

Magnetic Properties of $\text{Fe}_x\text{V}_{1-x}\text{O}_2$ ($0 < x < 0.05$)

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The magnetic properties of the $\text{Fe}_x\text{V}_{1-x}\text{O}_2$ system ($0 < x < 0.05$) were investigated by magnetic susceptibility, magnetization, and also by Mössbauer effect measurements. As a result, it is confirmed that the magnetic properties are very similar to those of the $\text{Cr}_x\text{V}_{1-x}\text{O}_2$ system previously studied. At lower temperatures, the exchange-coupled cluster model can well explain the results obtained in this experiment.

Introduction

Several vanadium oxides show temperature-induced metal-nonmetal transitions at T_i . The transition of pure VO_2 takes place at 340°K and the low-temperature semiconducting phase is temperature-independent paramagnetic. To clarify the mechanism of the transition, much work has been done: electrical resistivity, thermoelectric power, Hall coefficient, NMR, ESR, and optical measurement (1).

On the other hand, impurity effects on the phase transitions of VO_2 have also been investigated extensively. Recent work on the impurity effects has been devoted mainly to the system $\text{Cr}_x\text{V}_{1-x}\text{O}_2$ (2). In this system, there appear three phases $M_1 \rightarrow T \rightarrow M_2$ (all of them are insulating) with increasing x at room temperature. The crystal structure of each phase is shown schematically in Fig. 1, which was determined by X-ray crystallography and also complementarily by NMR (2). The high-temperature metallic phase R has a tetragonal

($P4_2/mnm$) rutile structure, in which metal ions are equispaced along c -axis. In the M_1 phase ($P2_1/c$), all the metal ions pair and twist from the rutile positions. In the M_2 phase, metal ions occupy two sites; half of the vanadium atoms pair but do not twist and the other half form unpaired zig-zag chains. Between the M_1 and M_2 phases, there appears the T -phase ($C\bar{1}$), in which two sites can be resolved by NMR measurement. The two sites are progressively differentiated on heating. This can be interpreted as arising from two sets of inequivalent paired chains, one of which is depairing with increasing temperature, while the other set keeps pairing through the phase transitions; $M_1 \rightarrow T \rightarrow M_2$ (both twisting and pairing appear only in the M_1 phase). Pouget *et al.* (2, 3) suggested that the magnetic properties of the $\text{Cr}_x\text{V}_{1-x}\text{O}_2$ system can be interpreted as a set of noninteracting linear Heisenberg chains and the $M_2 \rightarrow T$ transition as a bonding or dimerization of a linear Heisenberg chain.

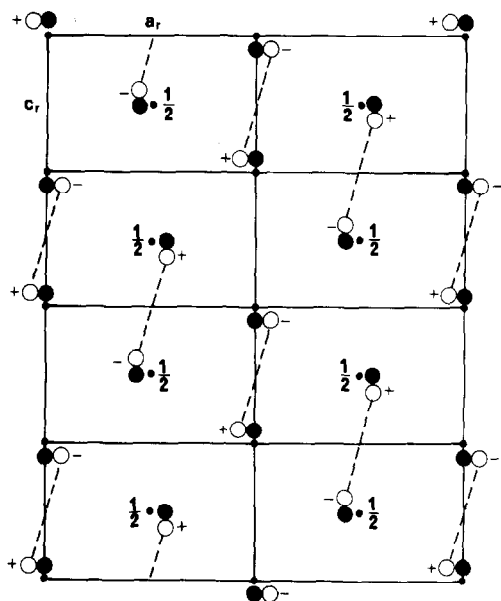


FIG. 1. Schematic crystal structure of the R (\circ), M_1 (\circ), and M_2 (\bullet) phases viewed along the tetragonal b -axis of rutile.

Recently, Pollert *et al.* (4), Kosuge and Kachi (5), and Brückner *et al.* (6) determined the phase diagram of the $\text{Fe}_x\text{V}_{1-x}\text{O}_2$ system, as shown in Fig. 2. The phase relation is very similar to the system $\text{Cr}_x\text{V}_{1-x}\text{O}_2$. The magnetic and electrical properties of this system, however, have been investigated fragmentarily by magnetic susceptibility (4–7), Mössbauer effect (7–10) and electrical resistivity measurement (6, 10).

This paper is concerned with the magnetism of the system $\text{Fe}_x\text{V}_{1-x}\text{O}_2$ ($0 < x < 0.05$), mainly with the magnetic properties of Fe ions, studied by magnetic susceptibility, magnetization, and also by Mössbauer effect measurements.

Experimental

The powder samples used in this experiment were prepared by the same method as that described in (5). For the Mössbauer effect measurement, the 0.5 and 1.0% ($x = 0.005$ and 0.01) samples were enriched up to 95% in ^{57}Fe , while for the 2.0 and 4.0% samples, the

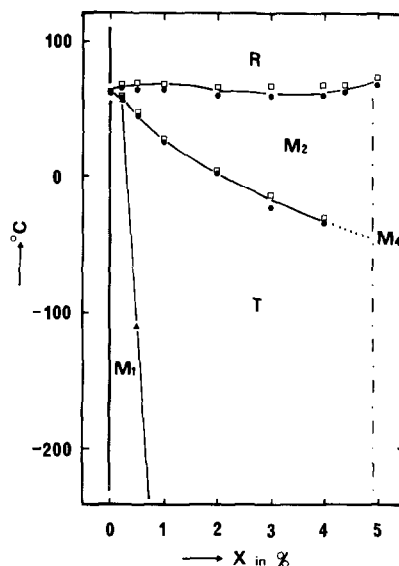


FIG. 2. Phase diagram of the $\text{Fe}_x\text{V}_{1-x}\text{O}_2$ system (5). The dash-dotted line shows the phase boundary. \square : on heating by DSC; \bullet : on cooling by DSC; \blacktriangle : on heating by X-ray diffraction.

enrichment was approximately 50 and 30%, respectively. These samples were checked by DSC measurement.

The susceptibility measurements were made using a torsion balance in the temperature range from 1.7 to 350°K. The magnetization measurement under high magnetic field was done with a magnetometer by use of a superconducting magnet below 4.2°K.

Mössbauer measurement with or without external field was made with a commercial multichannel Mössbauer spectrometer. The velocity scale was calibrated using a natural iron absorber.

Results

1. Magnetic Susceptibility Measurement (χ)

In pure VO_2 , the χ vs T curve is in good agreement with the published data (1), in the insulating phase as well as the metallic phase down to liquid nitrogen temperature. Below liquid nitrogen temperature, χ increases with decreasing temperature, as shown in the inset of Fig. 3. This may be due to impurities

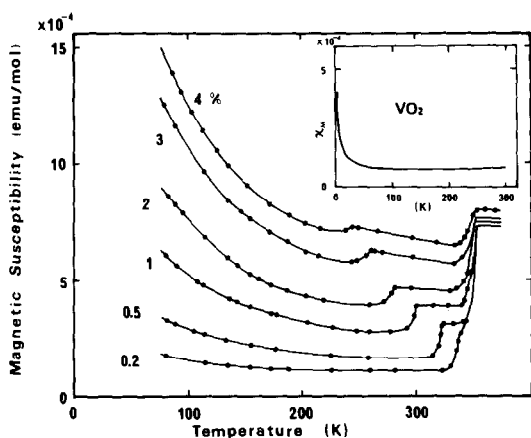


FIG. 3. Magnetic susceptibility of $\text{Fe}_x\text{V}_{1-x}\text{O}_2$ vs temperature above 77°K . The inset shows magnetic susceptibility vs temperature for pure VO_2 .

contained in the starting material and/or lattice defects (nonpairing vanadium ions).

Figure 3 shows the temperature dependence of the magnetic susceptibility above liquid nitrogen temperature. On cooling, χ shows the stepwise decrease, corresponding to the phase transitions $R \rightarrow M_2 \rightarrow T$ (see Fig. 2). The $T \rightarrow M_1$ phase transition, however, was neither detected by χ vs T nor by DSC measurements. This behavior is in good agreement with the published data on this system (4, 6), and is very similar to that in the $\text{Cr}_x\text{V}_{1-x}\text{O}_2$ system (2). As was confirmed by Pollert *et al.* (4), Kosuge and Kachi (5), and Brückner *et al.* (6), the phase relation of this system is quite similar to that of the $\text{Cr}_x\text{V}_{1-x}\text{O}_2$ system. It is probable that the temperature dependence can be interpreted in terms of noninteracting linear Heisenberg chains, as was done for the $\text{Cr}_x\text{V}_{1-x}\text{O}_2$ system.

Here, we define $\Delta\chi$ as

$$\Delta\chi = \chi_{\text{alloy}} - \chi_{\text{VO}_2}$$

where χ_{alloy} means the magnetic susceptibility of the samples $\text{Fe}_x\text{V}_{1-x}\text{O}_2$ and χ_{VO_2} that of pure VO_2 . Figure 4 shows the $(\Delta\chi)^{-1}$ vs T curves above 77°K . The linearity observed between 77 and 200°K corresponds to the Curie-Weiss law, i.e., $\Delta\chi = C/(T - \Theta)$. The parameters C and Θ are shown in Fig. 5 and

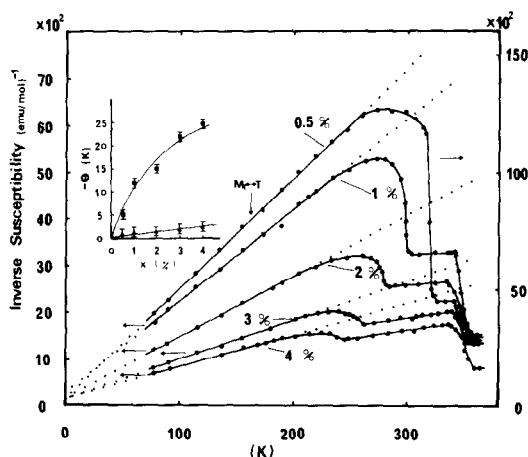


FIG. 4. Inverse of the susceptibility contribution due to the presence of Fe, $(\Delta\chi)^{-1} = (\chi_{\text{alloy}} - \chi_{\text{VO}_2})^{-1}$, in $\text{Fe}_x\text{V}_{1-x}\text{O}_2$ above 77°K . The inset shows the parameter Θ in $\Delta\chi = C/(T - \Theta)$ above 77°K (\blacksquare) and below 4.2°K (\blacktriangle).

the inset of Fig. 4, respectively. From the definition of $\Delta\chi$, it is clear that it originates from localized electrons of iron ions. The exchange interaction between iron ions is negative (antiferromagnetic) and rather strong, and the value of C is in rough agreement with the value calculated on the assumption of $3d^5$ (Fe^{3+}), as shown in Fig. 5.

Below liquid helium temperature, $(\Delta\chi)^{-1}$ vs T curves are straight lines as shown in Fig. 6.

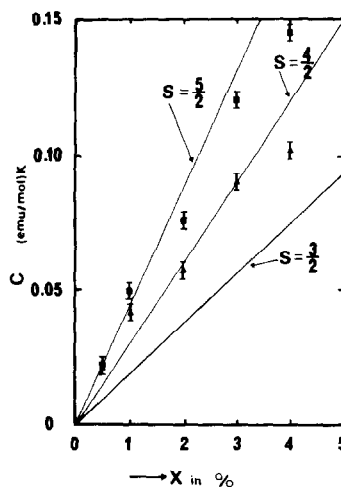


FIG. 5. Curie-Weiss constant C in $\Delta\chi = C/(T - \Theta)$ obtained above 77°K (\blacksquare) and below 4.2°K (\blacktriangle).

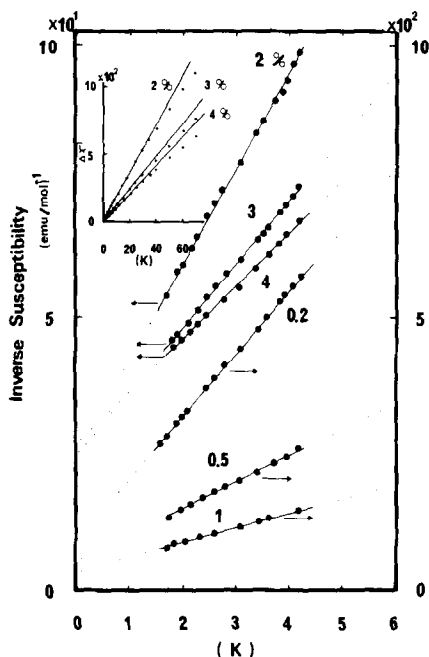


FIG. 6. Inverse of the susceptibility contribution due to presence of Fe in $\text{Fe}_x\text{V}_{1-x}\text{O}_2$ below 4.2°K . The inset shows $(\Delta\chi)^{-1}$ vs T in the temperature range 4.2 to 70°K . The straight lines correspond to the Curie-Weiss law below 4.2°K .

The parameters C and Θ are shown in Fig. 5 and the inset of Fig. 4, respectively. The values of Θ are fairly small in contrast to those obtained from above 77°K . As shown in the inset of Fig. 6, $(\Delta\chi)^{-1}$ gradually deviates downward from the straight line in the temperature range from 10 to 77°K , which means an increase of the magnetic moment with increase of temperature.

2. Magnetization Measurement

Figure 7 shows the magnetization vs external field curves for the compositions $x = 0.005, 0.02,$ and 0.04 at 4.2 and 1.3°K . The curves for the sample with $x = 0.005$ roughly obeys the Brillouin function. At 1.3°K , this curve shows paramagnetic saturation. The curves for $x = 0.02$ and 0.04 exhibit significant deviation from the function, and even at 1.3°K , these curves do not show paramagnetic saturation. From these results and the temperature dependencies of $\Delta\chi$, we can

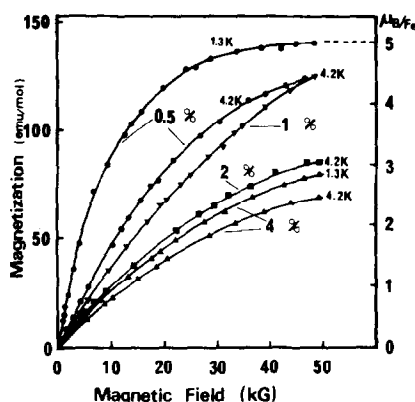


FIG. 7. Magnetization vs magnetic field at 4.2 and 1.3°K . It is to be noted that only the sample with $x = 0.005$ shows paramagnetic saturation at 1.3°K .

conclude that the exchange interactions between the magnetic spins are negligibly small in the case of $x = 0.05$, but are significant when $x = 0.02$ or 0.04 .

3. Mössbauer Effect Measurement

Blaauw and van der Woude (10) performed Mössbauer effect measurements on the $\text{Fe}_x\text{V}_{1-x}\text{O}_2$ system in detail, from which they deduced a somewhat erroneous phase diagram. We show here typical spectra of each phase.

The temperature dependence of the Mössbauer spectra for $x = 0.005$ and 0.04 are shown in Fig. 8a, b. The spectra in the R phase show only a single line. In the rutile structure, all metal positions are crystallographically equivalent. The isomer shift is about 0.50 mm/sec which is a typical value of Fe^{3+} . The linewidth increases remarkably with increasing x (0.28 to 0.85 mm/sec, x from 0.005 to 0.04). In the M_2 phase, the spectra consist of four absorption lines, in which two outer lines have larger quadrupole interaction (1.25 mm/sec; A -site) and the two inner lines a smaller one (0.25 mm/sec; B -site). The intensities of the absorptions from A - and B -site are almost identical, namely, iron atoms randomly have dissolved in the inequivalent two metal sites. The value of the isomer shift is about 0.50 mm/sec for both sites, which is also the

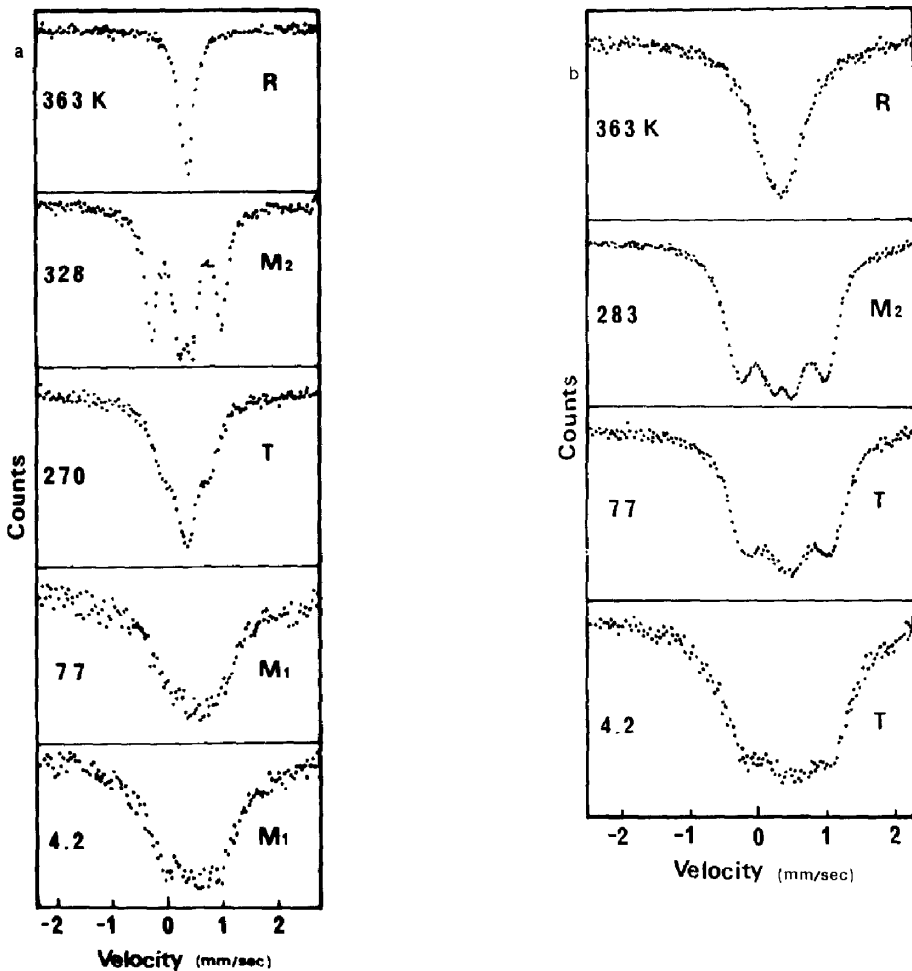


FIG. 8. Temperature dependence of Mössbauer spectra for $x = 0.005$ (a), and $x = 0.04$ (b).

typical value for Fe^{3+} . Temperature dependence of the absorption spectra for the M_2 phase was hardly observed.

In the T phase, the spectra are essentially the same as those of the M_2 phase. However, the difference between A - and B -site smears out gradually with decrease of the temperature (see, Fig. 8b). In the present experiment, the spectrum for the M_1 phase could be observed only for $x = 0.005$. The spectrum consists of a broad single line. There is no doubt, however, that in this system the broadness of the absorption lines does not originate from magnetic ordering. The broadness suggests distribution of the quadru-

pole interaction, although all the metal positions are crystallographically equivalent in the M_1 phase. It is very difficult to make a distinction between the T and M_1 phase by Mössbauer spectra.

Figure 9 shows the Mössbauer spectra for $x = 0.005$, 0.02, and 0.04 at 4.2°K under the high magnetic field of 45 kOe. Because the magnetic field was applied parallel to the direction of the γ -rays, the absorptions corresponding to $\Delta I_z = 0$ are inhibited. Accordingly the spectra consist of four lines instead of the usual six lines.

For the sample $x = 0.005$, the spectrum shows four rather sharp absorptions. The

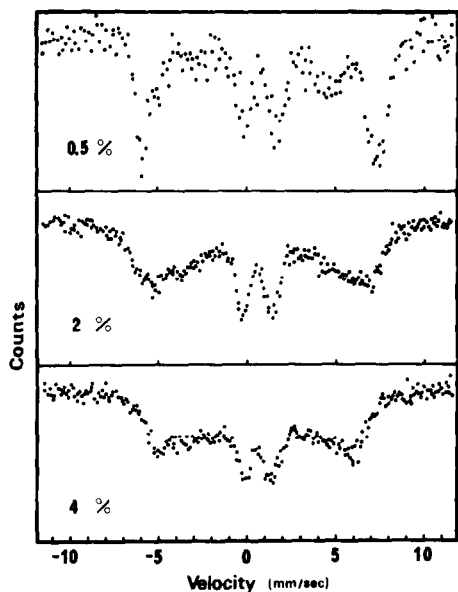


FIG. 9. Mössbauer spectra under the external field of 45 kOe (parallel to γ -ray) at 4.2°K. The hyperfine fields for $x = 0.005$ (M_1 phase), 0.02 (T phase), and 0.04 (T phase) are 430, 386, and 352 kOe, respectively.

linewidth is three times that of the pure iron. The magnetic field at the nuclei is about 430 kOe at 4.2°K. The magnetic field which the iron nucleus feels consists of two origins; one is the hyperfine field (negative) and the other is the applied external field (positive; 45 kOe in our case). In this case (paramagnetic state), the hyperfine field is obviously proportional to the value of the magnetization. As seen from Fig. 7, the magnetization at 4.2°K is about 90% of the complete paramagnetic saturation at 0°K. From these considerations, we can estimate the magnetic hyperfine field to be about 530 kOe. This value may be compared with the value of Fe^{3+} in Al_2O_3 (550 kOe).

On the other hand, the spectra for $x = 0.02$ and 0.04 show remarkable broadenings in comparison with that for $x = 0.005$. The linewidth of the two outer absorptions are remarkably larger than those of the two inner ones. If the origin of the line broadening comes from distribution of the electric field gradient or of the isomer shift, the linewidth of the four

lines must be the same. Therefore the origin of the broadening may be thought to be the distribution of the hyperfine field. We can estimate the distribution of the hyperfine field from the feature of the outer absorption lines. It is apparent from Fig. 9 that the number of nuclei feeling lower hyperfine fields increases with increasing x . The result will be discussed in the next section.

Discussion

We repeat the relation of crystal structures among the phases in the $\text{Fe}_x\text{V}_{1-x}\text{O}_2$ system (see Fig. 1). The simplest way to understand these phases is to view the rutile structure as two interpenetrating sublattices A and B of V chains parallel to $[001]_R$; each type of sublattice consists either of center vanadiums or of corner vanadiums in the rutile unit cell. In the M_2 phase, the V atoms of the A sublattice are paired along $[001]_R$ while those of the B sublattice form equispaced zig-zag chains along the same direction.

In the M_1 phase, all the metal ions pair and twist from the rutile position. In other words, the monoclinic M_1 phase can be presented as the result of a two-component distortion; one is a pairing along $[001]_R$ and the other is a zig-zag distortion along the octahedral axis. In this phase, the A and B sublattices are again equivalent.

Between the M_2 and M_1 phases, there appears the T phase. The phase corresponds to a progressive dimerization of the zig-zag chains in the B sublattice and a simultaneous tilting of the V pairs in the A sublattice leading to two equivalent V sublattices in the M_1 phase.

We briefly discuss here the magnetic properties above liquid nitrogen temperature. In this temperature range, the behavior is very similar to that of the $\text{Cr}_x\text{V}_{1-x}\text{O}_2$ system. Because the discussion is analogous to the one for the $\text{Cr}_x\text{V}_{1-x}\text{O}_2$ system made in detail by Pouget *et al.* (2), only a qualitative description has been made.

In the R phase, Mössbauer spectra show a single line absorption. The linewidth increases with increasing x . This suggests that the local distortion around Fe ion increases with increment of x .

In the M_2 phase the spectra show four absorption lines from two sites, corresponding to A , B sublattice. It is difficult, however, to say which absorption is from which site. The value of the isomer shift for the outer lines is about 0.50 mm/sec and that for the inner ones is also about 0.50 mm/sec. The linewidth of each absorption increases with increasing x . This comes from the distribution of the electric field gradient on each site. The equality of the absorption intensity from A and B sublattice is a matter of course, because the samples were prepared at high temperature (R phase). In this phase the magnetic susceptibility (χ_{alloy}) scarcely depends on the temperature. The vanadium of the A sublattice does not contribute to the temperature-dependent susceptibility, because the atoms of the A sublattice have finished pairing. Here we define $\delta\chi$ as follows,

$$\chi_{\text{alloy}} = \chi_{\text{VO}_2} + C/(T - \Theta) + \delta\chi.$$

From the definition, the magnitude of $\delta\chi$ means the deviation from the Curie-Weiss law. In the M_2 phase, $\delta\chi$ increases with increasing temperature. If we assume that the magnetic moment and also the exchange interaction of iron do not change in the M_2 phase, $\delta\chi$ comes from the vanadium ions ($S = \frac{1}{2}$) of the B sublattice. As mentioned above, these vanadium atoms are equispaced along the $[001]_R$ direction. The magnetic interaction between these chains will be very weak, since their nearest-neighbor chains have paired V^{4+} sites which are essentially nonmagnetic. It is possible to analyze the magnitude $\delta\chi$ using a set of noninteracting linear Heisenberg chains as a model, as was done by Pouget *et al.* for the $\text{Cr}_x\text{V}_{1-x}\text{O}_2$ system. From the magnitude of $\delta\chi$, we can get the value of the intrachain exchange constant $2J$, by using the calculation of Bonner *et al.* $2J$ is estimated to range from

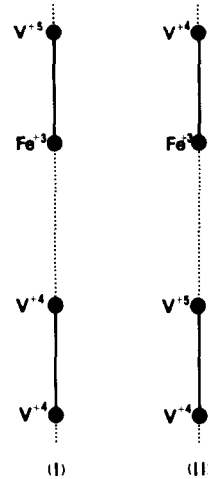


FIG. 10. Model of the pairing (see text).

100 to 700°K. More strictly speaking, the following must be taken into consideration. As for the A sublattice, there are two possibilities of pairing as shown schematically in Fig. 10. In the case of mode (I), the analysis mentioned above is reasonable. In the case of mode (II), however, it is evident that V^{4+} (unpaired) and $\text{V}^{4+}\text{-Fe}^{3+}$ (either paired or unpaired) contribute to the magnetic susceptibility not only in the M_2 phase but also in the T and M_1 phase. One of these modes must have lower energy than the other and presumably stabilizes the structure. As for the B sublattice, the nature of the impurity (Fe^{3+} in this case) in the noninteracting linear Heisenberg chain has been not well established so far.

In the T phase, Mössbauer spectra show the similar patterns as those of the M_2 phase. On cooling, the site difference between A and B , appearing in the Mössbauer profile, gradually smears out, leading to a broad single line in the M_1 phase. On the $\delta\chi$ vs T curves, the $\delta\chi$ decreases with decrease of temperature as shown in Fig. 4. The $M_2 \rightarrow T$ transition can be interpreted as the dimerization transition of a linear Heisenberg chain. Pouget *et al.* (2) analyzed qualitatively the $M_2 \rightarrow T$ transition in the $\text{Cr}_x\text{V}_{1-x}\text{O}_2$ system as dimerization (singlet-triplet phase transition). So, we do not repeat the same procedure for this system. At

the temperature with $\delta\chi = 0$, V atoms on B site have come to complete dimerization. Below the temperature, $(\Delta\chi)^{-1}$ vs T curves show straight lines down to about 70°K. The values of C are in rough agreement with the values calculated on the assumption of $3d^5$ (Fe^{3+}) as shown in Fig. 5. It seems likely that the mode (I) has lower energy than the mode (II). Above liquid nitrogen temperature, iron ions can be regarded as free (isolated) Fe^{3+} ion.

Below liquid nitrogen temperature, the main results obtained can be summarized as follows:

(1) On cooling, the $(\Delta\chi)^{-1}$ vs T curves gradually deviate from straight lines (free Fe^{3+} line) in the temperature range from 10 to 70°K. Below 10°K, the $(\Delta\chi)^{-1}$ vs T curves again show straight lines, from which we get smaller C and Θ values than those obtained above 77°K. In the low concentration region ($x \leq 0.01$), the C values are in fairly good agreement with the values calculated, assuming that the electronic state of iron is free Fe^{3+} .

(2) The absolute value of the magnetization at 4.2°K is much smaller than that calculated from the Brillouin function. The magnetization vs external field for $x = 0.005$, however, roughly obeys the Brillouin function as shown in Fig. 7.

(3) Mössbauer effect measurements under external field show that the magnetic field at the nucleus has a distribution as shown in Fig. 9. The magnetic field distribution appears to develop a minimum at zero field and a rather broad maximum at around 390 kOe (for $x = 0.02$). With increase of x , the distribution moves to lower field.

These findings suggest exchange-coupled (antiferromagnetically) Fe^{3+} clusters. These clusters consist of dimers, triads, or larger clusters. In the case of dimers, for example, the total spin $S = S_1 + S_2$ can be calculated to be 0, 1, 2, 3, 4, 5, and the multiplet spacing is determined by the exchange interaction J_{12} . The number of atoms with a particular orientation will be determined by the Boltzmann distribution. Even in the simplest dimers

case, there is a variety of exchange interactions J originating from the length and the path of the Fe^{3+} - Fe^{3+} ions. For the case of larger clusters, the situation is much more complicated. It is, however, to be noted that the samples do not contain such large clusters that show the magnetic phase transition.

It is evident that in the low-concentration region of iron, the great majority of irons is magnetically isolated, and so the magnetic properties can be interpreted as free Fe^{3+} ions. With increasing x , the clustering grows gradually. If the multiplet width is very narrow compared with kT , the value of the magnetic moment must coincide with the value of free Fe^{3+} ions. This situation may correspond to the χ vs T curves above liquid nitrogen temperature. If the multiplet width is comparable to kT or smaller than kT , the averaged magnetic moment must be reduced compared with that of free Fe^{3+} ions. In this case, the magnetic moment gradually decreases with decreasing temperature. This situation must correspond to the magnetic properties below liquid nitrogen temperature: the reduction of the averaged magnetic moment, the distribution of the hyperfine field, and the difficulty of the magnetic saturation. Thus, the exchange-coupled cluster model can explain the magnetic properties of the $\text{Fe}_x\text{V}_{1-x}\text{O}_2$ system qualitatively.

It is interesting to point out that in the $\text{Cr}_x\text{V}_{1-x}\text{O}_2$ system, D'Haenens *et al.* (12) confirmed exchange-coupled Cr^{3+} ions by electron spin resonance and, also, Pouget *et al.* (2) observed that $(\Delta\chi)^{-1}$ vs T curves deviate downward from the straight lines in the low temperature (below 10°K for $x = 0.05$), which suggests gradual reduction of the magnetic moment.

Acknowledgments

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