

**CRYSTALLOGRAPHIC PROPERTIES OF I_2 -Fe-IV-VI₄ MAGNETIC SEMICONDUCTOR COMPOUNDS**

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ABSTRACT

X-ray powder diffraction measurements were made at room temperature on sixteen polycrystalline samples of I_2 -Fe-IV-VI₄ (I: Cu, Ag; IV: Si, Ge, Sn, Pb; VI: Se, Te) magnetic semiconductor compounds. The diffraction patterns were analyzed to determine values of lattice parameter for each compound. The results showed that $Cu_2FeSiSe_4$, $Cu_2FeGeSe_4$ and $Cu_2FeSnSe_4$ have the tetragonal stannite structure ($I\bar{4}2m$), while the rest of the materials have an orthorhombic superstructure of wurtzite which is known as wurzt-stannite ($Pmn2_1$). It was found that, when the values of the effective parameter $a_e = (V/N)^{1/3}$ are plotted against the molecular weight W of the materials, the tetragonal and orthorhombic compounds lie on different straight lines. In addition, differential thermal analysis (DTA) measurements were made, and the peaks on the DTA cooling curves were used to determine values corresponding to the melting temperature for the compounds. © 2000 Elsevier Science Ltd

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INTRODUCTION

Magnetic semiconducting materials are of interest because of the manner in which the magnetic behavior associated with the concerned magnetic ion can modify and complement the semiconductor properties [1]. The materials that have been most studied are the semi-magnetic semiconductor alloys obtained from the tetrahedrally coordinated II-VI semiconductor compounds by replacing a fraction of the group II cations with manganese, giving alloys which show spin-glass behavior, very large magneto-optical effects, etc. [1]. It was recently suggested [2-4] that another set of magnetic compounds and alloys, which could show larger magneto-optical effect than the II-VI-derived alloys, can be obtained from the tetrahedral bonded I_2 -II-IV-VI₄ compounds by replacing the II cations with Mn, Fe, Co, and/or Ni ions. The crystal structure of various I_2 -Fe-IV-VI₄ compounds has been investigated by several workers [5-10], and it has been indicated that four tetrahedral structure types exist: (1) the stannite tetragonal structure based on zinc-blende; (2) an orthorhombic superstructure derived from wurtzite (known as wurtz-stannite); (3) an unknown structure type based on slightly deformed tetragonal, orthorhombic or monoclinic symmetry; and (4) an orthorhombic structure with probable space group *Imm2*. However, in the case of compounds involving Fe ions, only those with Cu, Si, Ge, Sn, and S or Se have been investigated, and no crystallography study made on Fe materials containing Cu, Ag, and Te. Also, it is to be noted that Fe compounds with Cu, Ag, Se, and Te involving Pb have not been investigated. The general composition diagram for these compounds together with its related binary and ternary compounds can be represented by a regular tetrahedron as shown in Figure 1 with I, Fe, IV, and VI elements at the four apices, giving the system $I_xFe_yIV_zVI_p$ ($x + y + z + p = 1$). In this diagram, the I_2 -Fe-IV-VI₄ compounds are found at $x = 0.25$, $y = z = 0.125$ and $p = 0.5$ with a multiplying factor value of 8.

In the present program of work, we are studying the properties of some I_2 -Fe-IV-VI₄ compounds with I = Cu, Ag; II = Mn, Fe; IV = Si, Ge, Sn, Pb; and VI = Se, Te. The aim of this paper is to show some results of the initial work on the crystallographic properties of these materials.

EXPERIMENTAL

The samples used were prepared by the melt and anneal technique. In each case, the components of 1 g sample were made from the appropriate amounts of the elements and were sealed under vacuum in small quartz ampoules, which had previously been carbonized to prevent interaction of the components with the quartz. The components were melted together at 1150°C for about an hour, annealed to equilibrium at 500°C, then cooled to room temperature by leaving the ampoule in the switched-off furnace.

The X-ray powder diffraction pattern of each compound was recorded at 300 K on Kodak DEF-392 film with a calibrated Guinier de Wolf camera (Enraf-Nonius FR 552), using Cu ($\lambda = 1.5406 \text{ \AA}$) radiation, to check the equilibrium conditions as well as the presence of secondary phases. It was found that an annealing period from 20 to 30 days produces specimens with good equilibrium conditions. After the equilibrium condition of the prepared sample was checked, the peak positions were measured visually with an Enraf-Nonius FR508V52 optical system.

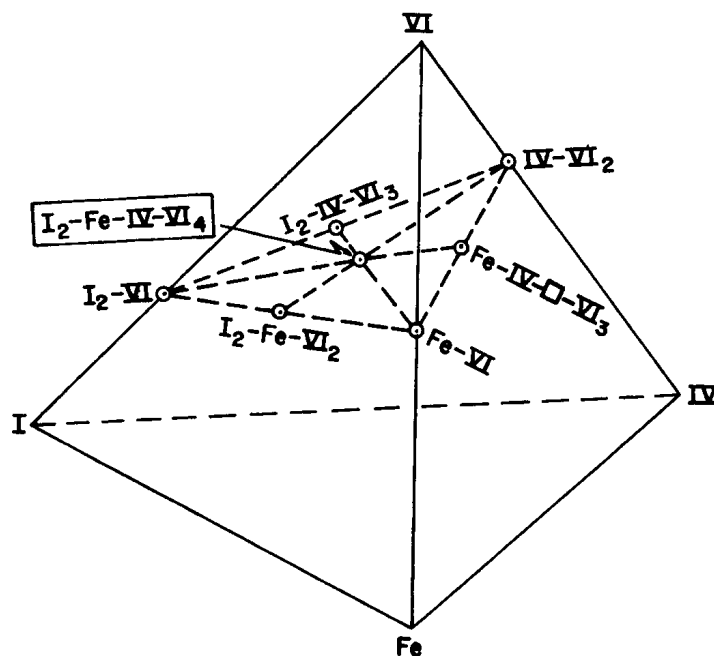


FIG. 1

General composition diagram showing the $I_2\text{-Fe-IV-VI}_4$ compounds investigated in this work.

Using Perkin-Elmer DTA-7 equipment and gold as reference material, differential thermal analysis runs were carried out on each sample prepared. The charge was of a powdered sample of approximately 100 mg weight. Values of the melting point for the compounds were obtained from the peaks on the DTA cooling curves. Each melting temperature was determined from the base line intercept of the tangent to the leading edge of the peak in the difference signal. A typical cooling DTA melting peak is shown in Figure 2 and the corresponding values of the melting temperatures, obtained as indicated above, are given in Table 1.

RESULTS

For all cases, the Guinier X-ray powder diffraction photographs showed sharp diffraction lines, indicating that the samples were in good equilibrium conditions. Values of 2θ , obtained for each compound as indicated above, were indexed with the computer program DICVOL91 [11] using an absolute error of 0.05° (2θ) in the calculations. It was found that the $\text{Cu}_2\text{FeSiSe}_4$, $\text{Cu}_2\text{FeGeSe}_4$, and $\text{Cu}_2\text{FeSnSe}_4$ compounds have the stannite structure ($I\bar{4}2m$) (Fig. 3). The compound $\text{Cu}_2\text{FePbSe}_4$ and the sets $\text{Cu}_2\text{-Fe-IV-Te}_4$, $\text{Ag}_2\text{-Fe-IV-Se}_4$, and $\text{Ag}_2\text{-Fe-IV-Te}_4$ were found to have an orthorhombic superstructure of wurtzite ($a_{\text{or}} = 2a_{\text{w}}$, $b_{\text{or}} = a_{\text{w}}(3)^{1/2}$, and $c_{\text{or}} = c_{\text{w}}$) with space group $Pmn2_1$ for which all $h0l$ reflections with $h + l = 2n + 1$ are systematically absent. This structure is shown in Figure 4. It is to be noted that another model that is compatible with the given rule is monoclinic Pc , with a chosen pseudo-orthorhombic cell described by Pn [6]. However, the authors of previous studies [6]

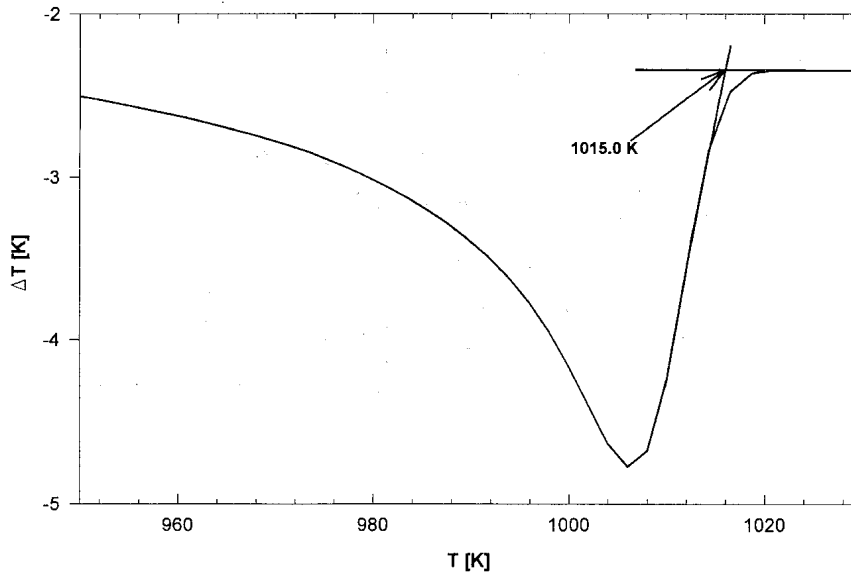


FIG. 2

Typical DTA cooling thermogram for $\text{Ag}_2\text{FeGeSe}_4$.

on single crystal specimens of $\text{Cu}_2\text{CdGeS}_4$, using Weissenberg and precession photographs, concluded that the actual space group is $Pmn2_1$ and the Pn proposal should be excluded.

The resulting X-ray powder diffraction data together with the visually estimated intensity I/I_0 values of the reflection lines and the De Wolf [12] and Smith-Snyder [13] figures of merit are available from the authors. The obtained lattice parameter values of each sample are given in Table 1.

The X-ray powder diffraction photographs taken of the $\text{I}_2\text{-Fe-IV-VI}_4$ compound prepared in this program also showed weak diffraction lines. These lines could be due to the presence of FeTe_2 (PDF 14-419) as a secondary phase. The traces also were observed in compounds such as CuFeTe_2 , AgFeTe_2 , MnFe_2Te_4 , and FeMn_2Te_4 , and these observations will be discussed elsewhere.

DISCUSSION

As has been shown previously [14] for these types of compounds, the quantity $a_e = (V/N)^{1/3}$, where V is the volume of the unit cell and N is the number of molecules per cell, varied smoothly with the molecular weight W depending of the crystal structure. Figure 5 shows the variation of a_e vs. W for the orthorhombic samples in the present case, together with the value for the orthorhombic $\text{Cu}_2\text{FeSiS}_4$ previously reported by Schafer and Nitsche [8]. For comparison, the values reported [8] for tetragonal $\text{Cu}_2\text{-Fe-IV-S}_4$ compounds are included. It is seen from Figure 5 that the orthorhombic and the tetragonal compounds lie on different straight lines. This result is in agreement with the one obtained earlier [15] for $\text{I}_2\text{-Fe-IV-VI}_4$ materials.

Another point of interest here is to use the determined values of a_e with the Phillips-Van Vechten scheme [16-20], to check the plot of the ionic gap C_i vs. the homopolar gap E_h as

TABLE 1
Lattice Symmetry, Melting Temperature, Lattice Parameter, and Ionicity Values f_i
for I_2 -Fe-IV-VI₄ Compounds

| Compound | Lattice | T (K) | a (Å) | b (Å) | c (Å) | V (Å ³) | a_c (Å) | W | f_i |
|--|---------|--------|---------|---------|---------|-----------------------|-----------|---------|-------|
| 1 ^a Cu ₂ FeSiS ₄ | orth | — | 7.404 | 6.411 | 6.140 | 291.448 | 5.262 | 339.269 | 0.631 |
| 2 ^a Cu ₂ FeGeS ₄ | tetr | — | 5.330 | 5.330 | 10.528 | 299.089 | 5.308 | 383.773 | 0.612 |
| 3 ^a Cu ₂ FeSnS ₄ | tetr | — | 5.460 | 5.460 | 10.725 | 319.729 | 5.427 | 429.873 | 0.585 |
| 4 ^a Cu ₂ FeSiSe ₄ | tetr | — | 5.549 | 5.549 | 10.951 | 337.197 | 5.524 | 526.853 | 0.655 |
| 5 Cu ₂ FeGeSe ₄ | tetr | 1012.0 | 5.591 | 5.591 | 11.030 | 344.741 | 5.551 | 571.357 | 0.635 |
| 6 Cu ₂ FeSnSe ₄ | tetr | 951.4 | 5.720 | 5.720 | 11.292 | 369.410 | 5.695 | 617.457 | 0.609 |
| 7 Cu ₂ FePbSe ₄ | orth | 830.0 | 7.676 | 6.691 | 6.355 | 326.350 | 5.465 | 705.957 | 0.575 |
| 8 Cu ₂ FeSiTe ₄ | orth | 730.0 | 7.393 | 6.797 | 6.510 | 326.490 | 5.469 | 721.413 | 0.651 |
| 9 Cu ₂ FeGeTe ₄ | orth | 965.0 | 7.656 | 6.567 | 6.506 | 327.070 | 5.469 | 765.917 | 0.626 |
| 10 Cu ₂ FeSnTe ₄ | orth | 935.6 | 7.687 | 6.741 | 6.579 | 340.920 | 5.545 | 812.017 | 0.591 |
| 11 Cu ₂ FePbTe ₄ | orth | 1080.0 | 7.681 | 6.850 | 6.599 | 347.220 | 5.579 | 900.517 | 0.581 |
| 12 Ag ₂ FeSiSe ₄ | orth | 842.0 | 7.653 | 6.529 | 6.638 | 318.790 | 5.422 | 615.513 | 0.633 |
| 13 Ag ₂ FeGeSe ₄ | orth | 1015.0 | 7.658 | 6.515 | 6.434 | 321.040 | 5.437 | 660.017 | 0.611 |
| 14 Ag ₂ FeSnSe ₄ | orth | 642.0 | 7.398 | 6.993 | 6.401 | 331.120 | 5.491 | 706.117 | 0.579 |
| 15 Ag ₂ FePbSe ₄ | orth | 835.0 | 7.116 | 6.930 | 6.840 | 337.290 | 5.525 | 794.617 | 0.570 |
| 16 Ag ₂ FeSiTe ₄ | orth | 842.0 | 7.721 | 6.657 | 6.588 | 338.650 | 5.532 | 810.073 | 0.653 |
| 17 Ag ₂ FeGeTe ₄ | orth | 990.0 | 8.048 | 6.668 | 6.450 | 346.150 | 5.573 | 854.577 | 0.630 |
| 18 Ag ₂ FeSnTe ₄ | orth | 920.0 | 8.098 | 6.785 | 6.335 | 348.050 | 5.583 | 900.677 | 0.586 |
| 19 Ag ₂ FePbTe ₄ | orth | 900.0 | 8.196 | 6.992 | 6.172 | 353.660 | 5.613 | 989.177 | 0.576 |

^aLattice parameter values from ref. 8.

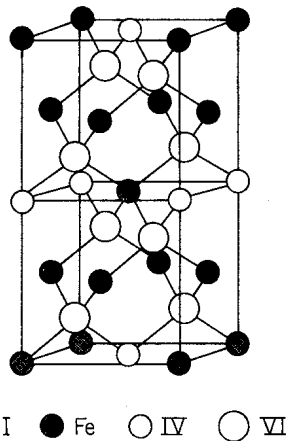


FIG. 3
Tetragonal stannite structure.

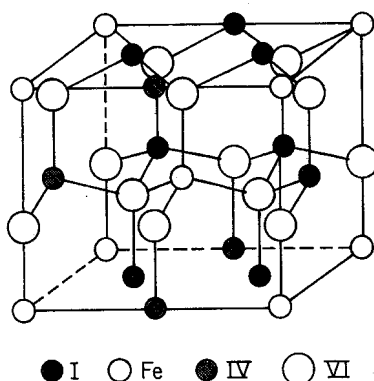


FIG. 4

Orthorhombic wurtz-stannite structure.

well as to estimate values of the ionicity f_i for the materials. For the present $I_2\text{-Fe-IV-VI}_4$ compounds, the values of E_h and C_i can be written as [21]

$$1/E_h^2 = 1/3[1/E_h^2(\text{AD}) + 1/E_h^2(\text{BD}) + 1/E_h^2(\text{CD})] \quad (1)$$

$$1/C_i^2 = 1/3[1/C_i^2(\text{AD}) + 1/C_i^2(\text{BD}) + 1/C_i^2(\text{CD})] \quad (2)$$

$$E_h^2(\text{AD}) = ad^{2.5}(\text{AD}) \quad (3)$$

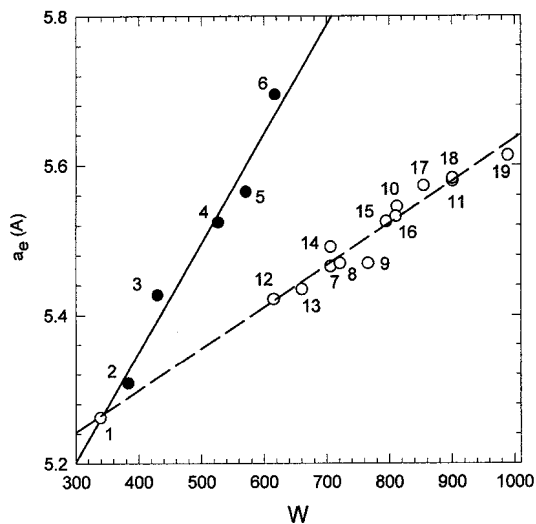


FIG. 5

Variation of effective lattice parameter a_e with molecular weight W for $I_2\text{-Fe-IV-VI}_4$ compounds. Dashed line: orthorhombic (wurtz-stannite) compounds; solid line: tetragonal compounds. See Table 1 for compounds corresponding to numbers 1–19. Data for compounds 1–4 are from ref. 8.

$$E_h^2(\text{BD}) = ad^{-2.5}(\text{BD}) \quad (4)$$

$$E_h^2(\text{CD}) = ad^{-2.5}(\text{CD}) \quad (5)$$

$$C_i(\text{AD}) = be^2(Z_A/r_A + Z_D/r_D)\exp[-k(r_A + r_D)] \quad (6)$$

$$C_i(\text{BD}) = be^2(Z_B/r_B + Z_D/r_D)\exp[-k(r_B + r_D)] \quad (7)$$

$$C_i(\text{CD}) = be^2(Z_C/r_C + Z_D/r_D)\exp[-k(r_C + r_D)] \quad (8)$$

$$f_i = C_i^2/(C_i^2 + E_h^2) \quad (9)$$

where d is the bond length between the concerned ions and is given by sum of the covalent radii of the element; $Z_A, Z_B, Z_C, Z_D, r_A, r_B, r_C, r_D$, and f_i are, respectively, the valence number of the atoms, the covalent radii of the atoms and the ionicity of the compound. k is the Thomas-Fermi screening parameter for a free electron gas with a density of four electrons per atomic volume given by $k = [4.045 \times 10^{-4}/(a_e)^{1/2}] \text{ cm}^{-1/2}$; and a and b are constants given by $a = 40.47 (\text{eV } \text{\AA})^{5/2}$ and $b = 1.5 (\text{eV } \text{\AA}/\text{coul}^2)$ [17]. Values of $b = 1.8$ [18] and 1.99 [22]

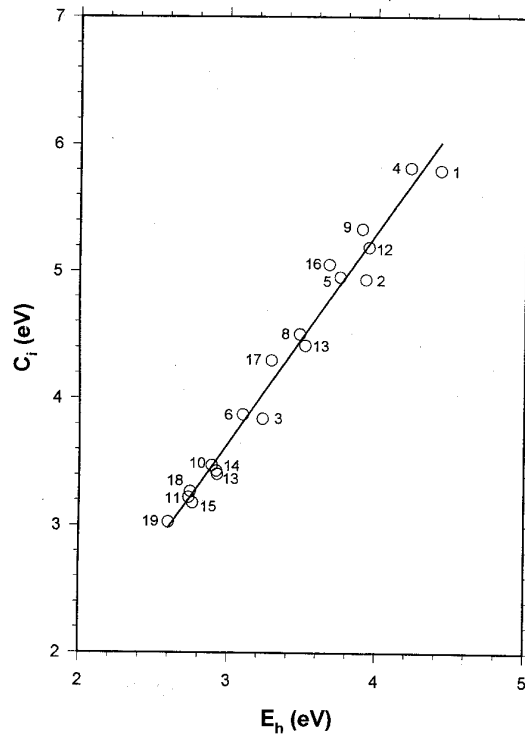


FIG. 6

Ionic C_i vs. homopolar E_h energy gaps for $\text{I}_2\text{-Fe-IV-VI}_4$ compounds. See Table 1 for compounds corresponding to numbers 1-19.

have been used previously; however, as a first approximation, the value $b = 1.5$ has been used here. Hence, using the covalent radii values given by the E.S.R.F. (European Synchrotron Radiation Facility) for the elements [23], values of E_h , C_i , and f_i were calculated from eqs. 1 to 9. The resulting plot of C_i vs. E_h is shown in Figure 6 and the obtained values of f_i are listed in Table 1. It is seen from Figure 6 that, independent of the crystal symmetry and the type of anion involved, all the compounds lie on the same straight line, as was recently reported [24] for the I-III-VI₂ and II-IV-V₂ chalcopyrite compounds.

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