through the ternary Sb-Ge-Si melts in a thermal gradient to the cooler part of the melt where the growth of the doped solid solutions took place. Seven weeks were required to grow these crystals at a temperature of about 1050°C in a thermal gradient of ~1°C/cm. The resulting crystals were very small, just large enough for the preparation of samples for diodes and x-ray analyses. Large crystals (1 in. $\times\frac{3}{8}$ in. diam) of Ge-Si alloys have been grown by using larger thermal gradients. However, the gradient was purposely kept low here in an attempt to grow more homogeneous material free from occlusions. From three crystals grown for this study, samples were prepared for Hall effect measurements. Room-temperature measurements of the Hall constant indicated a carrier concentration of 1 to 2×10^{19} cm^{-3} for all crystals.

The lattice parameters of the alloys, obtained from x-ray powder patterns, are summarized in Table I. The compositions given in Table I were obtained from the measured lattice parameters and the curve in Fig. 1 which in our opinion best fits the available data on the lattice parameter as a function of composition.[12,16] This curve differs somewhat from that of Johnson and Christian.[16] In the present work the donor concentrations are sufficiently low, $\sim1-2\times10^{19}$ cm^{-3}, so that their effect on lattice parameter can be neglected within the limits of experimental error.

B. Junction Fabrication

The *p-n* junctions were made by alloying aluminum wire containing 1% boron into wafers of the *n*-type semiconductors approximately 0.1 cm on each edge using a fast heating cycle in which a maximum temperature of about 725°C was reached. An ohmic contact was made by alloying a gold wire to the opposite side of the wafer at a slightly lower temperature. Because of the presence of boron in the aluminum wire, the aluminum concentration is a lower limit to the acceptor concentration in the *p*-type regrowth. The acceptor concentration in the *p*-type regrowth is estimated to be $\gtrsim4\times10^{20}$ cm^{-3} in the germanium diodes (from the equilibrium solubility of Al in Ge[17]) and 2.3×10^{19} cm^{-3} in the silicon diodes (by direct measurement). If the solubility of aluminum is assumed to vary linerarly from that in silicon ($\sim9\times10^{18}$ cm^{-3}) to that in germanium ($\sim4\times10^{20}$ cm^3), then in the alloys the aluminum concentrations in the *p*-type region would be $\geq10^{20}$ cm^{-3} for those compositions studied. The *p* sides of the junctions in the alloys are therefore estimated to be relatively heavily doped compared to the *n* side where the donor concentration ranged from 1 to 2×10^{19} cm^{-3}.

It is unlikely that the *p*-type regrowth obtained in forming the junction is of the same alloy composition as that in the *n*-type base wafer. However, due to the asymmetric doping levels in the *p* and *n* regions, the electric field exists predominantly on the *n* side of the junction. Hence, the point of stationary phase[18] occurs on the *n* side and the phonons which assist the tunneling transitions should be characteristic of the *n* region, regardless of the composition of the *p*-type regrowth.

This effect may also account for several unsuccessful attempts that were made to observe the phonon energies in single-crystal alloys containing about 90% Si. While tunneling junctions were readily made in these crystals, only weak phonon effects characteristic of pure silicon were observed. Since the doping level in the *p* and *n* regions are estimated to be comparable in this case, the tunneling transitions may occur in the nonuniform *p*-type regrowth.

[15] F. A. Trumbore, C. R. Isenberg, and E. M. Porbansky, Phys. Chem. Solids **9**, 60 (1959).

[16] A. Smakula and J. Kalnajs, Phys. Rev. **99**, 1737 (1955); H. Stöhr and W. Klemm, Z. Anorg. Allgem. Chem. **241**, 305 (1939); E. R. Johnson and S. M. Christian, Phys. Rev. **95**, 560 (1954).

[17] F. A. Trumbore, Bell System Tech. J. **39**, 205 (1960).

[18] E. O. Kane (see Ref. 3, p. 204).

C. The Derivative Measurement

After fabrication the diodes were mounted so that a four terminal measurement of the I-V characteristic could be made. The diodes were immersed in liquid helium which could be pumped to 0.8°K when necessary. At helium temperatures, the I-V plots for Ge and Si diodes showed distinct inflections at biases equal to the phonon energies, but the alloy diodes in most cases exhibited only very weak inflections. These weak inflections were easily located, however, by plotting d^2I/dV^2 versus V using continuously recording equipment.

The equipment used for these studies was developed for measurements of the fine structure observed in superconductor tunnel diode I-V characteristics. A 500-cps signal is applied to the diode and the 1000-cps harmonic recorded as a function of the dc bias swept across the diode. The harmonic signal is closely proportional to d^2I/dV^2 when the changes in dI/dV are small. The traces of Fig. 2 are taken from 10-in.×15-in. X-Y recorder sheets. The advantages of this technique over

TABLE I. Summary of phonon energies.

Atomic fraction of silicon	Lattice constant (Å)	Phonon energy (mV) TA	LA	LO	TO
0		7.6±0.2	27.5±0.2	31.1±0.2	36.3±0.2
0 (Ref. 6)		8.0±0.2	26.6±1.2	30.5±1.2	34.6±1.2
0.07	5.640	9.0	30.7	34.3	39.3
0.22	5.600	10.8	34.3	not observable	48.5
0.46	5.544	12.3	36.3	43.0	49.6
0.70	5.491	14.5	36.8	44.0	50.3
0.79	5.472	16.0	37.5	45.0	50.6
1.00		18.7±0.2	47 ±2	56.2±1.0	59.1±0.2
1.00 (Ref. 7)		17.9±0.6	43.7±2.1	53.2±2.1	58.5±1.2

that used in earlier work are that the dc bias can be swept very slowly (~10 min for a typical run over a bias range 0–75 mV) with consequent improvement in precision, and the 500 cps signal can be kept smaller than kT for good resolution.

The phonon energies are located as the peaks in the d^2I/dV^2 versus V plot; the validity of this assignment has been discussed previously.[4] The use of low temperatures (~1°K) narrows the peak width appreciably in Ge and Si diodes, but in the alloys the width is practically unchanged below 4.2°K.

RESULTS

Typical measurements of the bias dependence of d^2I/dV^2 are shown in Fig. 2 for diodes of Ge, Si and the alloy containing 46% Si. (All junctions exhibit structure near zero bias and this will be described in a later section.)

In germanium diodes (Fig. 2a), as the bias is increased, four well-defined peaks are observed in the

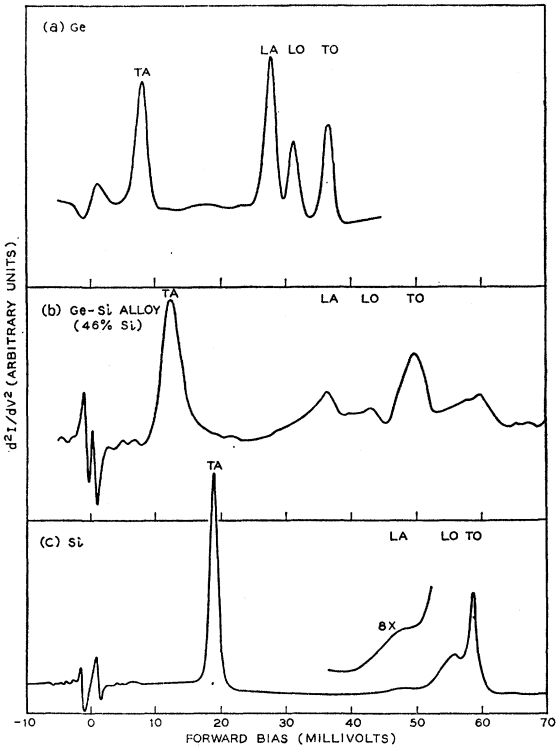

FIG. 2. Curves of d^2I/dV^2 against bias for junctions of (a) Ge, (b) Ge-Si alloy containing 46% Si and (c) Si at 0.8°K.

derivative which correspond in energy to the four fundamental phonons, the transverse acoustic (TA), the longitudinal acoustic (LA), the longitudinal optic (LO) and the transverse optic (TO). The positions of these peaks, whose half-width is about 2 mV, are listed in Table I where a comparison is made with the corresponding phonon energies obtained from neutron-scattering studies. While the phonon-energy determinations are in reasonable agreement considering the experimental uncertainties, it is noted that the precision of the second derivative technique exceeds that using neutron scattering. Within experimental error, the results are in agreement with those reported in previous tunneling studies.[3,4]

In silicon diodes (Fig. 2c), the relative phonon contributions to the tunneling current vary so that only the TA and TO phonons are as prominent as in the Ge diodes, with half-widths of about 1.5 mV. The LO phonon contribution is weaker than that of the TO and is not completely resolved from the latter due to the small difference in energy. The peak associated with the LO phonon has an estimated half-width of 4 mV. The LA phonon peak is so small that it is only observed in some of the diodes with very high gain in the differentiation circuitry. As listed in Table I, the phonon energies in silicon determined from tunneling measurements and by Brockhouse[6,7] are also in agreement to within the precision of the two methods, but our values

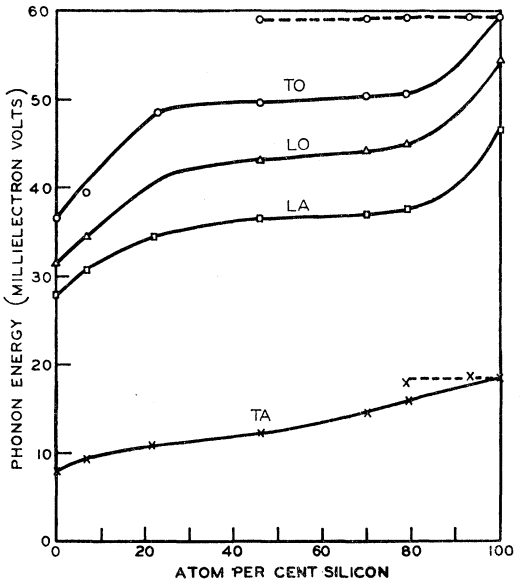

FIG. 3. The phonon energies plotted against the atom percentage of Si in the Ge-Si alloy.

are consistently higher. While our results agree within experimental error with those observed in similar studies,[3,4] it is noted that the increased resolution in the present work has permitted a more precise determination of the phonon energies in Si and Ge than in previous tunneling measurements; in particular, the values for the three high-energy phonons in Si are significantly changed from those previously reported.

Figure 2(b) displays the bias dependence of d^2I/dV^2 for a diode made with a Ge-Si alloy containing 46% Si. This result is typical for the alloy diodes where (1) four well-defined peaks are observed whose position, relative size, and shape shift smoothly as a function of alloy composition from pure Ge to pure Si, (2) the half-width of the peaks is 4 ± 1 mV in contrast to the narrower peaks observed in pure Ge and Si diodes, and (3) the position of the peaks varied less than 0.4 mV from diode to diode made from the same single crystal. While the last is an indication of the homogeneity of the alloys, it was observed that in silicon-rich compositions greater than 46% Si, the TO phonon of pure Si is present and in diodes made with Si-rich alloys of composition greater than 79% Si, the TA phonon of pure Si was also observed. While the presence of the silicon phonons in the silicon-rich alloys may be ascribed to microscopic inhomogeneities in the alloys, it may also indicate the occurrence of localized vibrational modes in the alloy.

Table I summarizes the observed phonon energies as a function of alloy composition; each energy represents an average value observed in two to five diodes made from each crystal.

The data of Table I are presented graphically in Fig. 3 where the characteristic variation of phonon energy with composition may be more readily compared with calculations of the phonon spectrum using specific models for the ordered alloy.

DISCUSSION

The energies of the fundamental phonons have been measured as functions of alloy composition in the Ge-Si alloy system. The technique used obtains the phonon energies from the characteristics of diodes made with the Ge-Si alloys and is ideally suited to this problem where only very small amounts of single-crystal material are available. We believe that the results are more accurate than those obtained by other methods and by previous tunneling measurements, both in the alloys and in Ge and Si alone.

We find that the energy of the fundamental phonons varies smoothly as the concentration of Si in Ge is increased. For the three high-energy phonons (LA, LO, and TO), the variation of energy with concentration is very similar for each phonon. The energy varies rapidly between 0 and 20% Si and between 80 and 100% Si, being practically unchanged between 20 and 80% Si. The variation for the TA phonon is almost linear with a slight hint of the characteristic curve of the higher energy phonons. The variation of phonon energies with alloy compostition observed here differs in detail from that reported in earlier work.[11] Although a slight change in phonon energy was observed at each end of the composition range, in qualitative agreement with that observed here, the greatest change in energy was observed in the middle of the composition range, in disagreement with our data. As mentioned above, the optical-absorption measurements permit phonon-energy determinations from the observed combination energies only by assuming that the LA and LO phonons are equal in energy; whereas the LO phonon exceeds the LA by about 15% in both Ge and Si. The large discontinuities observed by Braunstein[11] in the conbination bands as the composition varied from Ge- to Si-rich samples suggests that the samples employed were less homogeneous than those used here. Ando[19] has reported phonon energies in Si-rich alloys determined by observation of the inflections in the I-V characteristics of tunnel junctions, but the large experimental uncertainty in the determined phonon energies does not permit a comparison with the present data.

Two models of the Ge-Si alloy have been considered by Braunstein *et al.*[10,11] in an attempt to calculate the phonon spectrum. The first, a virtual crystal approximation, replaces the actual alloy by an equivalent crystal in which each lattice site is occupied by identical atoms whose mass is determined by the alloy composition. This model predicts an essentially linear variation with composition for all the normal modes and would be expected to be a good approximation for the long-wavelength acoustic modes, where many lattice sites are involved in the determination of the character-

[19] K. Ando, J. Phys. Soc. Japan **15**, 2360 (1960).

istic vibration frequencies. As our results show, the low-energy TA phonon does vary with composition in the way the virtual crystal model predicts, but the high-energy phonons depart strongly from a linear relationship with composition.

In the second model, Si and Ge atoms are placed in the diamond-type lattice in all physically possible arrangements. In this way, 15 distinct arrangements of Ge and Si atoms may be produced in the unit cube, which give rise to 8 different atom-fraction compositions. For these ordered crystals, the normal modes were calculated using a force model involving nearest neighbor interactions only and the results permit a determination of the variation of phonon energy with composition. A different behavior was estimated for two subseries of the 15 different arrangements, one where the minority atoms occur only as next nearest neighbors in the lattice and the other where similar atoms tend to cluster together as nearest neighbors. The characteristic curve of the high-energy phonons in Fig. 3 is obtained for the former subseries. The experimental results thus suggest that the Ge-Si alloys form in an ordered diamond-type lattice where the minority atoms avoid each other on neighboring lattice sites.

CONDUCTANCE NEAR $V=0$

In addition to the peaks in the d^2I/dV^2 versus V plots of Fig. 2 which are associated with phonon emission, an additional structure is observed near zero bias. In the Ge junction of Fig. 2a, this structure corresponds to a dip in conductance centered at $V=0$. In the Si and alloy junctions of Figs. 2b, 2c, the structure indicates a peak in conductance at $V=0$. In the latter case, superimposed upon the characteristic is that expected for tunneling from a metal or semiconductor into a superconductor with an energy gap of about 0.3 mV. While the conductance dip or peak grows slowly as the temperature is decreased from 20° to 1° the superconductor tunneling characteristic, which is observed in many diodes, appears abruptly at temperatures in the range 1.6° to 2°K. To investigate which portion of the diode structure was undergoing a superconducting transition, separate resistance measurements at low temperatures were made on the diode components. While Al, Al+1%B, and the Ge-Si alloys did not have superconducting transitions at temperatures as low as 1.3°K, superconducting transitions were measured for a number of alloy mixtures and are listed in Table II.

The alloys listed in Table II are nonhomogeneous mixtures of an Al-rich superconducting phase containing Ge or Si and a Ge, Si or Ge-Si rich nonsuperconducting phase. The transition temperatures for all of the alloys are seen to be higher than for pure aluminum. The increase in T_c for the Al-Si and Al-Ge eutectic mixtures, where solid solubility data are available,[20] is roughly proportional to the Ge or Si solubility in Al. The higher T_c values for the Al-Ge-Si alloys suggest higher combined solubilities of Ge and Si in the Al crystallized from these melt compositions. It is, therefore, not unreasonable to assume that alloys with transition temperatures as high as 2.0°K could be obtained in fabricating the diodes and that the superconducting tunneling occurs between the Al, Ge, and/or Si alloy and the p-type regrowth. The conductance peaks and dips are ascribed to tunneling transitions in the p-n junction since they vary in relative magnitude with the doping level on the n side of the junction. These effects are currently being studied and will be described more fully at a later date.

TABLE II. Superconducting transition temperatures, T_c, for a number of Al-Ge-Si alloys.

Alloy composition (atom %)	T_c°K	Solid solubility of Ge (or Si) in Al (atom %)
Al	1.2	...
88 Al–12 Si (Al–Si Eutectic)	1.4	1.6[a]
70 Al–30 Ge (Al–Ge Eutectic)	1.6	2.8[a]
75 Al–12.5 Ge–12.5 Si	1.75	...
20 Al–40 Ge–40 Si	1.8	

[a] See Ref. 20.

Note added in proof. The most precise measurements of the variation of lattice parameter with alloy composition in the Ge-Si system have recently been reported by J. P. Dismukes, L. Ekstrom, and R. J. Paff, J. Phys. Chem. **68**, 3021 (1964). Their data lies slightly above the curve drawn in Fig. 1 but agree to within 1 at.% over the entire composition range.

ACKNOWLEDGMENTS

The authors wish to thank E. O. Kane, M. L. Cohen, and M. A. Short for valuable discussions about this work. The advice of D. E. Thomas on the circuitry problems was invaluable. The Ge-Si alloys were grown by P. Freeland and M. Kowalchik. The determinations of lattice parameters were made by R. Barns, D. Nitti, and A. D. Mills. The general assistance of H. G. White and L. Kopf in all phases of the experiments is gratefully acknowledged.

[20] M. Hansen and K. Anderko, *Constitution of Binary Alloys* (McGraw-Hill Book Company, Inc., New York, 1958).