JOURNAL OF SOLID STATE CHEMISTRY 38, 112–115 (1981)

The Resistivity and Magnetic Susceptibility of V_3O_5 Single Crystals

H. JHANS AND J. M. HONIG

Department of Chemistry, Purdue University, West Lafayette, Indiana 47907

Received June 30, 1980

New resistivity studies on single-crystal V_3O_5 show that the phase transformation at 427 K involves an insulator–metal transition; the resistivities reported here lie somewhat below those cited in numerous earlier investigations. Magnetic susceptibility (χ) measurements exhibit only very small changes at the transition. It is pointed out that the maximum in χ at 125 K should be correlated with the onset of antiferromagnetic ordering near 76 K.

The physical properties of V_3O_5 have been repeatedly investigated; this compound is of interest because it exhibits a metal–insulator transition near $T_u = 430$ K which is separate from a magnetic ordering transition that commences at $T_l = 76$ K and extends over a considerable temperature range. The resistivity study described below was motivated by the fact that there is disagreement in the electrical properties reported by several groups of investigators (*1, 4, 10–12, 14, 16, 18, 20–23, 25*). Not only is there a considerable spread in resistivities, but there also are qualitative variations in the quoted temperature dependence of resistivity both above and below the transition temperature T_u. There is even some doubt whether the phase transformation at 430 K involves a metal–insulator transition or whether it connects two insulating phases. In addition, magnetic susceptibility investigations were carried out by us for a more complete characterization of the material.

Single crystals of V_3O_5 were grown by a chemical vapor transport technique as specified elsewhere. (*3*). A four-probe method was employed for the resistivity (ρ) study with provision for periodic current reversal to permit averaging out of spurious thermoelectric signals. The magnetic susceptibility (χ) was determined by the conventional Faraday technique, using $HgCo(SCN)_4$ as a calibration standard. Great care was taken to preserve sample stoichiometry by rigid exclusion of oxygen from the system.

The electrical resistivity measurements reported in the literature to date are reproduced in Fig. 1 as plots of log ρ or log (R/R_0) vs $1/T$; here R/R_0 is the resistance ratio relative to $T_0 = 410$ K. The following items are noteworthy:

(1) The resistivities reported in the present study lie below all others in the temperatures range $T > 210$ K. Presumably this reflects differences in sample quality associated with the various preparative techniques. The overall spread in resistivities reported by various workers exceeds one order of magnitude.

(2) The transition temperature observed by us occurs sharply at $T_u = 427$ K, which falls well within the range of 400 to 445 K

0022-4596/81/070112-04$02.00/0

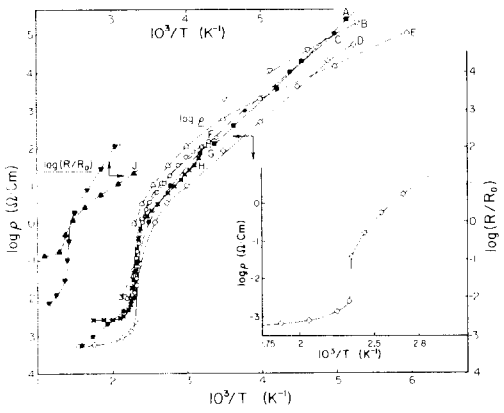

FIG. 1. Variation of electrical properties of single-crystal V_3O_5 with temperature, T; ρ is the resistivity, R/R_0 is the resistance ratio relative to T = 410 K. Curve A, Ref. (*4*, *11*, *12*); Curve B, Ref. (*1*); Curve C, Ref. (*25*); Curve D, present work; Curve E, Ref. (*18*); Curve F, Ref. (*14*, *16*); Curve G, Ref. (*21*); Curve H, Ref. (*22*); Curve I, Ref. (*20*); Curve J, Ref. (*23*). Inset shows detailed variation of resistivity near the transition temperature.

reported by other investigators. The jump in resistivity $\Delta\rho$ at $T = T_u$ observed by all workers covers aproximately one order of magnitude; while the transition reported in most of the earlier publications extends over a considerable temperature interval, it was found to be confined to less than 2° in the present study.

(3) The plot of log ρ vs $1/T$ obtained by us was fairly linear in the range $T < 400$ K; there is some curvature in the plot as T_u is approached on heating. These findings are consistent with those of other investigators. The activation energy for conductivity below 400 K is $\epsilon_a = 0.34$ eV, as compared to a range of values $0.17 \leq \epsilon_a \leq 0.68$ eV shown in Fig. 1.

(4) High-temperature resistivity measurements were carried out by us over a wider temperature range $T > T_u$ than by prior workers. The results depicted in Fig. 1 show a modest decline in ρ with rising T above 500 K with an apparent activation energy of 0.05 eV in this region. These results reinforce earlier findings by Brückner and coworkers (*22*) of resistivities that were virtually independent of temperature between 500 and 570 K. In almost all other cases shown in Fig. 1 the resistivity shows a much sharper drop with temperature $T > T_u$. Our results are thus consistent either with a semimetal for which the degree of band overlap increases slightly with $T > T_u$ or with a degenerate semiconductor whose bandgap is small compared to kT in the range $T > T_u$.

The hypothesis that the high-temperature phase is quasi-metallic receives independent support from thermoelectric and optical measurements. Again, there is some spread in Seebeck coefficients (α) reported in three publications (*15*, *21*, *25*) (in a fourth (*4*), α is stated to be negative at low temperatures, compared to positive values reported by the others, but this study did not encompass the transition region T_u); however, all three groups reported a sharp drop in α near T_u, a sign reversal at the transition, and small negative values for α that increased numerically and linearly with $T > T_u$. This is what one would expect for a material undergoing an insulator–metal transition. As regards the optical studies, Chudnovskii and co-workers (*25*) have determined the optical reflectivity in the range 0.1 to 3.5 eV both above and below T_u; they report significant changes in reflectivity below 1 eV and cite the optical characteristics in the infrared region as showing that the high-temperature phase is quasi-metallic.

The magnetic susceptibility (χ) studies reported in the literature and our own measurements are assembled in Fig. 2; again, a significant spread in measurements may be noted, but the trends are in good accord. In common with prior work by Brückner *et al.* (*16*), we observed a slight kink in χ vs T and in $1/\chi$ vs T plots which is absent in the results cited by Ueda et al. (*24*). This kink coincides with the electrical transition at $T = T_u$. The insert in Fig. 2 shows the reciprocal spin-susceptibility $1/\chi_d$ vs T; only the

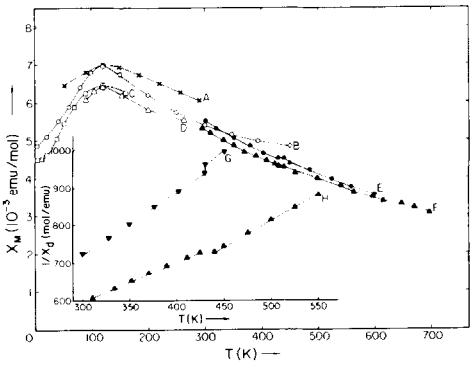

FIG. 2. Molar magnetic susceptibility vs temperature for single crystals of V_3O_5. Curve A, Ref. (*3, 9, 10, 12*); Curve B, Ref. (*24*); Curve C, Ref. (*26, 27*); Curve D, Ref. (*2*); Curve E, Ref. (*16, 21*); Curve F, present work. Inset shows plot of $1/\chi_d$ vs T, where χ_d is the molar spin susceptibility of V_3O_5. Curve G, Ref. (*25*); Curve H, present work.

work in Ref. (*25*) was also analyzed in this specific manner. Our results in the range 290–700 K may be fitted to a Curie–Weiss law $\chi = C/(T-\Theta) + \chi_0$, where χ_0 is the temperature-independent term. For $T < T_u$, $C = 0.97$ emu-deg/mole ($\mu_{eff} = 2.78\ \mu_B$), $\Theta = -282$ K; for $T > T_u$, $C = 0.75$ emu-deg/mole ($\mu_{eff} = 2.45\ \mu_B$), $\Theta = -110$ K; $\chi_0 = 100 \times 10^{-6}$ emu/mole in both temperature ranges. These parameters differ substantially from those cited by earlier investigators, but this is not surprising, considering that only a limited temperature range is available for fitting of the parameters, and that allowance must be made for the contributions to χ_0. What emerges from this and the earlier studies (*16, 21, 25*) is the fact that χ changes very little at the transition temperature T_u. The fact that the Curie–Weiss law applies both at $T < T_u$ and $T > T_u$ has occasionally been cited as indicating that the high-temperature phase of V_3O_5 is a semiconductor. However, it should be noted that for Cr-doped V_2O_3, which undergoes a well-documented metal–insulator transition near room temperature (*5, 6, 19*) (in addition to a metal–antiferromagnetic-insulator transition near 150 K), χ is also describable in terms of a Curie–Weiss law (*7*); the parameters change by less than 10% in the course of the metal–insulator transition. It thus appears that the applicability of the Curie–Weiss law does not provide a reliable criterion for establishing whether a given material is metallic or not; Rubinstein (*8*) and Mott (*13*), among others, have discussed at some length the various mechanisms by which an enhancement in Pauli paramagnetism can be brought about in narrow-band materials or in metallic alloys.

It also bears repeating that the maximum encountered in χ vs T near 125 K does not indicate that a transition in V_3O_5 takes place at that point, as has sometimes been asserted. Rather, the antiferromagnetic ordering transition as ascertained by neutron scattering (*17*), magnetic torque (*24*), or specific heat (*28*) measurements occurs at 76 K; it has recently been proposed (*28*) that the shift in the maximum of χ to higher temperatures reflects the lower-dimensional magnetic interactions between V ions aligned in chains.

Acknowledgment

This research was supported by NSF Grant DMR 790356A1.

References

1. S. KACHI, T. TAKADA, AND K. KOSUGE, *J. Phys. Soc. Japan* **18**, 1839 (1963).
2. K. KOSUGE, *J. Phys. Chem. Solids* **28**, 1613 (1967).
3. K. NAGASAWA, Y. BANDO, T. TAKADA, *Japan. J. Appl. Phys.* **8**, 1267 (1969).
4. H. OKINAKA, K. NAGASAWA, K. KOSUGE, Y. BANDO, T. TAKADA, AND S. KACHI, *J. Phys. Soc. Japan* **27**, 1366 (1969).
5. A. JAYARAMAN, D. B. MCWHAN, J. P. REMEIKA, AND P. D. DERNIER, *Phys. Rev. B* **2**, 3751 (1970).
6. D. B. MCWHAN AND J. P. REMEIKA, *Phys. Rev. B* **2**, 3734 (1970).
7. A. MENTH AND J. P. REMEIKA, *Phys. Rev. B* **2**, 3756 (1970).
8. M. RUBINSTEIN, *Phys. Rev. B* **2**, 4731 (1970).
9. K. NAGASAWA, *Mater. Res. Bull.* **6**, 853 (1971).

10. K. NAGASAWA, Y. BANDO, AND T. TAKADA, *Bull. Inst. Chem. Res. Kyoto Univ.* **49,** 322 (1971).
11. K. NAGASAWA, Y. BANDO, AND T. TAKADA, *J. Cryst. Growth* **17,** 143 (1972).
12. S. KACHI, K. KOSUGE, AND H. OKINAKA, *J. Solid State Chem.* **6,** 258 (1973).
13. N. F. MOTT, "Metal–Insulator Transition," Taylor & Francis, London (1974).
14. E. I. TERUKOV AND F. A. CHUDNOVSKII, *Sov. Phys. Semicond.* **8,** 797 (1974).
15. W. BRÜCKNER, W. MOLDENHAUER, B. THUSS, AND G. FÖRSTERLING, *Phys. Status Solidi A* **35,** K49 (1976).
16. V. BRÜCKNER, G. WICH, E. I. TERUKOV, AND F. A. CHUDNOVSKII, *Sov. Phys. Solid State* **17,** 1452 (1976).
17. A. HEIDEMANN, K. KOSUGE, AND S. KACHI, *Phys. Status Solidi A* **35,** 481 (1976).
18. N. N. KHOI, T. R. SIMON, AND H. K. EASTWOOD, *Mater. Res. Bull.* **11,** 873 (1976).
19. H. KUWAMOTO, H. V. KEER, J. E. KEEM, S. A. SHIVASHANKAR, L. L. VAN ZANDT, AND J. M. HONIG, *J. Phys.* **37,** C4-35 (1976).
20. W. MOLDENHAUER AND W. BRÜCKNER, *Phys. Status Solidi A* **37,** K143 (1976).
21. E. I. TERUKOV, F. A. CHUDNOVSKII, W. REICHELT, H. OPPERMANN, W. BRÜCKNER, H. P. BRÜCKNER, AND W. MOLDENHAUER, *Phys. Status Solidi A* **37,** 541 (1976).
22. W. BRÜCKNER, E. WIESER, W. MOLDENHAUER, AND W. REICHELT, *Phys. Status Solidi A* **44,** K95 (1977).
23. E. I. TERUKOV, W. REICHELT, M. P. VOLOTZKOI, F. A. CHUDNOVSKII, AND H. OPPERMANN, *Phys. Status Solidi A* **41,** 125 (1977).
24. Y. UEDA, K. KOSUGE, AND S. KACHI, *Mater. Res. Bull.* **12,** 763 (1977).
25. F. A. CHUDNOVSKII, E. I. TERUKOV, AND D. I. KHOMSKII, *Solid State Commun.* **25,** 573 (1978).
26. S. NAGATA, B. F. GRIFFING, G. D. KHATTAK, AND P. H. KEESOM, *J. Appl. Phys.* **50,** 7575 (1979).
27. S. NAGATA, P. H. KEESOM, AND S. P. FAILE, *Phys. Rev. B* **20,** 2886 (1979).
28. B. F. GRIFFING, S. P. FAILE, AND J. M. HONIG, *Phys. Rev. B* **21,** 154 (1980).