

$$\frac{d\bar{\mu}}{dc_{Al}}(c_{Al} \rightarrow 0) = -\mu_{Fe-Ni}(c_{Ni}) - \begin{cases} c_{Ni} \sum_k c_k \Delta\mu_{Ni}^k & (\text{if less than } 2\mu_B) \\ 2\mu_B & (\text{else}) \end{cases}, \quad (2)$$

where  $\mu_{Fe-Ni}(c_{Ni})$  is the average magnetization of the binary Fe-Ni alloy of composition  $c_{Ni}$ , and from the average magnetization measurements  $\sum_k c_k \Delta\mu_{Ni}^k \approx 11\mu_B$ .

The curve of Fig. 1 calculated on the basis of Eq. (2) gives a good fit to the experimental data of Bardos *et al.*<sup>6</sup> We cannot determine from the average magnetization measurements alone the change of the Ni moment in each coordination sphere, nor the extent of the perturbed range, but if we assume, for example, that the latter is limited to the first and second neighbors of Al, then the Ni moments in both coordination shell(s) must disappear entirely.

$d\bar{\mu}/dc_{Al}(c_{Al} \rightarrow 0)$  varies nearly linearly with Ni concentration up to 16 at.% Ni, after which it exhibits a saturation effect, corresponding to the acceptance of the two whole excess Al electrons by

the Ni atoms. This agrees well with the 18-at.%-Ni concentration necessary for the formation of a Ni band in Fe. This condition is the formation of an infinite chain of Ni atoms—a typical percolation problem,<sup>15</sup> where  $c_{Ni}$  gives the step probability.

The above simple model seems to explain the different experimental data well, although the detailed theoretical treatment is greatly complicated by the broadening of energy levels in the metal.

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<sup>1</sup>D. Parsons, W. Sucksmith, and J. W. Thompson, *Phil. Mag.* **3**, 1174 (1958).

<sup>2</sup>J. Crangle and M. J. C. Martin, *Phil. Mag.* **4**, 1006 (1965).

<sup>3</sup>J. B. Comly, T. M. Holden, and G. G. Low, *J. Phys. C* **1**, 458 (1968).

<sup>4</sup>T. M. Holden, J. B. Comly, and G. G. Low, *Proc. Phys. Soc. (London)* **92**, 726 (1967).

<sup>5</sup>N. F. Mott, *Advan. Phys.* **13**, 325 (1964).

<sup>6</sup>D. I. Bardos, J. L. Beeby, and A. T. Aldred, *Phys. Rev.* **177**, 878 (1969).

<sup>7</sup>M. J. Besnus and A. J. Meyer, *Phys. Rev. B* **2**, 2999 (1970).

<sup>8</sup>J. L. Beeby, *Phys. Rev.* **141**, 781 (1966).

<sup>9</sup>I. Vincze and L. Cser, *Phys. Status Solidi (b)* **50**, 709 (1972).

<sup>10</sup>C. E. Johnson, M. S. Ridout, and T. E. Cranshaw, *Proc. Phys. Soc. (London)* **81**, 1079 (1963); and our own unpublished data.

<sup>11</sup>D. A. Shirley, S. S. Rosenblum, and E. Matthias, *Phys. Rev.* **170**, 363 (1968); I. A. Campbell, *J. Phys. C* **2**, 1338 (1969).

<sup>12</sup>C. Reale, *J. Mater. Sci.* **6**, 33 (1971).

<sup>13</sup>A. Wenger, G. Bürri, and S. Steinemann, *Solid State Commun.* **9**, 1125 (1971).

<sup>14</sup>J. A. Seitchik and R. H. Walmsley, *Phys. Rev.* **137**, A143 (1965).

<sup>15</sup>J. M. Ziman, *J. Phys. C* **1**, 1532 (1968).

## Order-Disorder Transformation in Tellurium-Selenium Alloys by Mössbauer Effect

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A study of the quadrupole splitting at  $Te^{125}$  sites in the  $Te_{1-x}Se_x$  system with Se concentration  $x$  shows that these alloys are disordered copolymers except at concentrations of  $x=0, 0.5, 1.0$ , where ordering occurs.

The material characterization of disordered and amorphous semiconductors in terms of composition and structure is fundamental to a study of the properties of these materials. In this paper we demonstrate the use of the Mössbauer-effect technique to study compositional order-disorder

in the tellurium-selenium system. We show the existence of the Te-Se bond in the solid state and suggest (a) that alloys of tellurium and selenium form disordered copolymers and (b) that the equimolecular alloy  $Te_{0.5}Se_{0.5}$  is an ordered copolymer involving alternating tellurium and selenium atoms

in a helical chain.

Crystal structures of the covalent semiconductors tellurium and selenium (hexagonal) are known to be isomorphous and belong to the trigonal space group  $D_3^6$  or  $D_3^4$ . This structure<sup>1</sup> is rather unique and consists of atoms arranged in infinitely long spiral chains. Solid solutions of these semiconductors are known to exist in all atomic proportions, and measurements of the lattice parameters with concentration show a slight departure from Vegard's law.<sup>2</sup> It has been suggested that the structure of the  $\text{Te}_{1-x}\text{Se}_x$  system is either a mixture of tellurium and selenium polymers or a copolymer involving a covalent Te-Se bond. In the present work, we have used the Mössbauer effect in  $\text{Te}^{125}$  and have observed an increase of 24% in the quadrupole splitting (QS) at Te in the  $\text{Te}_{0.5}\text{Se}_{0.5}$  alloy over that of pure tellurium. This large increase in the QS can be understood, as we show, as being due to a Te site covalently bonded to two Se neighbors. We propose a model to explain the observed increase in the QS with selenium concentration. We point out that this model also explains the deviation from Vegard's law that was observed in the x-ray measurements of Ref. 2. Both the Mössbauer and x-ray measurements support the existence of a covalent Te-Se bond.

The electric field gradient (EFG) in pure tellurium has been studied extensively in single crystals.<sup>3</sup> The Te atom possesses a partially filled  $p$  shell. The principal contribution to the EFG comes from the unbalanced  $p$  electron density which implies an overwhelming importance for the covalent bonds with the two nearest neighbors. The sizable increase in the QS at Te in the  $\text{Te}_{1-x}\text{Se}_x$  system that is reported here then clearly demonstrates the copolymer nature of the system. We suggest the existence of three types of inequivalent Te sites: site  $\alpha$  covalently bonded to two Te near neighbors; site  $\beta$  covalently bonded to one Te and one Se near neighbor; and site  $\gamma$  covalently bonded to two Se near neighbors. The increase in the QS at the  $\beta$  and  $\gamma$  sites over that at the  $\alpha$  site can be understood as due to the presence of a smaller atom closer to the Te site in question.

Solid solutions of  $\text{Te}_{1-x}\text{Se}_x$  ( $x=0.0, 0.1, 0.2, 0.5, 0.7, 0.8$ ) were prepared by heating 99.9999% pure elemental<sup>4</sup> tellurium and selenium in vacuum followed by subsequent annealing at a temperature of about 175 °C. The elements in a powder form were thoroughly mixed and then sealed in a quartz ampoule in a vacuum of  $5 \times 10^{-7}$  Torr and fired to 1000 °C for 3 h. The furnace temperature was then slowly lowered to about 175 °C to anneal the alloys for a period of 36 h. The alloys were then crushed to a powder and annealed again in vacuum for about 24 h to ensure homogeneity and avoid

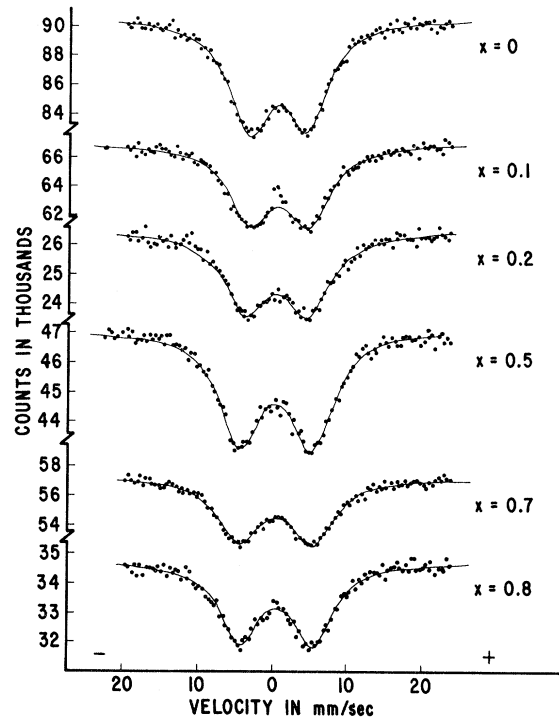


FIG. 1.  $\text{Te}^{125}$  Mössbauer spectra of  $\text{Te}_{1-x}\text{Se}_x$  alloys.

minor structural damage that was noticed in x-ray-diffraction patterns of the crushed alloy. The re-annealed alloys were used for preparing absorbers containing approximately 55 mg/cm<sup>2</sup> of Te of natural enrichment.

The Mössbauer experiments<sup>3</sup> were carried out using  $\text{I}^{125}$  in Cu as a source of 35.5-keV  $\gamma$  rays, and the resonant absorption was observed by detecting the 6-keV escape peak in a Xe proportional counter. To enhance the effects, both the source and the absorber were cooled to 4.2 K in an exchange-gas cryostat. In all cases the spectra consisted of a pair of doublets and are summarized in Fig. 1.

The analysis of the data was carried out by least-squares-fitting the spectra to a pair of Lorentzians of equal linewidth with no restrictions on line positions, intensities, and geometrical parameters. The result of this analysis is plotted in Fig. 2 and it shows that the separation between the peaks increases almost linearly with  $x$  in the range  $0 < x < 0.5$  and is independent of  $x$  in the range  $0.5 < x < 1.0$ . In order to understand this behavior, we calculated the relative populations of the  $\alpha$ ,  $\beta$ , and  $\gamma$  Te sites for a given Se concentration  $x$ . These calculations were made in the approximation that the  $\text{Te}_{1-x}\text{Se}_x$  system is a copolymer where the van der Waals forces between separate spiral chains and the interactions between non-nearest neighbors can be neglected in

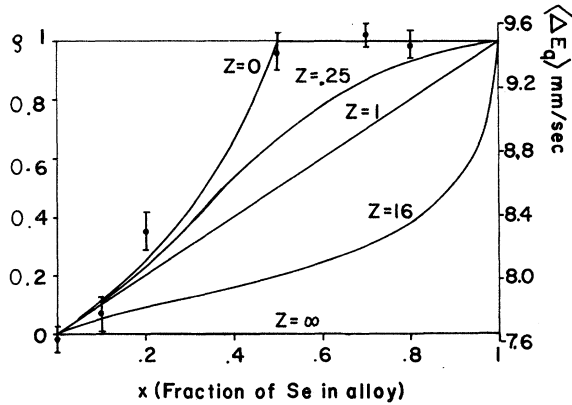


FIG. 2. Expected dependence of  $\rho$  on  $x$  at different values of  $Z$  and observed  $\langle \Delta E_Q \rangle$ , as a function of  $x$ .

comparison to the covalent binding between nearest neighbors in the same chain. In this approximation the problem reduces to a one-dimensional Ising model<sup>5</sup> with the only difference being that one asks questions which are slightly different from the usual ones; viz., what is the relative population of the three inequivalent Te sites for a given value of  $x$ . If the total number of atoms in a helix is  $n = n_1 + n_2$ , where  $n_1$  is the number of Te atoms and  $n_2$  the number of Se atoms, then the total number of  $\alpha$ ,  $\beta$ , and  $\gamma$  Te sites is equal to the number of Te atoms in the chain, i. e.,

$$n_\alpha + n_\beta + n_\gamma = n_1.$$

Neglecting the effects following from the finite length of the chain, we obtain the statistical weight  $e^S$ , where  $S$  is the entropy:

$$e^S \approx \binom{n_1 - \frac{1}{2}n_\beta - n_\gamma}{\frac{1}{2}n_\beta} \binom{\frac{1}{2}n_\beta + n_\gamma}{\frac{1}{2}n_\beta} \binom{n_2}{\frac{1}{2}n_\beta + n_\gamma}. \quad (1)$$

The total energy of a helix is made up of the sum of the binding energies of neighbors:

$$\begin{aligned} E &= (n_1 - n_\gamma - \frac{1}{2}n_\beta) E_{TT} + (n_2 - n_\gamma - \frac{1}{2}n_\beta) E_{SS} \\ &\quad + (2n_\gamma + n_\beta) E_{ST} \\ &= n_1 E_{TT} + n_2 E_{SS} + (n_\gamma + \frac{1}{2}n_\beta) (2E_{ST} - E_{SS} - E_{TT}), \end{aligned} \quad (2)$$

where  $E_{TT}$ ,  $E_{SS}$ , and  $E_{ST}$  are the binding energies of Te-Te, Se-Se, and Te-Se covalent bonds.

Optimizing the free energy in the number of  $\beta$  and  $\gamma$  sites, we obtain the expectation value of  $n_\beta$  and  $n_\gamma$  Te sites in the limit of infinitely long chains,

$$n_\gamma/n_1 = \rho^2, \quad n_\beta/n_1 = 2\rho(1 - \rho), \quad (3)$$

where

$$\rho = [2(1-x)(1-Z)]^{-1} \{1 - [1 - 4x(1-x)(1-Z)]^{1/2}\}, \quad (4)$$

where  $x = n_2/n$  is the fraction of Se atoms in the chain and

$$Z = \exp[(kT)^{-1}(2E_{ST} - E_{SS} - E_{TT})]. \quad (5)$$

The parameter  $\rho$  changes smoothly from 0 to 1 with  $x$  and has been plotted in Fig. 2 for a few values of  $Z$ . In the Mössbauer experiments, one observes an average QS of the three Te sites weighted by their respective populations and isomer shifts. To a first approximation one may not expect to see significant changes in the isomer shifts at the three inequivalent Te sites. One may then expect the average QS to be given by

$$\langle \Delta E_Q \rangle = n_1^{-1} (n_\alpha \Delta E_\alpha + n_\beta \Delta E_\beta + n_\gamma \Delta E_\gamma), \quad (6)$$

where  $\Delta E_\alpha$ ,  $\Delta E_\beta$ , and  $\Delta E_\gamma$  represent the QS of the first excited state of  $\text{Te}^{125}$  at  $\alpha$ ,  $\beta$ , and  $\gamma$  sites. It is reasonable to expect the increase in the QS at the  $\gamma$  site to be twice the increase of the QS at the  $\beta$  site, i. e.,

$$\Delta E_\gamma - \Delta E_\alpha = 2(\Delta E_\beta - \Delta E_\alpha) = 2\Delta. \quad (7)$$

This assumption simplifies Eq. (6) to read

$$\langle \Delta E_Q \rangle = \Delta E_\alpha + 2\rho\Delta \quad (8)$$

and one observes that the average QS  $\langle \Delta E_Q \rangle$  as a function of Se concentration  $x$  has a behavior (Fig. 2) determined by  $\rho$  alone. The theoretical curve for  $Z=0$  fits the data rather well. The small value of  $Z \leq 0.02$  inferred from our data clearly suggests that the binding of a Se-Te bond is stronger than the average of the Se-Se and Te-Te bond. One must therefore conclude that for a given Se concentration the tendency of the  $\text{Te}_{1-x}\text{Se}_x$  system is to form as many  $\gamma$  Te sites as possible. In particular, for the equimolecular alloy, it is then clear that one has an almost completely ordered system with Te and Se atoms alternating in a chain. Using the annealing temperature of 175 °C we calculate  $|E_{ST} - \frac{1}{2}(E_{SS} + E_{TT})|$  to be larger than +0.07 eV. The final value of  $\Delta$  was obtained after fitting the data for  $x=0.1, 0.2$  to three pairs of doublets with suitable constraints on line positions and intensities determined by Eqs. (3) and (7). This procedure yielded a value of

$$\Delta = 0.923 \pm 0.044 \text{ mm/sec}.$$

The proposed model also permits one to derive the dependence of the average lattice parameters  $c$  and  $a$  for these disordered alloys. One can write an expression similar to Eq. (2) for the average lattice parameter  $c$  as follows (the data for the parameter  $a$  are somewhat unreliable owing to their probable dependence on the thermal treatment of the alloy<sup>2</sup>):

$$c = (1-x)C_{TT} + x(C_{SS}) + \rho(1-x)(2C_{ST} - C_{SS} - C_{TT}). \quad (9)$$

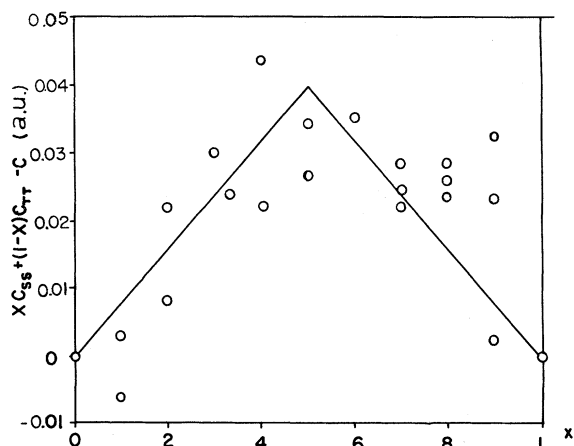


FIG. 3. Observed (Ref. 2) and predicted [Eq. (10)] deviation of  $c$  from the value given by Vegard's law as a function of  $x$ .

Using Eq. (4) for  $Z=0$ , we obtain

$$c = C_{TT} + (C_{ST} - C_{TT})2x \quad \text{if } 0 < x < 0.5$$

$$= 2C_{ST} - C_{SS} + 2x(C_{SS} - C_{ST}) \quad \text{if } 0.5 < x < 1.0, \quad (10)$$

where we have denoted the  $c$  lattice parameters corresponding to pure Se, pure Te, and the  $\text{Te}_{0.5}\text{Se}_{0.5}$  lattice by  $C_{SS}$ ,  $C_{TT}$ , and  $C_{ST}$ . The lattice parameters as a function of  $x$  taken from Ref. 2 are reproduced in Fig. 3 and fit well Eq. (10). The lattice parameter  $C_{ST}$  (the only fitted parameter) is slightly smaller than  $\frac{1}{2}(C_{TT} + C_{SS})$  and we obtain

$$[C_{ST} - \frac{1}{2}(C_{SS} + C_{TT})]/C_{ST} = -0.007.$$

This deviation from Vegard's law is consistent with the slightly negative value of  $E_{ST} - \frac{1}{2}(E_{SS} + E_{TT})$ . Both results support the view that the Se-Te bond in the solid state is stronger than the average of the Se-Se and Te-Te bond. This is a familiar result in covalent-bond theory<sup>6</sup> and is generally ascribed to a certain amount of ionic character in the Se-Te bond. The result of a 24% larger QS at the Te site in going from pure Te to  $\text{Te}_{0.5}\text{Se}_{0.5}$  is in fact quite similar to the reported increase of 34% in the QS at  $\text{I}^{129}$  between

hosts of solid  $\text{I}_2$  and  $\text{IBr}$ .<sup>7</sup> This analogy is particularly significant when one realizes that  $\text{IBr}$  and  $\text{I}_2$  are structurally isomorphous,<sup>6</sup> much like  $\text{Te}_{0.5}\text{Se}_{0.5}$  and pure tellurium. In both cases, the nuclear resonant atom on forming a shorter covalent bond length with a smaller-size near neighbor clearly experiences a larger QS.

One may attribute the increase in the QS for both Te and I to an increase in  $V_{zz}$ , resulting from a larger time average of the unbalanced  $5p$  valence-electron density. For the present experiments on Te, the  $\text{QS} = \frac{1}{2}e^2 Q V_{zz} (1 + \frac{2}{3}\eta)^{1/2}$ . It is unlikely that  $\eta$ , the asymmetry parameter of the EFG, would change significantly at the different inequivalent Te sites. Single-crystal experiments on Te metal<sup>3</sup> ( $\alpha$ -Te sites only) have shown that  $\eta = 3 \cos \theta$ , where  $\theta = 103.2^\circ$  is the Te-Te-Te bond angle<sup>8</sup> in polymeric chains. For the  $\beta$  and  $\gamma$  Te sites one may expect the corresponding Se-Te-Te and Se-Te-Se bond angles in copolymeric chains to be the same within a couple of degrees. In fact, recent x-ray measurements<sup>8</sup> have revealed that the Te-Te-Te bond angle in Te metal and the Se-Se-Se bond angle in hexagonal Se are the same within  $0.2^\circ$ .

Finally, a small amount of ionic contribution to EFG is also present. One estimates<sup>9</sup> this contribution from the known electronegativity differences between Te-Se and I-Br; in both cases it is about 8%. Isomer-shift measurements are insensitive to changes in QS at the different Te sites in  $\text{Te}_{1-x}\text{Se}_x$  alloys. This is a consequence of the 8.9-times-larger natural linewidth and the 6-times-smaller  $\delta \langle r^{-2} \rangle$  value<sup>10</sup> of the  $\text{Te}^{125}$  resonance in comparison to  $\text{I}^{129}$ . The present experiments suggest that it should be possible to grow single crystals of the ordered alloy  $\text{Te}_{0.5}\text{Se}_{0.5}$ . It is likely that further investigations using x-ray, Raman, and infrared spectroscopy on such a system will enhance our understanding of the Te-Se bond.

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<sup>1</sup>R. W. G. Wyckoff, *Crystal Structures*, 2nd ed. (Interscience, New York, 1963).

<sup>2</sup>E. Grison, *J. Chem. Phys.* **19**, 1109 (1951).

<sup>3</sup>P. Boolchand, B. L. Robinson, and S. Jha, *Phys. Rev. B* **2**, 463 (1970).

<sup>4</sup>Bought from Spex Industries, Methuen, N. J.

<sup>5</sup>K. Huang, *Statistical Mechanics* (Wiley, New York, 1965).

<sup>6</sup>A. F. Wells, *Structural Inorganic Chemistry* (Clarendon, Oxford, England, 1961), p. 32.

<sup>7</sup>M. Pasternak and T. Sonnino, *J. Chem. Phys.* **48**, 1997 (1968).

<sup>8</sup>P. Unger and P. Cherin, *The Physics of Selenium and Tellurium*, edited by W. Charles Cooper (Pergamon, New York, 1961), p. 223.

<sup>9</sup>T. P. Das and E. L. Hahn, *Nuclear Quadrupole Resonance Spectroscopy* (Academic, New York, 1958).

<sup>10</sup>G. K. Shenoy and G. M. Kalvius, in *Hyperfine Interactions in Excited States*, edited by G. Goldring and R. Kalish (Gordon and Breach, New York, 1971), Vol. IV.