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Preparation and Characterization of Compounds of the System $Fe(Sb_{1-x}Te_x)_2$ $(0 \leq x \leq 1.0)$

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The complete solid solution of $Fe(Sb_{1-x}Te_x)_2$ with the marcasite structure was synthesized. Electrical and magnetic measurements showed that the substitution of tellurium for antimony in the diamagnetic semiconductor $FeSb_2$ resulted in metallic and paramagnetic behavior in the composition range $0.1 \leq x \leq 0.3$, but in $0.4 \leq x \leq 0.6$ the products belonged to the arsenopyrite structure and were diamagnetic and semiconductive. The samples whose compositions were in the range $0.7 \leq x \leq 1.0$ were semiconductors. Mössbauer effect measurements showed that the isomer shift did not change, but the quadrupole splitting changed significantly from 1.28 mm/sec for $FeSb_2$ to 0.50 mm/sec for $FeTe_2$ in this solid solution.

Introduction

In recent years many investigations have been reported on the preparation and characterization of the compounds with the pyrite, marcasite, and arsenopyrite structures (*1–6*). Recently, Bachdadi and Wold (*7*) synthesized the compounds of $FeAs_{2-x}Se_x$ $(0 \leq x \leq 0.13)$ and reported that the substitution of selenium for arsenic in the diamagnetic semiconductor $FeAs_2$ results in paramagnetic and metallic behavior.

According to the neutron diffraction (*3*), magnetic and electrical (*6*), and Mössbauer effect (*8*) studies, $FeSb_2$ was diamagnetic and a semiconductor with an electronic energy gap of about 0.02 eV. Goodenough (*9*) pointed out that the metal–anion–metal angle α is approximately 76° for $FeSb_2$. This indicated that the d-orbitals directed along the c-axis (denoted as a_{11} by Goodenough (*9*)) were not orthogonal to the γ-bonding anion orbitals. Although $FeSb_2$ is in a low-spin state, in which the lower b-band is completely filled and the higher a_{11} band is empty, $FeSb_2$ was found to be a semimetal, showing paramagnetic behavior at a relatively high temperature for the thermal distribution of the $3d$-electron from b- to a_{11}-orbitals.

Steger and Kostiner (*8*) carried out a detailed investigation of the Mössbauer effect for $FeSb_2$ in the temperature range 6.4–560 K and showed that the temperature dependence of the quadrupole splitting was a result of an electronic process involving the thermal population of an empty conduction band. More recently, Kjekshus and Rakke (*10*) reported the results of room

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temperature ^{57}Fe Mössbauer data for 49 samples such as $Cr_xFe_{1-x}As_2$, $Fe_{1-x}Co_xAs_2$, $Fe_{1-x}Ni_xAs_2$, etc., which were discussed in relation to the crystal structures.

Although many experimental data on the preparation and characterization of the binary and ternary transition metal pnictides with the marcasite structure have been reported, there has been little investigation into the effect on the physical properties caused by the change of the number of $3d$-electrons of iron ions from $3d^4$ to $3d^6$ due to the replacement of anions such as $Fe(Y_{1-x}X_x)_2$, where X is a chalcogen and Y is a pnigogen.

We have undertaken the study of the full anion-substituted system $Fe(Sb_{1-x}Te_x)_2$ (*11*), in which iron atoms change their valence state from 4 to 2 depending on the x value, in order to investigate the phase relation, and physical properties in detail, and have succeeded in synthesizing the full solid solution of this system. The purpose of the present study is to characterize the electrical and magnetic properties of the compounds of $Fe(Sb_{1-x}Te_x)_2$.

Experimental

Eleven starting materials whose compositions were made up at 10 mole% intervals were prepared by mixing stoichiometric quantities of the elements of Fe (99.99%), Sb (99.999%), and Te (99.99%). They were fired in evacuated and sealed silica tubes. Samples of the $Fe(Sb_{1-x}Te_x)_2$ solid solutions were maintained for 12 hr at 1100°C and quenched into ice water. Then, all samples were annealed at 600°C for 2 weeks, and finally quenched to room temperature. The last step of the annealing process was repeated until the products were homogeneous.

Crystallographic parameters were determined by means of X-ray powder diffraction using silicon as internal standard.

Electrical conductivity measurements were carried out on powders pressed into the form of pellets by a conventional four-probe method in the temperature range of 77 to 300 K. Magnetic susceptibility measurements were performed using a magnetic torsion balance in the temperature range from 77 to 300 K in a field of 8 kOe. Mössbauer effect measurements were carried out using a 400-multichannel analyzer at 80 and 300 K. The γ-ray source was always kept at room temperature. Calibration of the velocity scale was made by using Fe metal as standard absorber.

Results and Discussion

The X-ray diffraction patterns of the products in this system were indexed on the basis of an orthorhombic unit cell, except in the cases of $x = 0.4$, $x = 0.5$, and $x = 0.6$. The products with $x = 0.4$, 0.5, and 0.6 belonged to the arsenopyrite structure with monoclinic symmetry. In the $Fe(Sb_{1-x}Te_x)_2$ system, both the *a*- and *b*-axes decreased with increasing x, but only the *c*-axis increased with increasing amounts of tellurium ion. This tendency was well in agreement with that reported by Bachdadi and Wold (*7*). The fact that FeSbTe ($x = 0.5$) had the arsenopyrite structure suggests that the electron configuration of the iron atom was $3d^5$ in a low-spin state.

The electrical resistivities of the representative compounds of the $Fe(Sb_{1-x}Te_x)_2$ system, measured as a function of temperature, are shown in Fig. 1. The thermal band gap calculated from the slope of the log ρ vs $10^3/T$ plot and the room temperature resistivity of $FeSb_2$ were about 0.02 eV and $1.1 \times 10^{-2}\ \Omega \cdot$ cm, respectively. These values agree with those reported by Fan *et al.* (*6*). As seen in Fig. 1, when tellurium was substituted for antimony in $FeSb_2$ by 10 and 20 mole% ($x = 0.1$ and $x = 0.2$), the electrical resistivity was found to vary linearly with increasing temperature from 77 to 300 K. The room

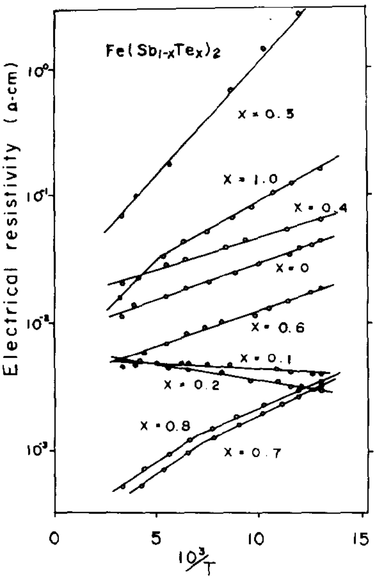

FIG. 1. Temperature dependence of the electrical resitivity.

temperature resistivity was $4.3 \times 10^{-3}\ \Omega \cdot cm$ for $FeSb_{1.6}Te_{0.4}$, i. e., slightly lower than that for $FeSb_2$. These results indicated that, in this composition range, the materials are metallic. However, the three arsenopyrite-type samples with composition $x = 0.4$, 0.5, and 0.6 showed semiconductive behavior. The electrical activation energies were about 0.01 eV for $FeSb_{1.2}Te_{0.8}$, 0.04 eV for FeSbTe, and 0.02 eV for $FeSb_{0.8}Te_{1.2}$. Above $x = 0.7$, all specimens were semiconducting with a higher electrical activation energy of about 0.1–0.4 eV.

The representative results of the bulk magnetic susceptibility measurements are listed in Table I. As seen in this table, the magnetic susceptibility of all samples seemed to be temperature independent, but the room temperature susceptibility and the ratio of $\chi_{77\,K}/\chi_{300\,K}$ increased rapidly with increasing x values and reached a constant at the compositional range $0.4 \leq x \leq 0.6$.

TABLE I

MAGNETIC SUSCEPTIBILITY OF $Fe(Sb_{1-x}Te_x)_2$

Compound	Magnetic susceptibility (emu/mole) 300 K	77 K	$\chi_{77\,K}/\chi_{300\,K}$
$FeSb_2$	5.22×10^{-4}	0.08×10^{-4}	0.017
$FeSb_{1.8}Te_{0.2}$	15.55×10^{-4}	11.66×10^{-4}	0.75
$FeSb_{1.6}Te_{0.4}$	181.9×10^{-4}	200.09×10^{-4}	1.1
$FeSb_{1.2}Te_{0.8}$	52.4×10^{-4}	54.50×10^{-4}	1.04
FeSbTe	24.23×10^{-4}	23.26×10^{-4}	0.96
$FeSb_{0.8}Te_{1.2}$	12.49×10^{-4}	12.12×10^{-4}	0.97
$FeSb_{0.6}Te_{1.4}$	6.66×10^{-4}	6.48×10^{-4}	0.97
$FeSb_{0.4}Te_{1.6}$	3.32×10^{-4}	3.27×10^{-4}	0.98
$FeSb_{0.2}Te_{1.8}$	2.07×10^{-4}	3.18×10^{-4}	1.54
$TeTe_2$	2.43×10^{-4}	3.64×10^{-4}	1.50

Mössbauer absorption spectra of the sample were measured at 80 and 300 K. Each hyperfine spectrum for these samples at 80 and 300 K consists of only one set of two-line spectra due to the quadrupole splitting and no magnetic hyperfine spectra were found down to 80 K. The Mössbauer parameters of isomer shift and the quadrupole splitting at both temperatures are summarized in Fig. 2.

The isomer shift relative to Fe metal and the quadrupole splitting of both $FeSb_2$ and $FeTe_2$ corresponding to the end members in this solid solution series at 80 and 300 K

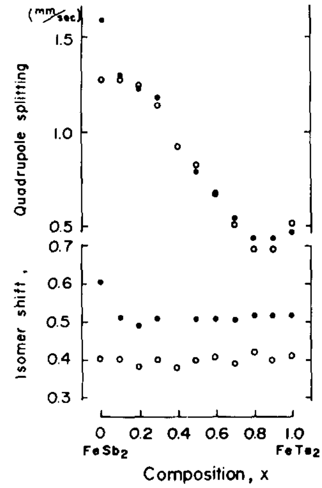

FIG. 2. Dependence of isomer shift and quadrupole splitting with x. Open circles, 300 K; solid circles, 80 K.

were quite in agreement with those reported by Steger and Kostiner (*8*) and Gupta *et al.* (*12*).

The differences in the observed isomer shifts for each sample at 80 and 300 K are probably almost entirely due to second-order Doppler shift, although there is another possibility that the shift occurs due to a change in lattice parameters. Since the correction required to convert these measurements to values at the same volume is not known, it is difficult to draw any definite conclusion about the relative Debye temperatures of these samples.

The quadrupole splitting at 80 and 300 K decreased with increasing x, but did not change linearly. Little change was observed in the compositional range $0 \leq x \leq 0.2$, but in $0.2 \leq x \leq 0.8$ the quadrupole splitting decreased monotonously with increasing x and reached a minimum value at $x = 0.8$. Beyond $x = 0.8$ the quadrupole splitting was slightly increased with increasing x. The tendency of change of the quadrupole splitting seems to be closely related to the change of the c-axis or cell volume.

Conclusion

The electrical and magnetic properties of the $Fe(Sb_{1-x}Te_x)_2$ series are divided into the four classes. $FeSb_2$ has semimetal and diamagnetic behavior. In the composition range $0.1 \leq x \leq 0.4$, the materials are metallic and temperature independent paramagnetic. On the other hand, in $0.4 \leq x \leq 0.6$, the compounds belong to the arsenopyrite structure and behave as semiconductors and diamagnetic materials. Beyond $x = 0.7$, the products are semiconductors with a high electrical activation energy of about 0.1–0.4 eV. According to Goodenough's band models for both the regular and the anomalous marcasite structure (*9*), $FeSb_2$ has almost filled b-bands and an empty a_{11}-band, corresponding to the low-spin configuration d^4 at each iron atom. In $FeTe_2$, the a_{11} and the two b-bands overlap and are filled by electrons due to the low-spin configuration d^6. In addition, the band structure for the arsenopyrite structures would be similar to that for the marcasite structures, but is accompanied by a splitting of the narrow a_{11}-band. The substitution of tellurium for antimony in $Fe(Sb_{1-x}Te_x)_2$ added one electron per tellurium atom in the composition range $0.1 \leq x \leq 0.3$ and added electrons would occupy donor a_{11}-orbitals according to the band scheme of compounds with the regular marcasite structure. The metallic conductivity and the ratio of $\chi_{77\,\mathrm{K}}/\chi_{300\,\mathrm{K}}$ for the compounds within the composition range $0.1 \leq x \leq 0.3$ indicate the addition of one electron per tellurium atom to a conduction band.

The present Mössbauer data of the isomer shift and quadrupole splitting suggest that the bonding is of a highly covalent nature. The isomer shift of $Fe(Sb_{1-x}Te_x)_2$ compounds does not change, in spite of the change in valence state of the iron ion from 4 to 2 depending on the x value. It is expected that the reason why the isomer shifts are constant at about 0.04 mm/sec relative to Fe metal in the full composition range is the high degree of covalent overlap between the metal atom and the ligands, in which the following two mechanisms occur: (a) metal-to-ligand donation into unfilled ligand γ-orbitals in $0.1 \leq x \leq 0.4$ and (b) ligand-to-metal γ-donation from filled ligand γ-orbitals in $0.6 \leq x \leq 1.0$. From the results obtained by the X-ray diffraction analysis, it is expected that the change of quadrupole splitting seems to be closely related to that of the c-axis or the cell volume for the $Fe(Sb_{1-x}Te_x)_2$ solid solution series. This fact indicates that the quadrupole splitting is strongly due to the octahedral symmetry and the distribution of electrons with the $3d$-orbitals rather than to different charge distributions.

References

1. F. HULLIGER AND F. MOOSER, *J. Phys. Chem. Solids* **26**, 429 (1965).
2. T. A. BITHER, R. J. BOUCHARD, W. H. CLOUD, P. C. DONOHUE, AND W. J. SIEMONS, *Inorg. Chem.* **7**, 2208 (1968).
3. H. HOLSETH AND A. KJEKSHUS, *Acta Chem. Scand.* **24**, 3309 (1970).
4. E. BJERKELUND AND A. KJEKSHUS, *Acta Chem. Scand.* **24**, 3317 (1970).
5. A. KJEKSHUS, *Acta Chem. Scand.* **24**, 411 (1971).
6. A. K. L. FAN, G. H. ROSENTHAL, H. L. MCKINZIE, AND A. WOLD, *J. Solid State Chem.* **5**, 136 (1972).
7. A. BACHDADI AND A. WOLD, *J. Phys. Chem. Solids* **35**, 811 (1974).
8. J. STEGER AND E. KOSTINER, *J. Solid State Chem.* **5**, 131 (1972).
9. J. B. GOODENOUGH, *Solid State Commun:* **5**, 144 (1972).
10. A. KJEKSHUS AND T. RAKKE, *Acta Chem. Scand. A* **28**, 1001 (1974).
11. G. YAMAGUCHI, M. SHIMADA, AND M. KOIZUMI, *J. Solid State Chem.* **9**, 63 (1976).
12. S. GUPTA, K. B. LAL, T. M. STRINVASAN, AND G. H. RAO, *Phys. Status Solidi A* **22**, 707 (1974).