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Semiconductor–Metal Transition in Ti_3O_5*

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Ti_3O_5 shows a first-order phase transition from the monoclinic structure to the pseudobrookite structure at 448°K, at which temperature a magnetic susceptibility anomaly has been reported earlier in the literature. There is an electrical conductivity discontinuity accompanying the phase transition. Incorporation of Fe stabilizes the high-temperature phase of Ti_3O_5; while with 2% Fe the transition temperature and enthalpy change are lowered, with 5% Fe there is no transition. Mössbauer spectra of 2% Fe-doped Ti_3O_5 are similar below and above the transition temperature and show no evidence for magnetic ordering in the low-temperature phase. These results are compared to the VO_2 transition.

Introduction

Åsbrink and Magnéli (*1*) reported that Ti_3O_5, the precursor of the Ti_nO_{2n-1} shear structures, possesses monoclinic structure at room temperature and transforms to the pseudobrookite (orthorhombic) structure near 393°K. Keys and Mulay (*2*) as well as Mulay and Danley (*2*) reported a sharp change in the magnetic susceptibility of Ti_3O_5 in the neighborhood of 460°K, with a 30-deg hysteresis on cooling; both above and below the transition the susceptibility was temperature-independent. Keys, Mulay, and Danley sugested that the susceptibility anomaly of Ti_3O_5 at 460°K may arise from a first-order semiconductor–metal transition; the magnetic transition temperature is, however, much higher than the crystallographic transition temperature reported by Åsbrink and Magnéli. Bartholomew and Frankl (*3*) have reported an abrupt change in slope, though no discontinuity, in the resistivity versus temperature curve for single crystals of Ti_3O_5. We note here that there is a striking resemblance between the magnetic susceptibility-temperature curve of Ti_3O_5 and that of VO_2; this compound is characterized by a sharp semiconductor–metal transition near 343°K, at which temperature the magnetic susceptibility also exhibits a marked change (*4–7*). Based on considerations of the localized *versus* collective behavior of the *d*-electrons in the Ti_nO_{2n-1} Magnéli phases, Goodenough (*8*) suggested that a semiconductor–metal transition could occur in Ti_3O_5, since it shows some Ti–Ti homopolar bonding at room temperature. We have presently investigated the phase transition of Ti_3O_5 employing differential thermal analysis (DTA), variable temperature X-ray crystallography, electrical conductivity measurements, electron spin resonance (ESR), and Mössbauer spectroscopy.

Experimental

High-purity Ti_3O_5 was prepared by arc melting TiO_2 and Ti (>99.99% purity) in proper stoichiometric proportions under an atmosphere of gettered argon (*9*). A rotating crystal photograph of a single crystal Ti_3O_5 was obtained in order to establish the identity and homogeneity of the prepared sample. X-ray powder diffraction patterns were recorded at different temperatures employing a G.E. X-ray diffractometer with an MRC high-temperature attachment. DTA curves were recorded employing

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an Aminco automatic differential thermoanalyser fitted with a voltage stabilizer and temperature programmer. The limitations and applications of DTA in the study of phase transformations in solids have been described by Rao and Rao (*10*).

We have not been able to grow single crystals of sufficient size for electrical conductivity measurements. We therefore recorded the conductivities of polycrystalline pellets in an inert atmosphere by the standard four-probe technique; the measurements were made after repeated thermal cycling through the transition temperature.

ESR spectra of polycrystalline powders were recorded at 77°K employing a Varian V4502 ESR spectrometer with a 9-in. magnet and 100 Kc modulation. Mössbauer spectra were recorded with ^{57}Co/Pd source at room temperature; the sample holder was surrounded by a furnace which enabled the spectra to be recorded up to 300°C.

Results and Discussion

DTA curves of Ti_3O_5 show a sharp reversible endothermic peak at 450°K, see Fig. 1(a), with a $\Delta H°$ of 1.6 ± 0.4 kcal/mol. This transition temperature agrees with the magnetic transition temperature of Refs. (*2*) and (*3*). We may note here that the $\Delta H°$ of the transition of Ti_2O_3 (in the range 400–800°K) is very much smaller (*11*); the DTA curve shows only a shallow peak [Fig. 1(d)] in Ti_2O_3 compared to that of Ti_3O_5. The DTA curves of Ti_3O_5 exhibited appreciable thermal hysteresis (~35°K), indicating that the transition is of first order; evidence has been adduced elsewhere (*6*, *12*, *13*) that the transition in Ti_2O_3 is of higher order.

X-ray studies of Ti_3O_5 as a function of temperature show that the monoclinic structure changes to the pseudobrookite structure sharply at ~448°K, instead of at 393°K as reported by Åsbrink and Magnéli (*1*). The lattice dimensions of the low ($a = 9.80$ Å, $b = 3.79$ Å, $c = 9.45$ Å, and $\beta = 91.75$ deg) and high ($a = 9.90$ Å, $b = 3.78$ Å, $c = 10.02$ Å, and $\beta = 90.75$ deg) temperature phases presently found are, however, close to those of Ref. (*1*). The reflections that showed maximum variations in the transition region were $00\bar{3}$, $20\bar{3}$, 203, $40\bar{2}$, 204, and 314. At 448°K the major change in the cell dimensions is in the *c*-parameter, see Fig. 2; similar changes have been reported in the transition of Ti_2O_3 (*14*, *15*). It is along the *c* direction that Ti_3O_5 possesses the characteristic endless flights of steps caused by the joining of the edges of the TiO_6 octahedra.

Doping Ti_3O_5 with Fe stabilizes the high-temperature phase of Ti_3O_5; thus, the degree of monoclinicity (of the room temperature structure) of Ti_3O_5 is considerably reduced on addition of Fe,

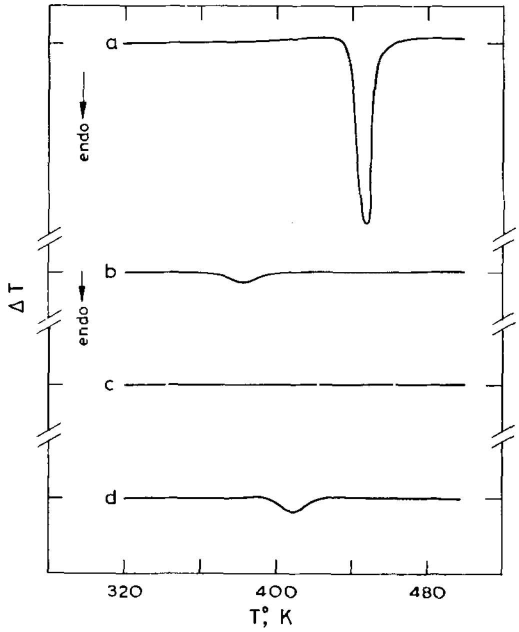

FIG. 1. DTA curves of (a) Ti_3O_5, (b) Ti_3O_5 doped with 2% Fe, (c) Ti_3O_5 doped with 5% Fe, (d) pure Ti_2O_3 (heating rate 16°/min).

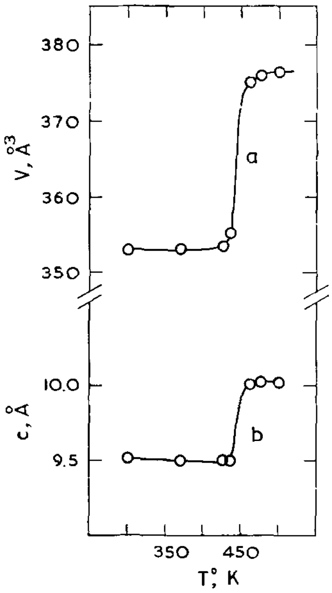

FIG. 2. Variations of (a) unit cell volume and (b) *c*-parameter of Ti_3O_5 with temperature.

as can be seen from the lattice parameters given below:

2% Fe: $a = 9.78$ Å, $b = 3.79$ Å, $c = 9.45$ Å, and $\beta = 91.7°$

5% Fe: $a = 9.95$ Å, $b = 3.80$ Å, $c = 10.04$ Å, and $\beta = 90.5°$

2% Fe in Ti_3O_5 decreases the transition temperature considerably (to ~375°K), as indicated by X-ray studies and the DTA curve [Fig. 1(b)]. The DTA peak is shallow and is associated with much lower $\Delta H°$; it is possible that with 2% Fe, the Ti_3O_5 transition acquires some higher-order components. Addition of 5% Fe to Ti_3O_5 stabilizes the high-temperature phase completely, and the room-temperature phase shows almost no monoclinic distortion. The DTA curve [Fig. 1(c)] also shows no evidence of a phase transition. We find that the accidental contamination of Ti_3O_5 by tungsten also stabilizes the high-temperature form. These results indicate that the low transition temperature reported by Åsbrink and Magnéli (*1*) may well have been due to the presence of some impurities in their sample. Unlike Ti_3O_5, the transition in VO_2 is not greatly affected by doping with Fe; the DTA curves in Fig. 3 serve to illustrate this point. The transition temperature of VO_2 is slightly lowered by Fe^{3+}, just as in solid solutions of VO_2 with other oxides (*16*, *17*). The transition, however, remains first order and links the semiconducting and metallic phases of VO_2.

Four-probe measurements of electrical conductivity of pure Ti_3O_5 showed an anomaly near 448°K, with roughly a 10-fold increase in conductivity, see Fig. 4(a). The magnitude of the jump in conductivity at the transition temperature, T_t, is probably lower than the actual discontinuity, since the present measurements were carried out on pressed pellets. The conductivity jump observed in polycrystalline pellets of VO_2 is also smaller than that found in single crystals, even after repeated cycling (*18*). The activation energy for conduction below the transition temperature is about 0.29 eV. Above T_t the conductivity gradually approaches the characteristics of metallic behavior, whereas the metallic character of VO_2 becomes immediately evident after the transition occurs. The temperature-independent magnetic susceptibility above T_t reported by Keys and Mulay (*2*) and by Mulay and Danley (*2*) is further evidence in favor of the metallic nature of the high-temperature phase of Ti_3O_5. Our findings differ significantly from those of Bartholomew and Frankl (*3*), in that we observe a sharp transition, in contrast to a minimum in

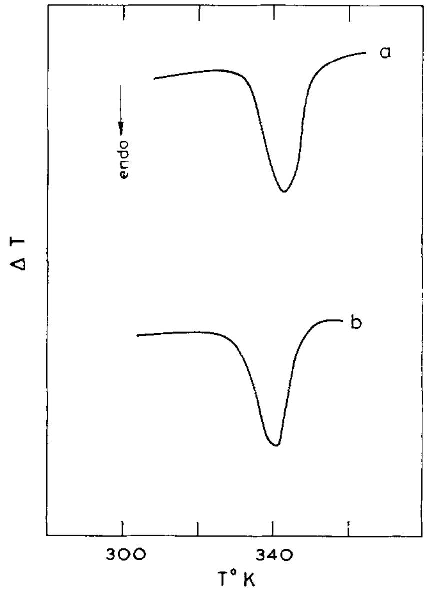

FIG. 3. DTA curves of (a) pure VO_2 and (b) VO_2 doped with 5% Fe (heating rate 16°/min).

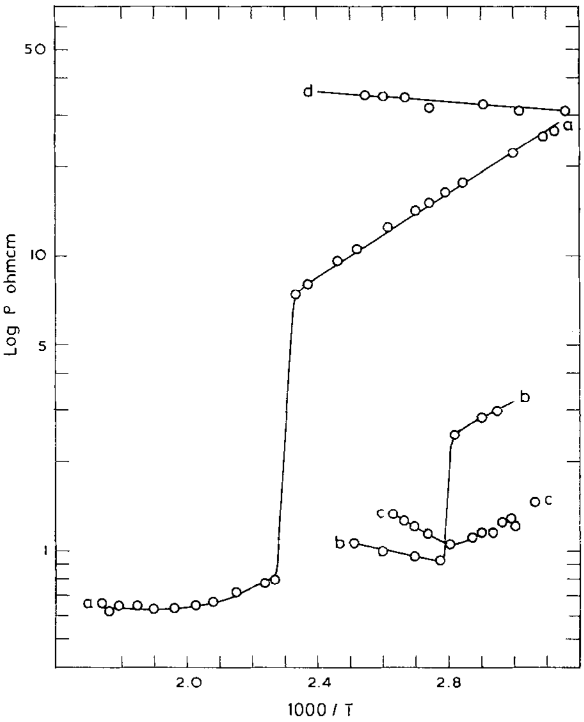

FIG. 4. Plots of logarithm of resistivity against reciprocal of absolute temperature for (a) pure Ti_3O_5, (b) Ti_3O_5 with 1.5% Fe, (c) Ti_3O_5 with 2% Fe, and (d) Ti_3O_5 with 5% Fe.

resistivity reported by the latter investigators. As will be shown later, the addition of impurities tends to mask the transition. Since the single crystals used by Bartholomew and Frankl were grown from a flux and were imperfect, it is possible that impurities in amounts sufficient to suppress the sharp transition were present in their crystals.

The electrical conductivity of Ti_3O_5 doped with 1.5% or 2% Fe is not significantly different from that of the metallic phase of pure Ti_3O_5. The magnitude of the conductivity discontinuity diminishes with increasing Fe content, see Fig. 4, and the transition shifts to lower temperatures in the more heavily doped samples; this is consistent with the onset of the monoclinic distortion at lower temperature in these solids. Figure 4(c) shows how, with sufficient doping, the discontinuity is supplanted by a break in the curve. Above T_t the conductivity behavior is metallic, a situation similar to that found in Fe^{3+}-doped VO_2 samples. Ti_3O_5 with 5% Fe shows no conductivity anomaly and the temperature-dependence of conductivity is typical of metals throughout the temperature range studied. Even though this phase is metallic, the magnitude of conductivity is rather small, probably because of the predominance of impurity scattering.

To establish the mechanism of the conductivity anomaly it is important to ascertain whether antiferromagnetic ordering occurs in the low-temperature phase of Ti_3O_5. The Mössbauer spectrum of Ti_3O_5 doped with 1.8% of enriched (97%) ^{57}Fe was identical above and below the transition temperature; see Fig. 5. The spectra show that Fe is present in two nonequivalent sites, both exhibiting quadrupole splitting. These observations are somewhat similar to those reported by Kosuge (*5*) on VO_2. Apparently, the transition in 1.8% ^{57}Fe-doped Ti_3O_5 is not accompanied by a change in magnetic order; both phases are paramagnetic. In this connection we have reexamined the Mössbauer spectra of 1.8% ^{57}Fe-doped VO_2 and find the presence of only one type of Fe site, with quadrupole splitting at room temperature, see Fig. 6, rather than two Fe sites reported by Kosuge (*5*). The origin of the discrepancy is not clear, though it may perhaps be related to a smaller degree of contamination in our samples. The Mössbauer spectrum of VO_2 remains unaffected by the transition at 372°K. It must be clearly understood that these Mössbauer results cannot be taken as evidence for the absence of magnetic order in the low-temperature phase of pure Ti_3O_5, since (unlike in VO_2) the incorporation of ~2% Fe causes stabilization of the high-temperature phase of Ti_3O_5 as described earlier. Attempts to record the Mössbauer spectra with ~1% ^{57}Fe-doped Ti_3O_5 were unsuccessful. To determine whether pure Ti_3O_5 exhibits magnetic order, different types of studies must be attempted.

Keys (*19*) has reported the ESR spectrum of Ti_3O_5 and has interpreted the multiplet structure as due to the hyperfine interaction between ^{47}Ti and ^{49}Ti, both of which have appreciable natural

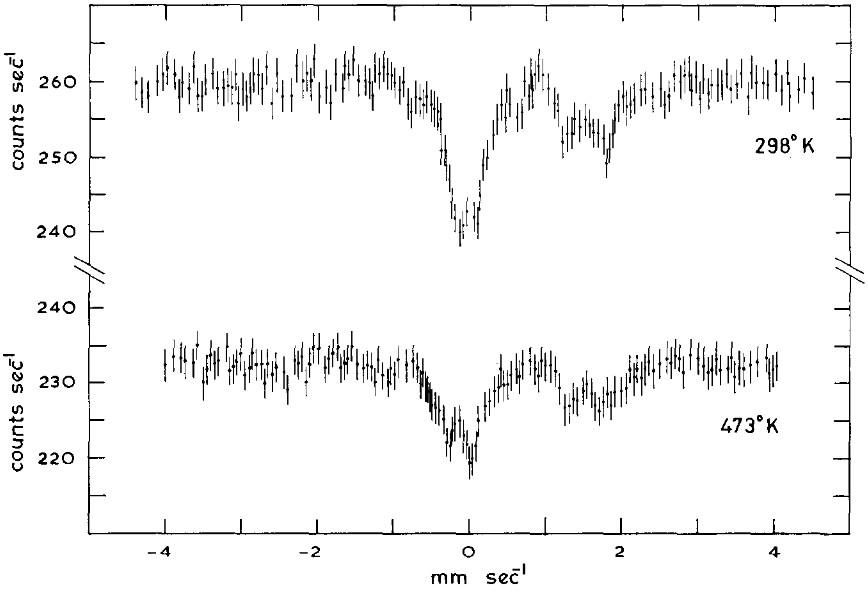

FIG. 5. Mössbauer spectra of Ti_3O_5 containing 1.8% of enriched ^{57}Fe at 298 and 478°K.

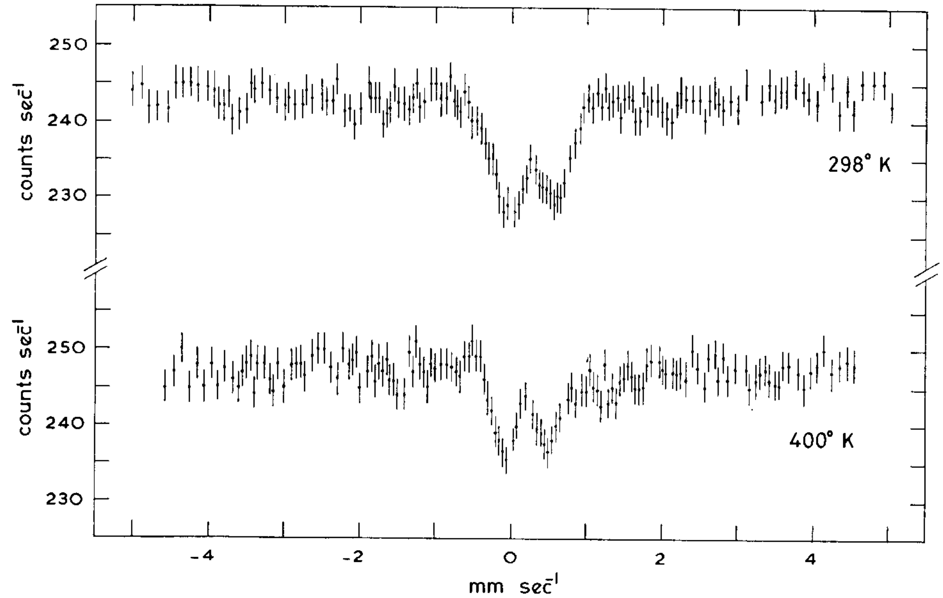

FIG. 6. Mössbauer spectra of VO_2 containing 1.8% of enriched ^{57}Fe at 298 and 400°K.

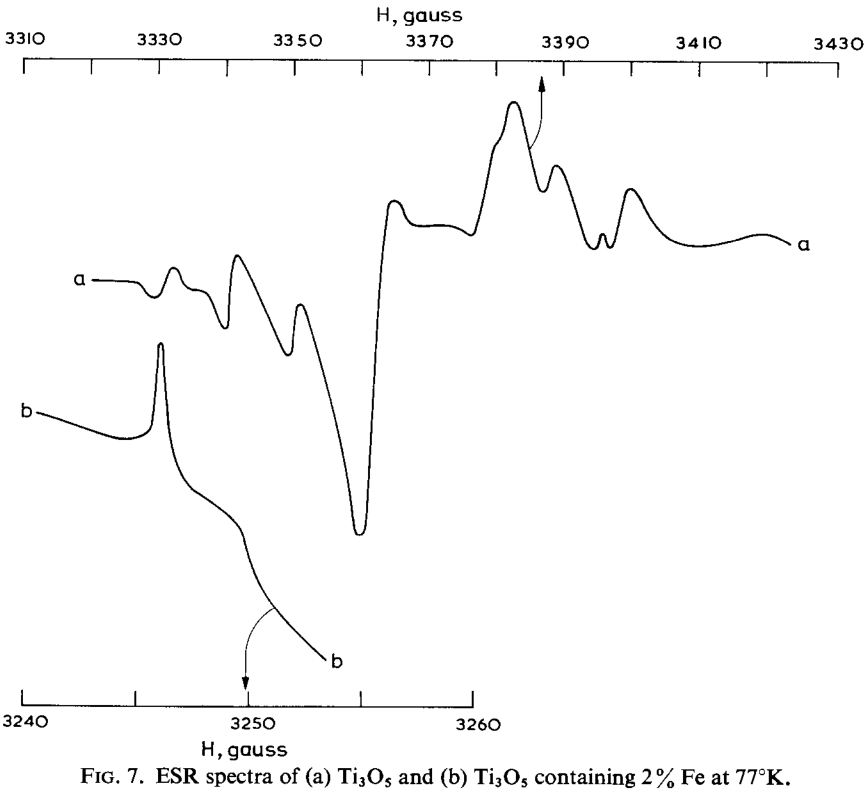

FIG. 7. ESR spectra of (a) Ti_3O_5 and (b) Ti_3O_5 containing 2% Fe at 77°K.

abundance. The hyperfine splitting has been taken to indicate the existence of a semiconductor–metal transition by Keys (*19*) and Adler (*20*). We have examined the ESR spectra of pure Ti_3O_5 and Fe-doped Ti_3O_5 at 77°K; the spectrum of Ti_3O_5 shows a multiplet structure similar in form, though not in detail, to that of Keys (*19*); see Fig. 7. The eight signals found by us at 3329, 3340, 3349, 3362, 3380, 3388, 3392, and 3396 G all occur at higher fields than those reported by Keys. It is possible that the sample of Keys was contaminated by some impurities; our 2% Fe-doped Ti_3O_5 exhibits an ESR spectrum at nearly the same field strengths as the signals reported by Keys. We believe that the multiplet structure in the spectrum of Ti_3O_5 is due in large measure to the presence of inequivalent sites; the hyperfine interaction, if any, may only be one of several contributing factors. The Ti_3O_5 sample with 2% Fe does not show the multiplet structure (Fig. 7) possibly because of the higher symmetry of the system and/or because of the decreased homopolarity of the bonds in the low temperature phase. The 5% Fe-doped sample does not show any ESR signal. It is likely that, in addition to the higher symmetry and presence of heteropolar bonds, the metallic characteristics of the heavily doped Ti_3O_5 sample may be responsible for the absence of the signal.

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