

## Preparation and Properties of Iron Vanadium Telluride, $\text{FeV}_2\text{Te}_4$ \*

ROSS H. PLOVNICK

*Materials Science Center, Cornell University, Ithaca, New York 14850*

Received August 5, 1971

Iron vanadium telluride,  $\text{FeV}_2\text{Te}_4$ , has been prepared and found to have the monoclinic defect NiAs type structure with unit cell parameters  $a_0 = 6.641 \pm 0.005 \text{ \AA}$ ,  $b_0 = 3.727 \pm 0.005 \text{ \AA}$ ,  $c_0 = 12.36 \pm 0.01 \text{ \AA}$ ,  $\beta = 91.75 \pm 0.05^\circ$ . Electrical resistance measurements show  $\text{FeV}_2\text{Te}_4$  to be metallic, and magnetic susceptibility *vs.* temperature data indicate magnetic ordering at approximately  $5^\circ\text{K}$ .

### Introduction

Since 1956, when the monoclinic defect NiAs structure type (space group  $I2/m$ ) was first proposed for  $\text{Fe}_3\text{Se}_4$  (1), more than 50 isomorphous ternary transition metal sulfides, selenides, and tellurides with the general formula  $\text{MM}_2\text{X}_4$  have been reported (2). The iron-containing sulfides and selenides show especially interesting and diverse magnetic properties: antiferromagnetism in  $\text{FeV}_2\text{S}_4$ ,  $\text{FeTi}_2\text{Se}_4$ ,  $\text{FeV}_2\text{Se}_4$ , and  $\text{FeCr}_2\text{Se}_4$  (3, 4); ferrimagnetism in  $\text{MFe}_2\text{Se}_4$  ( $\text{M} = \text{Ti, V, Cr, Fe, Co, Ni}$ ) (5); complex field-dependent behavior in  $\text{FeTi}_2\text{S}_4$  (6). The present investigation is a result of an attempt to prepare and characterize the previously unreported telluride analogs  $\text{FeTi}_2\text{Te}_4$  and  $\text{FeV}_2\text{Te}_4$ , and also  $\text{FeCr}_2\text{Te}_4$  for which only scant data is available (7).

Reaction of elemental mixtures corresponding to the stoichiometries  $\text{FeTi}_2\text{Te}_4$  and  $\text{FeCr}_2\text{Te}_4$  did not yield single-phase products; X-ray diffraction analysis indicated the presence of  $\text{FeTe}$  as a minor constituent of the product mixtures. The stoichiometric composition  $\text{FeV}_2\text{Te}_4$ , however, was successfully prepared in polycrystalline powder form and subsequently as small crystals. Structural, electrical, and magnetic properties of this new compound were then surveyed and are reported here.

\* Supported by the Advanced Research Projects Agency through the Materials Science Center at Cornell University.

### Experimental

#### Preparation and Crystal Growth

Polycrystalline  $\text{FeV}_2\text{Te}_4$  was prepared by reaction of stoichiometric amounts of the powdered, high-purity elements in sealed, evacuated ( $10^{-5}$  Torr) fused quartz tubes. The Fe and Te used were spectrographically certified (Johnson, Matthey and Co., Ltd.), the V was 99.7% (Ventron Corp.). The Fe was reduced in hydrogen at  $600^\circ\text{C}$  just prior to use.

The reactants were heated at  $400^\circ\text{C}$  for one day, then at  $600^\circ\text{C}$  for four days. After the resulting binary telluride mixture was ground with a mechanical agate mortar grinder for one hour under dry nitrogen, it was refired at  $600^\circ\text{C}$  for one day, then at  $800^\circ\text{C}$  for three days. The black product was reground for 30 minutes under dry nitrogen, then annealed at  $700^\circ\text{C}$  for two days followed by a programmed cooling to room temperature at the rate of  $4^\circ\text{C/hr}$ .

Crystals of  $\text{FeV}_2\text{Te}_4$  in the form of silver platelets up to 2 mm across were obtained both by prolonged annealing (several weeks) of powder samples in sealed, evacuated fused quartz tubes at  $800^\circ\text{C}$ , and by chemical transport (8) in such tubes using HCl as the transporting agent at an approximate pressure of 0.1 atm, with the charge zone at  $850^\circ\text{C}$  and the growth zone at  $800^\circ\text{C}$ . Crystals from both methods were verified as being identical with the polycrystalline  $\text{FeV}_2\text{Te}_4$  charge via X-ray diffraction analysis of pulverized crystal samples.

### Chemical analysis

Samples weighing approximately 100 mg were dissolved under reflux with 10–15 ml of fuming sulfuric acid (15–18%), and the solutions then diluted to 200 ml with distilled water. Tellurium was quantitatively precipitated via sulfur dioxide and hydrazine from diluted aliquots adjusted to about 2 N in HCl, filtered, and dried to constant weight. Iron and vanadium were determined by atomic absorption spectroscopy on other aliquots. Standards used in conjunction with the iron and vanadium determinations contained iron, vanadium, and tellurium in the molar ratio Fe:2V:4Te. *Anal.* Calcd. for FeV<sub>2</sub>Te<sub>4</sub>: Fe, 8.36; V, 15.25; Te, 76.39. Found: Fe, 7.85 ± .3; V, 15.06 ± .32; Te, 77.43 ± .14.

### Physical Measurements

Crystallographic parameters were determined on powder samples using a General Electric XRD-5 diffractometer with Ni-filtered radiation from a Cu source. Cell parameters were calculated and refined using an IBM 360 computer program of a modified Cohen least-squares method (9). Attempts to obtain an independent set of accurate cell parameters from zero-layer precession and Weissenberg X-ray photographs of crystal samples were abandoned when several crystals so studied were found to be intimately twinned.

Density was calculated from the specific gravity measured for crystals using standard pycnometric technique with water at 23°C as the liquid.

Electrical resistance of FeV<sub>2</sub>Te<sub>4</sub> crystals was measured between 80°K and room temperature. The magnetic susceptibility of polycrystalline FeV<sub>2</sub>Te<sub>4</sub> was studied as a function of temperature in the range 1.6–150°K and at 296°K using a Faraday balance which is described in detail elsewhere (10).

### Results and Discussion

Every peak in the X-ray diffraction pattern for polycrystalline FeV<sub>2</sub>Te<sub>4</sub> could be indexed on a monoclinic unit cell with  $a_0 = 6.641 \pm 0.005$  Å,  $b_0 = 3.727 \pm 0.005$  Å,  $c_0 = 12.36 \pm 0.01$  Å,  $\beta = 91.75 \pm 0.05^\circ$ . (Calculated cell volume  $V = 305.8$  Å<sup>3</sup>). All observed reflections satisfy the condition  $h + k + l = 2n$  ( $n = \text{integer}$ ) which is required by space group I2/m of the monoclinic defect NiAs structure type.

The calculated density of FeV<sub>2</sub>Te<sub>4</sub> is 7.259 g/cm<sup>3</sup>, using the experimentally obtained unit

cell volume,  $V = 305.8$  Å<sup>3</sup>, and assuming two molecules per unit cell. The observed pycnometric density of  $7.27 \pm 0.01$  g/cm<sup>3</sup> is in close agreement with the calculated density.

Electrical measurements indicate that FeV<sub>2</sub>Te<sub>4</sub> is metallic. The approximate room temperature resistivity is less than  $10^{-3}$  ohm cm.

Results of the magnetic measurements are shown in Fig. 1, a plot of the magnetic susceptibility *vs.* temperature. Below 20°K there is a slight field dependence; in this temperature region, measurement of force on the sample as a function of field strength in fields up to 6 kG indicated variations in force on the order of 10%. The values plotted in Fig. 1 are those measured at 6 kG. Furthermore, the susceptibility values have been corrected for the diamagnetism of the ions involved,  $\chi/(\text{dia}) = -0.47 \times 10^{-6}$  emu/g, using the values (11) of  $-13$ ,  $-10$ , and  $-70 \times 10^{-6}$  emu/g-ion for Fe<sup>2+</sup>, V<sup>3+</sup>, and Te<sup>2-</sup>, respectively (The correction is the same to two significant figures for the case of Fe<sup>3+</sup>, V<sup>2+</sup>, V<sup>3+</sup>, Te<sup>2-</sup>, for which the values are  $-10$ ,  $-15$ ,  $-10$ , and  $-70 \times 10^{-6}$  emu/g-ion, respectively.)

The peak in the susceptibility *vs.* temperature curve for FeV<sub>2</sub>Te<sub>4</sub> at approximately 5°K (Fig. 1) suggests magnetic ordering at this temperature, but the overall shape of the thermomagnetic curve does not resemble that of a "classical" antiferromagnet. Although the susceptibility above 5°K decreases with increasing temperature, it does not follow the Curie-Weiss law,  $\chi = C/T - \theta$ . A plot of  $1/\chi$  *vs.*  $T$  is not linear, and therefore paramagnetic moment and Weiss parameter cannot be determined from such a plot. The susceptibility above 22°K is well described, however, by the more complex equation

$$\chi = [C/(T + \theta) - (a/T - b)] \quad (1)$$

with the values of the various constants selected as  $C = 3.64 \times 10^{-3}$  emu-°K/g,  $\theta = 160^\circ\text{K}$ ,  $a = 1410^\circ\text{K}^2$ ,  $b = 10^\circ\text{K}$ . Values of  $\chi$  calculated from Eq. (1) have also been plotted in Fig. 1, where the good fit of this plot to the experimental data above 22°K is evident. This equation is of the form derived from molecular field calculations based on a ferrimagnetic model (12).

Comparing the ordering temperature 5°K observed for FeV<sub>2</sub>Te<sub>4</sub> with those previously reported (3) for antiferromagnetic FeV<sub>2</sub>S<sub>4</sub> and FeV<sub>2</sub>Se<sub>4</sub>, 130 and 94.5°K, respectively, one notes a trend toward lower ordering temperature with increasing anion size in the isomorphous series

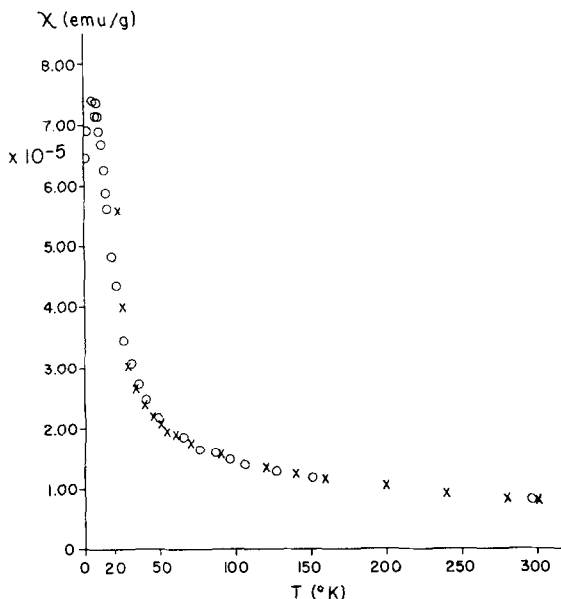


FIG. 1. Magnetic susceptibility vs. temperature for  $\text{FeV}_2\text{Te}_4$ . 0 = experimental data points; X = points calculated from the equation  $\chi = [C/(T + \theta) - (a/T - b)]$  (see text).

$\text{FeV}_2\text{X}_4$  (X = S, Se, Te). This trend probably arises from the fact that in these monoclinic defect NiAs-type compounds, iron cations occupy octahedral sites between layers of essentially hexagonal close-packed anions. The larger the anion, the greater the distance between iron cations, and as a result, the weaker the exchange interactions responsible for magnetic ordering between iron cations. The consequently smaller quantity of thermal energy required to overcome these diminished interactions is reflected in the trend toward lower ordering temperature with increasing anion size.

The unusual magnetic behavior observed for  $\text{FeV}_2\text{Te}_4$  may result from competing antiferro- and ferromagnetic interactions of the type discussed by Andron and Bertaut (13) with regard to  $\text{NiCr}_2\text{S}_4$ , and more recently by Morris *et al.* (14) for  $\text{FeCr}_2\text{Se}_4$  and related compounds. Further work, in particular low temperature neutron diffraction study, is needed to determine the detailed nature of the magnetic order in  $\text{FeV}_2\text{Te}_4$ .

#### Acknowledgments

I thank J. L. Krause for the Faraday measurements and helpful conversations, P. W. Bless for the precession and Weissenberg photographs, V. Johnson (of E. I. duPont Central Research Dept.), and E. S. Kostiner for stimulating discussions, and J. R. Roth and N. G. Nunez of the

Cornell Analytical Chemistry Facility for the chemical analyses.

#### References

1. A. OKAZAKI AND K. HIRAKAWA, *J. Phys. Soc. Japan* **11**, 930 (1956).
2. F. HULLIGER, *Struct. Bonding (Berlin)* **4**, 158 (1968).
3. B. L. MORRIS, R. H. PLOVNIK, AND A. WOLD, *Solid State Commun.* **7**, 291 (1969).
4. M. CHEVRETON AND B. ANDRON, *Compt. Rend.* **264**, 316 (1967).
5. D. BABOT, G. BÉRODIAS, AND B. LAMBERT-ANDRON, *J. Phys.* **32**, C1-985 (1971).
6. B. L. MORRIS, V. JOHNSON, R. H. PLOVNIK, AND A. WOLD, *J. Appl. Phys.* **40**, 1299 (1969).
7. W. ALBERS, G. VAN ALLER, AND C. HAAS, *Colloq. International sur les Dérivés semi-métalliques*, Orsay, 1965; *Propriétés des Dérivés semi-métalliques*, p. 19, Ed. CNRS Paris, 1967.
8. H. Schäfer, "Chemical Transport Reactions," Academic Press, New York, 1964.
9. M. U. COHEN, *Rev. Sci. Instr.* **6**, 68 (1935).
10. J. E. YOUNG, JR., Ph.D. Thesis, Cornell University (1971).
11. P. W. SELWOOD, "Magnetochemistry," 2nd ed., p. 78, Interscience Pub., New York, 1956.
12. See, for instance, S. Chikazumi, "Physics of Magnetism," p. 94, John Wiley and Sons, Inc., New York, 1964.
13. B. ANDRON AND E. F. BERTAUT, *J. Phys.* **27**, 619 (1966).
14. B. L. MORRIS, P. RUSSO, AND A. WOLD, *J. Phys. Chem. Solids* **31**, 635 (1970).