

Electrical and magnetic studies of iron(III) vanadate

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Abstract. Iron(III) vanadate (FeVO_4) is an n-type semiconductor between 300 and 800 K. Electrical conduction in this phase occurs due to small deviation from oxygen stoichiometric composition. The mechanism of electrical transport is of a thermally activated hopping of charge carriers (electrons) on equivalent iron lattice sites. The FeVO_4 obeys Curie–Weiss law between 80 and 300 K. The measured magnetic moment (μ_{eff}) of Fe^{3+} ion in FeVO_4 is 5.270 BM at 298 K, which is lower than the μ_{spin} only value. The predominant exchange interactions are the weak 90° M–O–M superexchange and M–O–O–M super-superexchange. The negative Weiss constant $\theta = -30$ K of the phase indicated the possibility of an antiferromagnetic ordering of the iron(III) vanadate lattice. The IR absorption spectrum of FeVO_4 gave bands at 990, 900, 825 and 725 cm^{-1} due to the presence of distorted VO_4 polyhedra of the lattice.

Keywords. Conduction; stoichiometric composition; superexchange; antiferromagnetic ordering.

1. Introduction

Phase studies of the binary oxides Fe_2O_3 – V_2O_5 (Milligan *et al* 1949; Burdese 1957; Schwartz and Young 1962) have established the formation of only iron(III) vanadate of composition FeVO_4 . Its occurrence as an incongruently melting compound in the Fe_2O_3 – V_2O_5 system has been reported (Burdese 1957) along with the fact that it transforms under high pressures to an orthorhombic disordered wolframite structure type (Schwartz and Young 1962; Schwartz *et al* 1964). Levinson and Wanklyn (1970) reported crystal growth and magnetic behaviour of FeVO_4 indicating antiferromagnetic ordering with Neel temperature of 22 ± 1 K. Investigation of the crystal structure and Mössbauer effect was done by Robertson and Kostiner (1972). The crystal structure and symmetry of FeVO_4 is triclinic, $\text{P}\bar{1}$. Their Mössbauer spectroscopy result indicated iron in trivalent oxidation state (Fe^{3+}). In the crystal of FeVO_4 , they noticed that three independent iron atoms (two in distorted octahedral and one in a distorted trigonal bipyramidal environment) are joined to create a doubly bent chain of six edge shared polyhedra. No other information is available in the literature. As a part of investigation on MO – V_2O_5 (where M = 3d cation), we have undertaken a systematic study of the electrical, thermal and magnetic properties of iron(III) vanadate. The results are described in the present paper.

2. Experimental

FeVO_4 phase was obtained by heating an intimate mixture of Fe_2O_3 and V_2O_5 (both pure AR grade) in 1:1 molar ratio at 800°C for 4–5 days by conventional solid state

reaction technique. The DC electrical conductivity (σ) was measured by two-probe method and Seebeck coefficient (α) by the integral method between 300 and 800 K. The samples were in the form of sintered (high density) pellets, 18 mm in diameter and 2 mm thick. The magnetic susceptibility (χ) was measured in the temperature range 80–300 K by the Gouy technique using $\text{HgCo}(\text{CNS})_4$ as calibrant. The change in the weight of the sample was noted at magnetic field $H = 0, 2140, 4400$ and 6150 oersted on a single-pan sensitive balance (15×10^{-5} g, Praha, Czech make). For low-temperature measurements, a sample heater sensor (SHS) assembly coupled with automatic temperature controller ($\pm 0.2^\circ\text{C}$) was used. The sample was maintained at each temperature for about 15 min and the change in weight was recorded for $H = 0, 2140, 4400$ and 6140 oersted at temperatures between 80 and 300 K.

The electron spin resonance (ESR) spectrum of the sample was recorded on a Varian V4502 x-band spectrometer operating at 8.62–9.5 GHz with DPPH marker.

The IR spectrum of FeVO_4 phase was taken in nujol mull in the range 1200–600 cm^{-1} using a Perkin-Elmer spectrophotometer (237B). Differential thermal analysis (DTA) of FeVO_4 was done in a fabricated DTA unit using a sensitive strip chart recorder in static air.

3. Results and discussion

The X-ray diffraction (XRD) pattern of FeVO_4 phase agrees with one reported earlier (ASTM card No 15-294, Burdese 1957). DTA of the sample did not show any indication of phase transition in FeVO_4 upon increasing the temperature. However, it melts incongruently at $870 \pm 2^\circ\text{C}$.

Electrical conductivity (σ), Seebeck coefficient (α) and magnetic susceptibility (χ) data are shown in figures 1a, 1b and 2. The relationship between σ and T may be expressed as

$$\sigma = \frac{\sigma_0}{T} \exp(-\Delta G^*/KT), \quad (1)$$

where σ_0 is a constant and ΔG^* is the free energy of activation for electrical conduction process.

$$\log_{10} \sigma T = \log_{10} \sigma_0 - \Delta G^*/2.303K. \quad (2)$$

From figure 1a it can be seen that a plot of $\log_{10} \sigma T$ versus $1/T$ should be linear with slope of $\Delta G^*/2.303K$, provided (1) is obeyed. Figure 1a confirmed the validity of the expression in the case of FeVO_4 . It is observed that $\log_{10} \sigma T$ versus $1/T$ is linear for the sample between 300 K and 550 K with free energy of activation (ΔG^*) of 0.70 eV. However, it could be seen that there is a linear plot with deviation in the slope above 550 K.

Seebeck coefficient (α) is constant and temperature-independent for localized electrons (charge carriers) if the density of charge carriers are independent of temperature in the lattice of the sample. The Seebeck coefficient, α ($\mu\text{V}/\text{degree}$), of the sample showed a linear plot (figure 1b) typical of localized electrons; but the α value increased slightly with temperature and indicated a dependence of density of

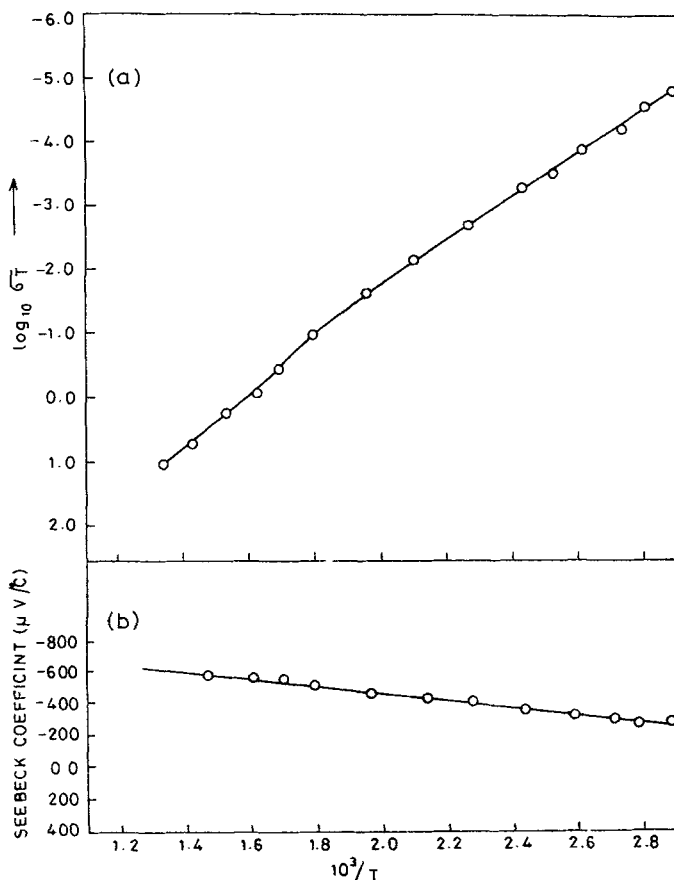


Figure 1. (a) Plot of $\log_{10} \sigma T$ versus $10^3/T$ and (b) Seebeck coefficient versus $10^3/T$.

charge carriers (electrons) on temperature. It could be shown in the lattice of Fe^{3+} (and or V^{5+}) in FeVO_4 that the Seebeck coefficient depends on the second term of (3) and (4):

$$\alpha = \frac{A}{eT} - K/e \ln \frac{(\text{Fe}^{3+})}{(\text{Fe}^{2+})}, \tag{3}$$

$$\alpha = \frac{A}{eT} - K/e \ln \frac{(\text{V}^{5+})}{(\text{V}^{4+})}, \tag{4}$$

where the terms have the usual significance. The term A represents the kinetic energy transported by the migrating electrons. The A/eT term is negligibly small ($> 10 \mu\text{V}/\text{degree}$) for ionic oxides. The second term predominates and determines the sign of α . In (3), (Fe^{3+}) is the density of states available to mobile electrons in the lattice and

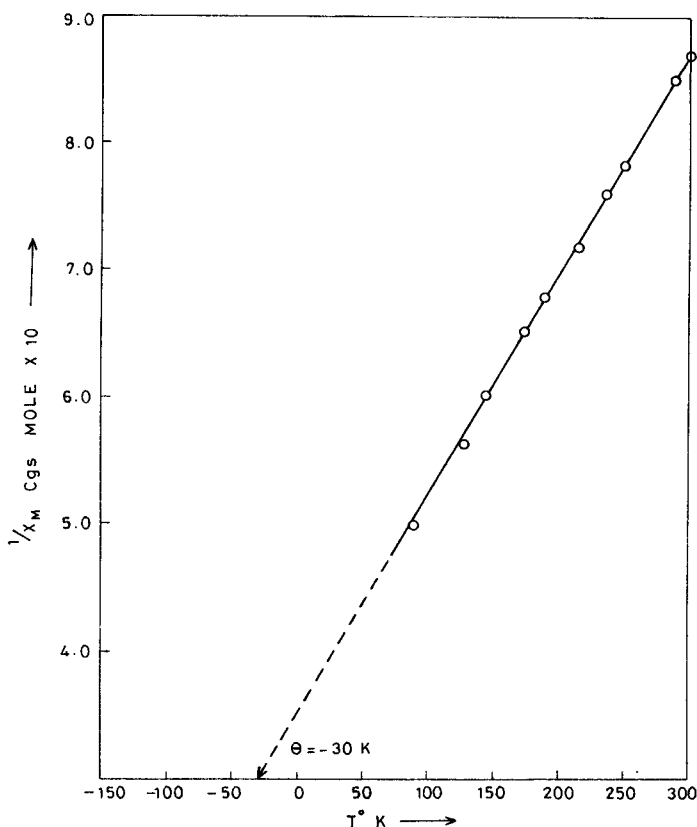
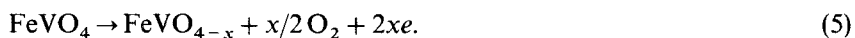


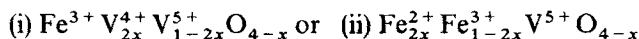
Figure 2. Plot of $1/x_M$ versus T° for iron(III) vanadate.

(Fe^{2+}) is the density of mobile electrons (cations in lower valency state) created due to very small deviation from oxygen stoichiometry.

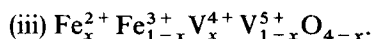
The above results indicated that FeVO_4 is an n-type semiconductor where the electrical conduction is due to the thermally activated mobility of electrons. This is quite expected because the phase is predominantly ionic so that the charge carriers (electrons) are localized. Therefore the only mode of charge transport is via thermally activated jumps on equivalent cationic sites. The sign of α is negative which indicated that it is an n-type semiconductor between 300 and 800 K. One can expect FeVO_4 to be a good insulator in pure and stoichiometric compositions. Semiconduction observed in FeVO_4 phase is due to deviation from stoichiometric composition of the phase. The Seebeck coefficient is negative which could be due to oxygen vacant model structure of the lattice. Thus one can attribute n-type semiconduction of the sample to the following reason: Under normal conditions of temperature and pressures, oxygen vacancies (defect structure) occur in FeVO_4 lattice, leaving behind two electrons per half molecule of oxygen leaving the lattice:



In other words, iron(III) vanadate can be represented as



and/or



The following results confirm the above. (i) Mössbauer spectroscopy (Robertson and Kostiner 1972) identified the iron in FeVO_4 lattice as Fe^{3+} (trivalent). (ii) ESR spectrum of the sample consisted of a small signal at $g = 1.96$, which is typical of a localized electron (V^{4+}) in the lattice. (iii) FeVO_4 phase exhibited n-type semiconduction and the Seebeck coefficient is negative between 300 and 800 K. (iv) The observed magnetic moment (μ_{eff}) of Fe^{3+} in FeVO_4 lattice is 5.270 BM from the magnetic susceptibility measurements, which is slightly lower than the μ_{spin} only value for Fe^{3+} ion.

In the crystal structure of FeVO_4 , Robertson and Kostiner (1972) found three independent iron atoms (two in distorted octahedral and one in a distorted trigonal bipyramidal environment) in polyhedra which are joined to create a doubly bent chain of six edge shared polyhedra as shown in figure 3. The bond lengths ($\text{Fe}^{3+}-\text{O}^{2-}$) range from 1.8690 to 2.114 Å. The chains are linked by VO_4 tetrahedra. The VO_4 tetrahedra share corners with up to four polyhedra within a single chain, but none of them share an edge with an individual polyhedron in a chain. The three independent vanadium atoms are each in a slightly distorted tetrahedral environment of oxygen atoms. The bond lengths ($\text{V}^{5+}-\text{O}^{2-}$) range from 1.666 to 1.806 Å, depending on the environment of oxygen atoms. The $\text{Fe}^{3+}-\text{Fe}^{3+}$ interatomic distance (figure 3) within the chain ($\text{Fe}(1)-\text{Fe}(2) = 3.073$ Å, $\text{Fe}(2)-\text{Fe}(3) = 3.048$ Å, and $\text{Fe}(3)-\text{Fe}(3) = 3.119$ Å) showed

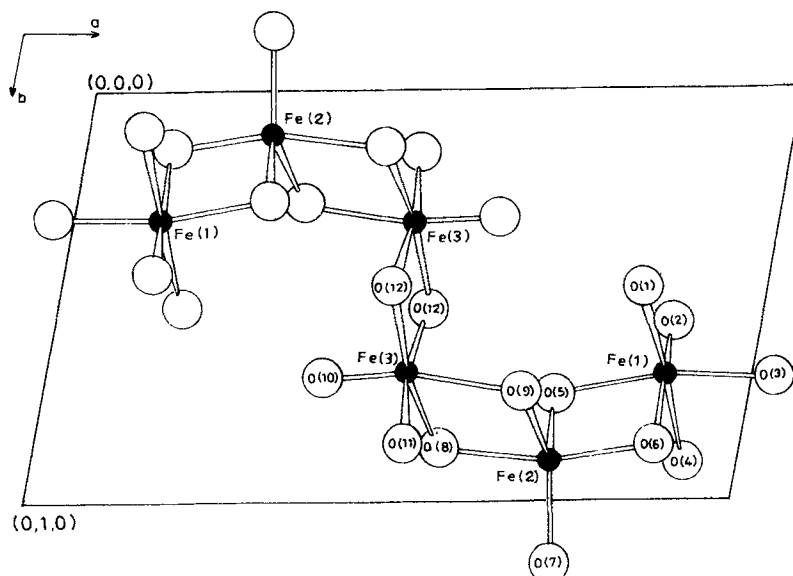


Figure 3. The doubly bent chain of six iron atoms in FeVO_4 projected onto the a - b plane. The large circles are oxygen atoms and the small ones are iron atoms.

the largest separation between the two octahedrally coordinated iron atoms at the centre of the chain.

n-Type semiconduction observed in FeVO_4 can be explained as follows: Both Fe^{3+} (d^5) and V^{5+} (d^0) are in their highest oxidation state in FeVO_4 and thus the formation V^{6+} and O^- ions is not energetically favourable in the iron vanadate lattice. FeVO_4 phase has oxygen-deficient lattice structure due to deviation from oxygen stoichiometry (5). The $2x$ electrons released per $\frac{1}{2}\text{O}_2$ are trapped on either (a) Fe^{3+} or (b) V^{5+} and or (c) both the lattice sites as localized electrons for conduction which results in the formation of Fe^{2+} (d^6) or V^{4+} (d^1) sites in the lattice of FeVO_4 . Therefore the only mode of charge transport in FeVO_4 is via thermally activated hopping of electrons on equivalent ($\text{Fe}^{2+}-\text{O}-\text{Fe}^{3+}$) lattice sites (type ii) of the doubly bent chain of edge shared polyhedra (figure 3) or the corner shared VO_4 polyhedra within a single chain. It can be remarked from the perspective view of the crystal structure of FeVO_4 projected on to $b-c$ plane (Robertson and Kostiner 1972) that the most favoured path for activated electrons to jump is the continuous chains of Fe^{3+} sites of the lattice rather than the V^{5+} sites. However, thermally activated hopping of electron on equivalent V^{5+} sites also cannot be overlooked for electrical conduction in the lattice. It is clear from DTA and other available data that there is neither structural transformation nor electronic transition in FeVO_4 lattice upon increasing temperature, though figure 1a indicated a deviation in slope at about 550 K. This observed behaviour could possibly be due to the additional path available for activated hopping of electrons at the vanadium sites (type iii) of a corner shared VO_4 tetrahedron within a single chain in the lattice. The presence of such localized (V^{4+}) centres in the lattice of the sample is confirmed by the observed ESR signal at $g = 1.96$.

Figure 1b shows a linear plot, but the Seebeck coefficient increased slightly with temperature, as against an expected constant value of α for localized electrons with constant density of charge carriers in the lattice. This behaviour of the sample could be accounted for by a decrease in the density of Fe^{2+} sites in the lattice (3) upon increasing the temperature. It is well established that generally the Fe^{2+} state in oxides is not stable at higher temperatures, and it gradually changes to the Fe^{3+} state. Therefore one can remark that as the density of Fe^{2+} state decreases due to the above reason the Seebeck coefficient value would be expected to increase proportionately (3) with increase in temperature as observed in the present work. However, increase in the electrical conduction of the sample is due to thermally activated mobility of the electrons, which increased exponentially with temperature. Moreover, one would expect a very small increase in deviation from oxygen stoichiometry of the lattice upon increasing the temperature, which would increase the density of charge carriers (electrons) in the lattice. These electrons may not be located at Fe^{3+} sites in the high temperature range of the investigation as localized electrons but would be trapped at V^{5+} sites of the lattice as typical localized electrons (V^{4+} centres) for conduction and would hop on to equivalent sites with little higher free energy of activation above 550 K, as is evident from figure 1a.

The magnetic susceptibility of FeVO_4 measured between 80 and 300 K is shown in figure 2. It may be observed that (a) FeVO_4 is paramagnetic down to 80 K and obeys Curie-Weiss law, (b) the Weiss constant (θ) is negative and (c) the μ_{eff} observed is slightly lower than μ_{spin} only value for Fe^{3+} ions.

The magnetic susceptibility of FeVO_4 sample at 300 K is 6.73×10^{-5} cgs/mole. Figure 2 shows a linear plot of $1/\chi_M$ versus temperature. It is evident that the Weiss

constant of FeVO_4 is -30 K , which indicates, possibly, an antiferromagnetic ordering of the FeVO_4 lattice. The observed magnetic moment (μ_{eff}) value of Fe^{3+} ion is 5.270 BM which is lower than 5.92 BM for μ_{spin} only value of Fe^{3+} ($t_{2g}^3 e_g^2$). It is clear from the crystal structure of FeVO_4 (Robertson and Kostiner 1972) that the predominant exchange interactions are $\text{M}^{3+}-\text{O}-\text{M}^{3+}$ (superexchange) and $\text{M}^{3+}-\text{O}-\text{O}-\text{M}^{3+}$ (super-superexchange). Direct cation-cation magnetic exchange interactions and cation-anion-cation superexchange interactions between adjacent iron atoms of FeVO_4 (figure 3) with d^5 configuration give antiferromagnetic coupling (Goodenough 1963). The cation-anion-cation superexchange energy term allows antiferromagnetic coupling over the full range of $\text{Fe}^{3+}-\text{O}-\text{Fe}^{3+}$ angles from 90° to 180° with maximum energy expected at 180° . Because of sharing of FeO_6 polyhedral edges in FeVO_4 structure, the $\text{Fe}^{3+}-\text{O}-\text{Fe}^{3+}$ angles are limited to 100° and therefore indicate small superexchange interaction, which resulted in a value (5.270 BM) lower than μ_{spin} only value (5.92 BM) for Fe^{3+} ion. Interestingly, it can be observed that the presence of certain number of Fe^{2+} (d^6) ($t_{2g}^4 e_g^2$) ions in the lattice of Fe^{3+} ($t_{2g}^3 e_g^2$) ions of FeVO_4

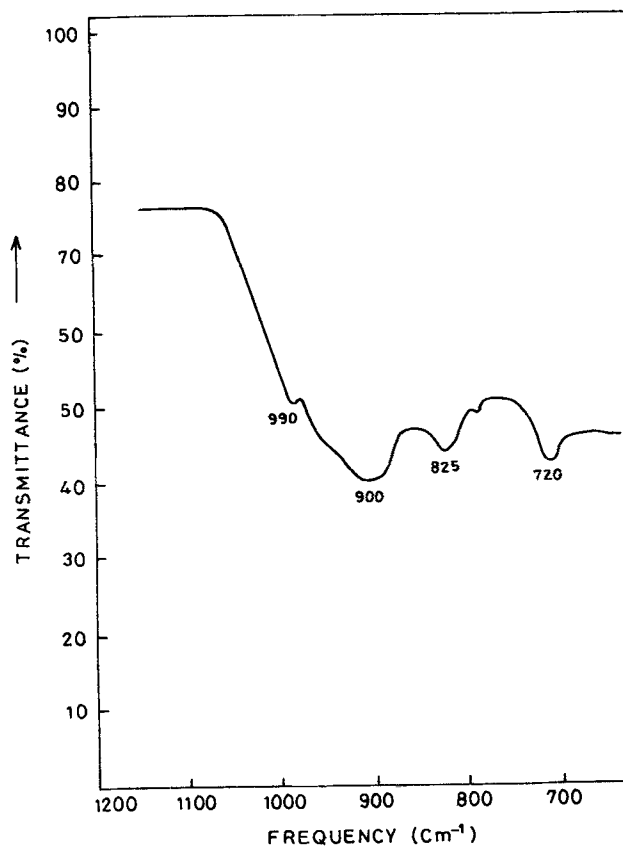


Figure 4. IR spectrum of iron(III) vanadate.

could contribute less to the effective magnetic moment (μ_{eff}) of the cation, depending on the concentration of Fe^{2+} ions in the lattice.

The IR spectrum of FeVO_4 (figure 4) indicates bands at 990, 900, 825 and 720 cm^{-1} . Siebert (1954) and Ayamonino *et al* (1978) have obtained the IR spectra of VO_4^{3-} group of many divalent cations, while Fotiev *et al* (1971) obtained IR spectra of VO_4^{3-} group with cations in the trivalent oxidation state. It can be seen from figure 4 that the IR spectrum of VO_4^{3-} group in FeVO_4 lattice is different from the spectra obtained for VO_4^{3-} group of T_d symmetry (Siebert 1954) in orthovanadates. In the crystal structure of FeVO_4 , Robertson and Kostiner (1972) found that the iron is in the trivalent oxidation state and the three V^{5+} ions are each distorted in distorted tetrahedral environment of oxygen atoms, whose V–O bond lengths ranged from 1.660 to 1.806 Å; the average V–O bond length in many orthovanadates is 1.720 Å. Thus one can expect that these three distorted VO_4^{3-} polyhedra of FeVO_4 would give bands (990, 900, 825, 725 cm^{-1}) different from the ones observed for orthovanadate lattice having one kind of VO_4^{3-} polyhedra (Siebert 1954; Ayamonino *et al* 1978).

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