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Phase Transition in V_5O_9

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Electrical resistivity, magnetic susceptibility, and heat capacity of V_5O_9 have been measured through its phase transition temperature (T_t) around 129 K. The associated changes in enthalpy and entropy were found to be 2095 J/mole and 19.24 J/mole · deg., respectively. A qualitative thermodynamic analysis has been attempted to correlate the crystal symmetry, electrical, magnetic, and heat capacity behavior at T_t. The metal–semiconductor transition appears as a consequence of the crystallographic order–disorder process, since the electrical and magnetic contributions to configurational entropy change are relatively small. © 1985 Academic Press, Inc.

Introduction

Transition metal oxides have been extensively investigated due to their important role in catalysis and thermistor industry. The Magnéli phases, V_nO_{2n-1} and Ti_nO_{2n-1} are known to undergo electrical transition as a function of temperature (*1*, *2*). From a fundamental point of view, such materials could serve as good prototypes for elucidation of the mechanism through determination of the major factor responsible for driving the transition. Honig *et al.* (*3*) have made a thermodynamic analysis of the sharp metal-semiconductor transition occurring in V_2O_3 around 170 K and concluded that the magnetic order–disorder process drives the transition. Subsequently, Salker *et al.* (*4*) extended this analysis to V_4O_7. In the present communication, the case of V_5O_9 is discussed, with reference to its structural, electrical, magnetic, and thermal behavior near its transition around 129 K. The heat capacity of V_5O_9, which has hitherto not been reported, was measured over the relevant temperature range, since it forms an essential component of such an analysis.

Experimental Procedure

V_5O_9 was synthesized by heating an appropriate mixture of V_2O_5 and V_2O_3 in evacuated quartz ampoules; the details of the

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procedure were similar to those employed by Salker *et al.* (*4*) for V_4O_7. Formation of a single phase compound was confirmed by examination of X-ray powder diffractograms recorded on a Philips X-ray diffractometer (Model PW 1140) using CuK_α radiation filtered through Ni.

The dc electrical resistivity and magnetic susceptibility were measured point by point, after stabilizing the temperature, in the range 90 to 400 K in an oxygen-free nitrogen atmosphere.

The heat capacity at constant pressure, C_p, with benzoic acid as the standard, was recorded in the temperature range 100–200 K employing a Perkin–Elmer Model DSC-2. The rate of heating/cooling was 5°/min.

Results and Discussion

The results are depicted in Figs. 1–3.

The X-ray analysis at room temperature showed that the composition is monophasic, the observed d_{hkl} values being in good agreement with those reported by Andersson and Jahnberg (*5*) and with the triclinic crystal structure parameters reported by Marezio *et al.* (*6*).

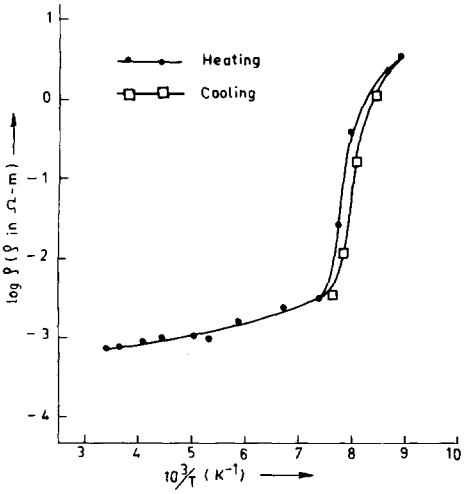

FIG. 1. Variation of electrical resistivity (ρ) of V_5O_9 with temperature (T).

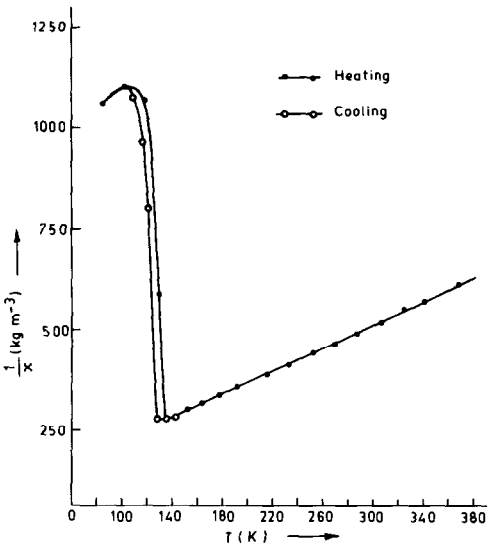

FIG. 2. Variation of magnetic susceptibility (χ) of V_5O_9 with temperature (T).

Figure 1 reveals that there is a sharp metal–semiconductor transition (T_t) around 129 K, accompanied by 2–3 orders of magnitude change in resistivity (ρ). This result

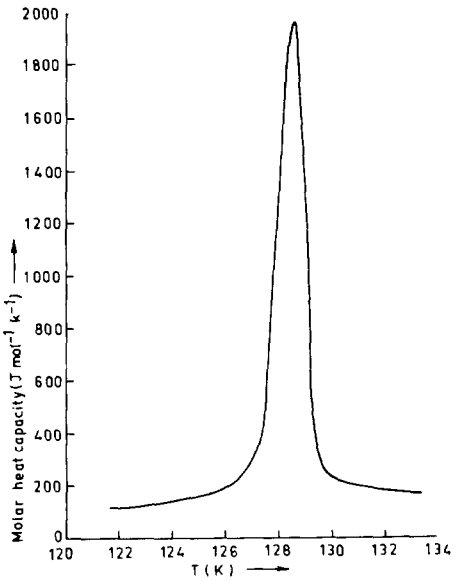

FIG. 3. Temperature variation of heat capacity (C_p) of V_5O_9 with temperature (heating cycle).

agrees well with the reports of Andrew and Chudnovskii (*2*) and Reichelt and Terukov (*7*). Figure 2 indicates a sudden change in the magnetic susceptibility (χ) at T_t. This is a paramagnetic–paramagnetic change, since the Néel temperature has been reported to be 30 K (*1*). Neglecting the Pauli paramagnetic contribution in the metallic state, the effective magnetic moment (μ_{eff}) values per formula unit are found to be 4.43 μ_B (just above T_t) and 2.02 μ_B (just below T_t) respectively. Assuming no orbital contribution to magnetic moment, the unpaired electrons below and above T_t come out to be one and three, respectively. DSC scans showed sharp peaks at 129 K (heating cycle) and 125 K (cooling cycle), respectively. Figure 3 depicts the heat capacity (C_p) variation with temperature during the heating cycle. The values of change in enthalpy (ΔH) and entropy (ΔS) of transition were determined to be 2095 ± 25 J/mole V_5O_9 and ΔS = 19.25 ± 0.05 J/mole · deg, respectively.

As a first approximation, it may be assumed that the structural, electronic, and magnetic contributions to the entropy are additive and that the thermal entropy change is the cumulative effect of the various order–disorder processes. Since the maximum number of unpaired electrons corresponding to ionic configuration of V_5O_9 ($V_2^{3+}O_3$, $3V^{4+}O_2$) is seven, the presence of three unpaired electrons above T_t indicates that the number of conduction electrons in the metallic phase cannot exceed four per formula unit. The Fermi energy (E_F) may thus be determined from the equation $E_F = (\hbar^2/2m)(3\pi^2 n)^{2/3}$, where m is the electronic rest mass, n the density of conduction electrons, $\hbar = h/2\pi$ and h, is Planck's constant. The calculated value of E_F is 1.035 eV. The entropy change associated with the electronic delocalization process may then be calculated from the relation $C_e = \pi^2 k^2 T/2E_F$ and $\Delta S_e = \int C_e \, d \ln T$, where C_e is the electronic heat capacity and k the Boltzmann constant. Thus ΔS_e = 0.437 J/mole · deg. Since the magnetic susceptibility data shows an increase of two unpaired electrons per formula unit through T_t, the magnetic entropy change is expected to be considerably less than $R \ln(2S + 1)$ = 9.13 J/mole · deg. Since the thermal entropy change is as high a 19.24 J/mole · deg, it is tempting to conclude that the major contribution to entropy comes from the structural order–disorder process.

From crystallographic studies, Marezio *et al.* (*6*) have observed that, at T_t: (a) the average V–O distance in each VO_6 octahedron changes markedly; (b) the metal–metal distances change by < 0.006 nm; and (c) the V–V distance increases across the shared octahedral faces by 0.001 nm. Although the interpretation of the displacements of different vanadium and oxygen atoms at T_t is not straightforward, because of the complexity of the triclinic structure and the correlations between displacements of neighboring atoms, it may still be concluded that this crystallogrpahic order–disorder is primarily responsible for the accompanying metal–semiconductor transition and for the magnetic susceptibility anomaly.

Finally, since the transition is accompanied by a change in unit cell volume (*6*) and a hysteresis in electrical, magnetic, and thermal parameters, it is first order in the thermodynamic sense. Therefore, it is possible to determine the pressure dependence of T_t from the Clapeyron equation. The calculated value of dT/dP comes out to be −0.0005 k/bar. This may be compared with the experimental value, −0.00087 k/bar cited by Terukov *et al.* (*8*).

References

1. J. M. Honig and L. L. Van Zandt, *Ann. Rev. Mater. Sci.* **5**, 225 (1975).
2. V. N. Andrew and F. A. Chudnouskii, *Inzh. Fiz. Zh.* **28**(5), 844 (1975).

3. J. M. HONIG, H. V. KEER, G. M. JOSHI, AND S. A. SHIVASHANKAR, *Bull. Mater. Sci.* **3**(2), 141 (1981).
4. A. V. SALKER, E. B. MIRZA, V. V. DESHPANDE, AND H. V. KEER, *Phys. Status Solidi A*, **84**(2), K105 (1984).
5. S. ANDERSSON AND L. JAHNBERG, *Arkiv Kemi* **21**(5), 413 (1964).
6. M. MAREZIO, P. D. DERNIER, D. B. MCWHAN, AND S. KACHI, *J. Solid State Chem.* **11**, 301 (1974).
7. W. REICHELT AND E. I. TERUKOV, *Z. Chem.* **17**(8), 309 (1977).
8. E. I. TERUKOV, YU. Z. SANFIROV, AND A. YU. ZYUZIN, *Fiz. Tverd. Tela* **21**(5), 1563 (1979).

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