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Crystal Growth and Magnetic Behavior of $FeVO_4$*

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Crystals of the incongruently melting compound $FeVO_4$ have been grown as rods or platelets by slowly cooling melts of composition 34 mol% Fe_2O_3, 66 mol% V_2O_5. Mössbauer and susceptibility measurements indicate that a transition to an ordered antiferromagnetic state occurs at $T_N = 22 \pm 1$°K.

1. Crystal Growth

The preparation of the compound $FeVO_4$ has been reported (*1-3*) previously, and the phase diagram for the system Fe_2O_3–V_2O_5 shows that $FeVO_4$ melts incongruently (*1*).

Attempts were made to prepare single crystals by slowly cooling compositions between the peritectic and eutectic points, 840°C and 635°C, respectively. Laboratory Reagent grade V_2O_5 and Fe_2O_3 were used. The materials were weighed, mixed, and pressed into 100-cc platinum crucibles with closely fitting lids. The muffle furnace used provided a small temperature gradient so that the crucible was approximately 2° cooler at its base than at the melt surface. It was found necessary to use a starting temperature considerably higher than that indicated by the phase diagram. Best results were obtained by slowly cooling a mixture of composition 34 mol% Fe_2O_3, 66 mol% V_2O_5, from 1130°C to 700°C at 10°C/hr. The crucibles were then inverted without cooling to room temperature, returned to the furnace, and heated to 740°C to allow the liquid to run off the crystals, most of which were lightly attached to the crucible base and sides. The crystals were finally cleaned in hot, dilute nitric acid.

Crystals having two habit modifications were produced; black rods 3-4-mm long by 1-1.5 mm thick, and thin plates, red by transmitted light, which floated on the melt surface [Figs. 1a, b)]. Reentrant facets on the rods showed these to be frequently twinned.

A powder sample of composition 50 mol% Fe_2O_3, 50 mol% V_2O_5, sintered for 12 hr at 740°C, gave an X-ray powder pattern identical to that given by the crystals, and showed no indication of the presence of the two initial components. The X-ray powder pattern data agreed closely with published data (*1*) for $FeVO_4$. According to a single-crystal investigation at present being carried out, $FeVO_4$ has a triclinic unit cell. Preliminary values[1] of unit cell parameters are given in Table I. Further work on the crystal structure will be reported later.

2. Magnetic Behavior

Due to the low crystal symmetry and the present lack of data regarding the crystal structure, Mössbauer and magnetic measurements were undertaken on crushed crystal material, with a view to establishing the main features of the magnetic behavior of

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[1] Private communication, F. L. Carter, Naval Research Laboratory, Washington, D.C.

$FeVO_4$. Control runs on sintered powders gave substantially the same results.

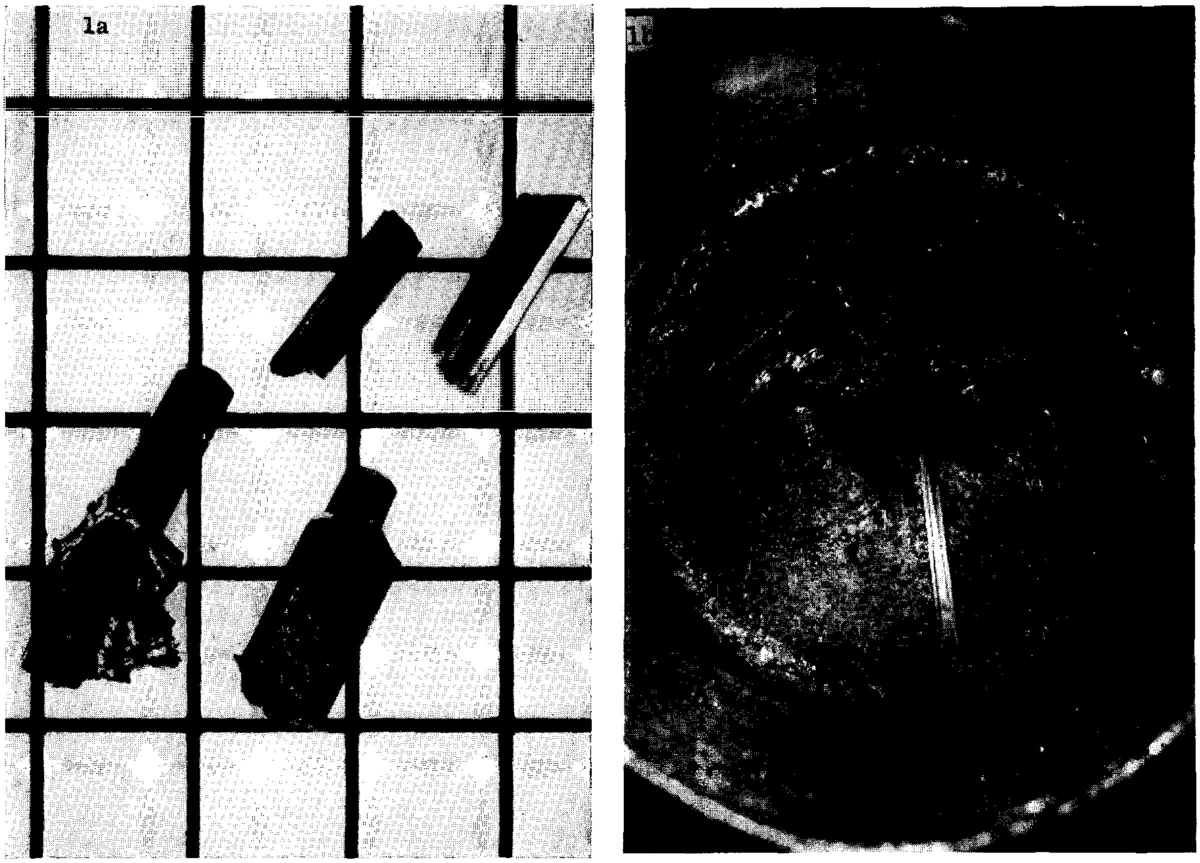

FIG. 1. (a) $FeVO_4$ rods (1 div. = 2.54 mm); (b) Platelets of $FeVO_4$ growing on the melt surface in a 6-cm diam. crucible.

TABLE I

UNIT CELL PARAMETERS, MÖSSBAUER, AND MAGNETIC DATA FOR $FeVO_4$[a]

Property	Symbol	Value
Unit-cell dimensions and angles	a_0	8.02 Å
	b_0	9.31 Å
	c_0	6.69 Å
	α	106.6°
	β	101.5°
	γ	96.7°
Density (pycnometric)	ρ	3.52 gm/cc
Susceptibility at room temp.	χ_{298}	$0.61 \pm 0.04 \times 10^{-4}$ emu/gm
Susceptibility at 4.2°K	$\chi_{4.2}$	$1.63 \pm 0.08 \times 10^{-4}$ emu/gm
Néel temperature	T_N	22 ± 1°K
Paramagnetic Curie temperature	θ	−133 ± 10°K
g-Factor	g	1.99 ± 0.03
Hyperfine field on the iron nucleus at 0°K	$H_i(0)$	470 ± 10 kG

[a] The Mössbauer results indicate that the iron is trivalent, and we have taken the spin $s = 5/2$ in the evaluation of g from the Curie–Weiss law.

The Mössbauer studies were undertaken upon naturally abundant Fe^{57}, using standard techniques (*4*). Spectra of powdered crystalline material were obtained as a function of temperature, using a commercially available, constant-velocity Mössbauer spectrometer.[2] A few typical spectra are given in Fig. 2. The absorption lines obtained are quite broad and complex. At least[3] two different Fe sites are evident, having a relative occupancy of about 1:3. A more detailed analysis of the Mössbauer spectra must await precise crystallographic data.

In Fig. 3, we plot the temperature dependence of the average hyperfine field $H_i(T)$ at the Fe^{57} nucleus. We find $H_i(0) = 470 \pm 10$ kG, which is somewhat low for Fe^{3+} in a $3d^5$–$^6s_{5/2}$ configuration. (Typical values (*4*) of $H_i(0)$ in oxides of trivalent iron are in

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[2] Manufactured by Elron, Inc., Haifa, Israel.

[3] A recent high-resolution Mössbauer spectrum taken at room temperature is consistent with three equally populated, nonequivalent Fe sites (private communication, E. Kostiner, Cornell University, Ithaca, N.Y.).

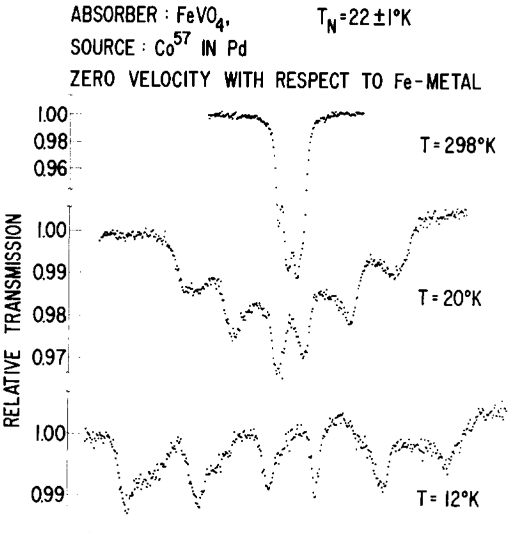

FIG. 2. Typical Mössbauer spectra of crushed crystal absorbers of $FeVO_4$. Zero velocity is given with respect to Fe–metal. The absorber thickness (≈20 mg/cm) was not a constant for the spectra shown.

the region of 520 kG.) On the other hand, the mean isomer shift of the room temperature spectrum (center of gravity of the spectrum) is $+0.35 \pm 0.05$ mm/sec with respect to Fe–metal. This isomer shift typifies (*5*) Fe^{3+}.

In Fig. 3 we also plot the susceptibility $\chi = M/H$ of $FeVO_4$, derived from the magnetic moment M measured in an applied external magnetic field $H = 15$ kG. The measurements were performed on powdered crystal material. The peak at about 22°K is indicative of antiferromagnetic ordering. The magnetic moment was proportional to the applied field at liquid helium temperature, for fields up to $H = 20$ kG, and no spontaneous moment was observed. Values of the susceptibility at 4.2°K and room temperature are given in Table I. Our room temperature value of the susceptibility is in agreement with the measurement of Burdese (*1*).

For $T \gtrsim 100$°K, the mass susceptibility χ follows the standard Curie–Weiss relation, $\chi = C/(T - \theta)$. The value of the paramagnetic Curie temperature θ is given in Table I, along with the g factor, computed from the Curie–Weiss constant C, assuming the spin s to be 5/2. We have ignored the fact that there is possibly more than one crystallographic site for the Fe^{3+} ions. The g factor obtained in this manner is in agreement with the theoretical value for Fe^{3+}.

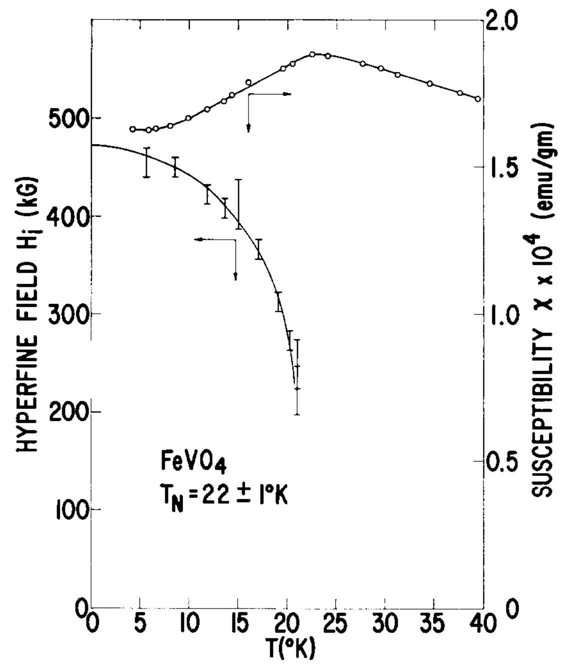

FIG. 3. Temperature dependence of the Fe^{57} hyperfine field and the susceptibility of crushed crystal samples of $FeVO_4$. The Néel temperature is estimated to be 22 ± 1°K. The magnetic moment was proportional to the applied field at 4.2°K, and no spontaneous moment was detected.

Further magnetic studies on single-crystal specimens will be of interest when the crystal structure is established.

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