

TGS using Eqs. (18)–(22). They are shown in Table I. It may be noted that for both crystals β seems to be slightly lower in the ferroelectric phase than in the paraelectric phase. It is conceivable that the small unit-cell distortions which accompany the transition may produce small changes in β . The number of dipoles per unit volume leads to $n = Nv_c$ (dipoles per unit cell) approximately 6 for TGS and slightly more than 12 for TGFB. These figures seem to be too high, since one would expect *two* dipoles per unit cell, corresponding to the two chemical units per unit cell. They differ by a factor of 2, which also seems unrealistic in view of the close crystallographic analogy of both systems. It may be noted, however, that for TGS⁷ and TGFB,⁸ the change in specific heat at the transition, which in the statistical dipolar theory is directly proportional to N , also indicates a factor of 2. In addition, the expected absolute value $\Delta C_p = \frac{3}{2} Nk$, with N given by

Eq. (20), while still somewhat too small (roughly by 50%) in comparison with the experimental data,⁹ is closer to these data with $n = 6$ (TGS) and $n = 12$ (TGFB) than with $n = 2$. The difference in elementary dipole moments for TGS and TGFB also seems too large, however, the resulting moments per unit volume $N\mu$ are closer to each other than the μ , as expected.

In summary, one can conclude that, while the statistical dipolar model discussed here appears too simple to be correct, it gives a fairly good picture of the transitions for TGFB and TGS, and that the characteristic parameters determined from different experimental data are reasonably consistent with each other.

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Heat Capacity of Metallic V_2O_3 at High Pressure

D. B. McWhan and J. P. Remeika

Bell Laboratories, Murray Hill, New Jersey 07974

S. D. Bader,* B. B. Triplett,*† and N. E. Phillips*

Inorganic Materials Research Division of the Lawrence Berkeley Laboratory and Department of Chemistry, University of California, Berkeley, California, 94720

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The heat capacity of V_2O_3 has been measured between 0.3 and 10 K at pressures of 1 and 25 kbar. The results confirm that the very high electronic heat capacities measured for doped samples are characteristic of pure V_2O_3 in the metallic phase.

Vanadium sesquioxide has a metal-to-antiferromagnetic-insulator transition at 1 atm and 150–160 K. The low-temperature insulating phase can be suppressed by doping [$(V_{1-x}Ti_x)_2O_3$ with $x \approx 0.05$]¹ or by changing the stoichiometry [$V_{2-x}O_3$ with $x \approx 0.03$]² or by pressure.³ In the first two cases,

heat-capacity studies at low temperatures on the metallic phases have revealed very large linear contributions.^{1,4} These have been attributed to the highly correlated nature of a metallic state on this verge of localizing to form a Mott insulator. The heat capacity and magnetic susceptibilities^{1,4} are

in qualitative agreement with the spin-fluctuation model of Brinkman and Rice.⁵ However, studies of the transport properties of doped metallic phases have shown an anomalously large dependence of the residual resistivity on doping, and this effect is at variance with the present theory.⁶ In order to establish whether the enhanced electronic contribution to the heat capacity is an intrinsic property of the metallic state or a result of doping or changes in stoichiometry, the heat capacity of metallic V_2O_3 has been measured at high pressure.

The heat-capacity measurements were made by the method used earlier for cerium⁷ and uranium,⁸ except that the pressure cell was redesigned to achieve the higher pressures that are needed to suppress the insulating phase of V_2O_3 . The sample is contained in a small piston-cylinder device in which the pressure is applied at room temperature in a conventional press and then retained by a mechanical clamp. The heat capacity of the sample plus the cell is then measured in a helium-3 cryostat by the heat-pulse method using calibrated germanium thermometers. The precision from run to run is of the order of a few tenths of 1%, so that reasonable accuracy is obtained even though the

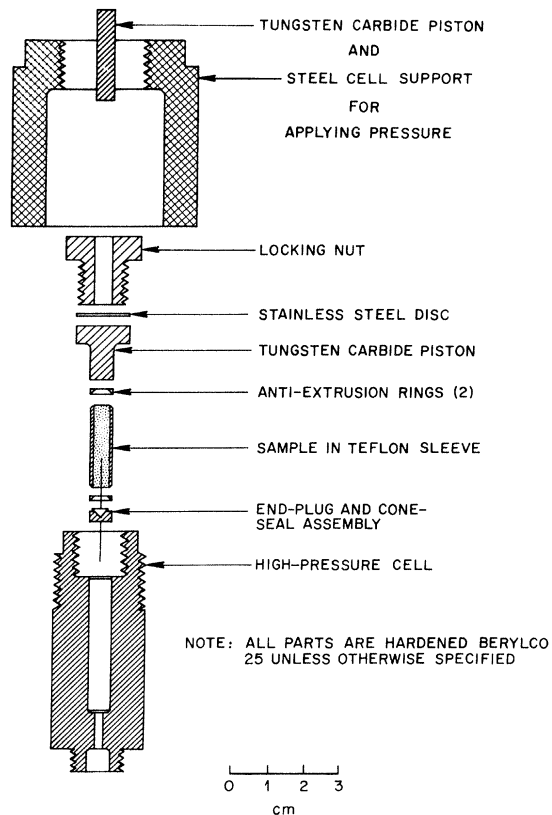


FIG. 1. Schematic drawing of high-pressure heat-capacity cell and related parts.

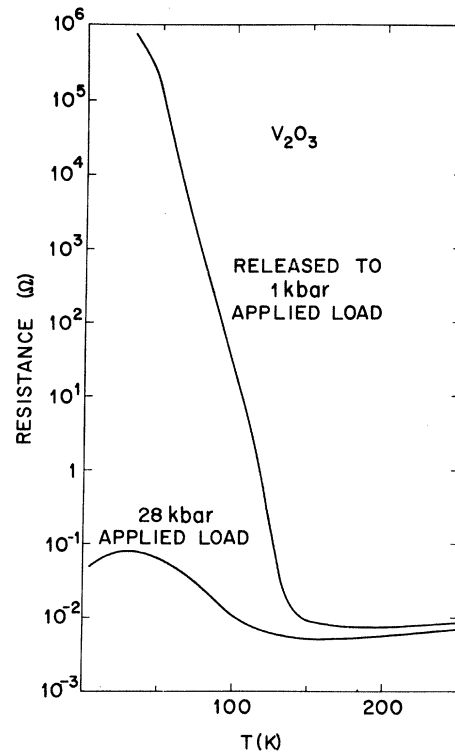


FIG. 2. Resistance vs temperature, showing partial suppression of insulating phase.

heat capacity of the sample is small relative to that of the cell.

The heat-capacity cell is shown schematically in Fig. 1. In order to achieve pressures in excess of 20 kbar, the body of the cell was made of hardened Berylco 25 (Ref. 9) and the mushroom-shaped piston was made of tungsten carbide.¹⁰ A single insulated electrical lead was added using a conventional cone seal, so that the resistance of the sample could be monitored. The cell was prestretched to 28 kbar using a tungsten-carbide end plug and a soft-copper sample, and then the inside diameter was bored to a uniform radius. A crushed crystal sample of V_2O_3 (2.93 g), which was made as described earlier,¹¹ was contained in a Teflon sleeve of 0.005-in. wall thickness. The total weight of the assembled cell was 258.6 g. The pressure was increased to 28 kbar and the locking nut was tightened. The resistance of the sample was measured as a function of temperature down to 4.2 K, where the pressure locked in was estimated¹² to be 25 kbar. The cell was warmed to room temperature, the pressure released, and the resistance measured again. The results, which are given in Fig. 2, show that some of the sample has transformed to the insulating phase in the high-pressure run. The applied pressure was again raised to the previous level and the heat-capacity was measured. A second heat-capac-

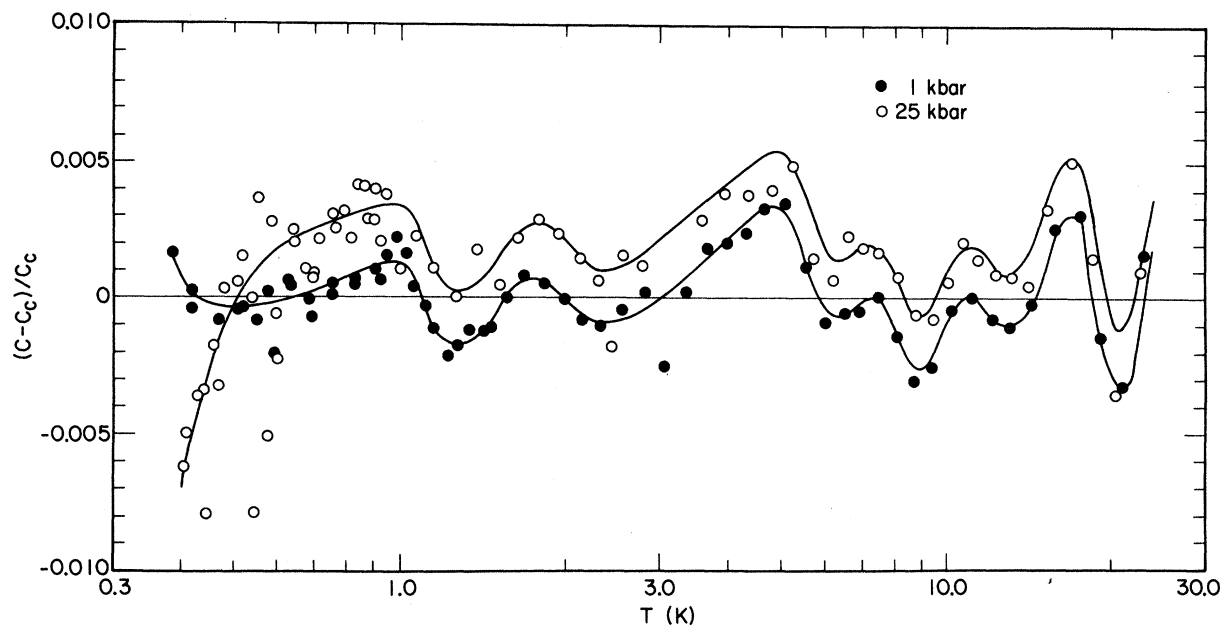


FIG. 3. Heat capacity of the empty cell at 1 and 25 kbar, plotted as deviations from Eq. (1) with the coefficients fitted to the 1-kbar data.

ity measurement was then made after the pressure was released to an estimated 1–2 kbar.

The heat capacity of the empty cell was determined at 1 and at 25 kbar by measuring the heat capacity of the cell filled with pure diamond powder, which has a negligible heat capacity compared with that of the cell.¹³ The heat capacity of the cell is shown as the deviation from

$$C_c = A_0 + \sum_{i=1}^4 A_{2i+1} T^{2i+1} \quad (1)$$

in Fig. 3. The coefficients¹⁴ in Eq. (1) were obtained by a least-squares fit to the 1-kbar data, and the heat capacity of the cell was represented by Eq.

(1) and tables that corresponded to the appropriate curve in Fig. 3. For the calculation of the heat capacities of the V_2O_3 samples, the heat capacity of the cell, as calculated from Eq. (1), was corrected by a factor found by interpolation in the proper table.

The heat capacities of V_2O_3 at 1 and at 25 kbar are plotted in Figs. 4 and 5, respectively, as CT^2 vs T^3 . In both figures the error bars indicate the effect of $\pm 0.5\%$ error in the total heat capacity.

These figures demonstrate a fit of the lowest temperature data to $C = AT^{-2} + \gamma T$, where the first term is the hyperfine heat capacity and the second term is the electronic heat capacity. At 1 kbar, $A = 7.0$

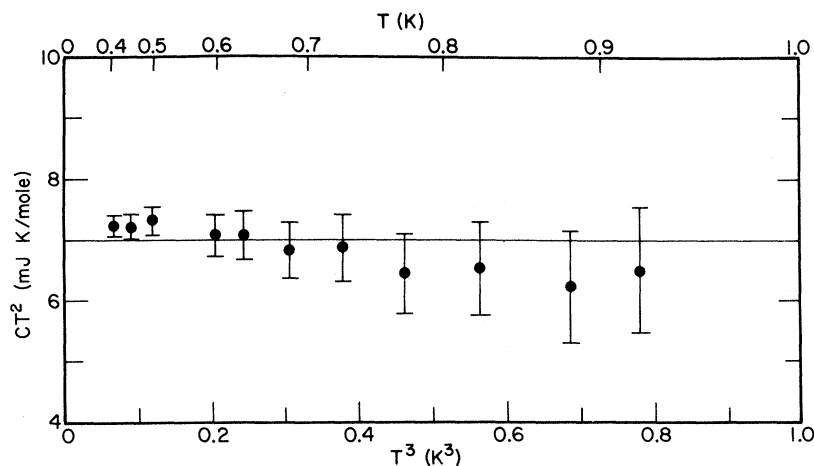


FIG. 4. Heat capacity of V_2O_3 at 1 kbar.

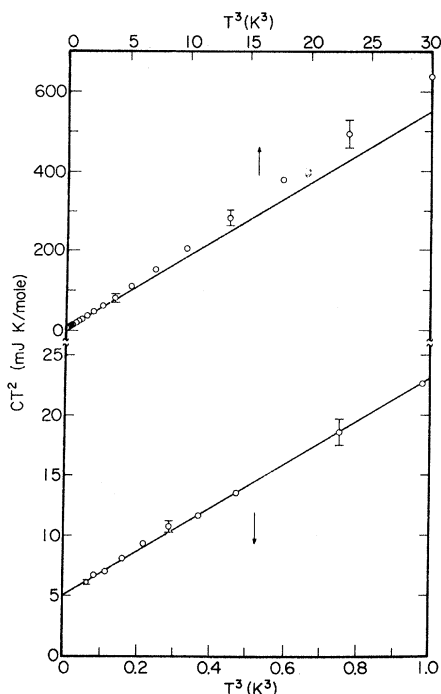


FIG. 5. Heat capacity of V_2O_3 at 25 kbar.

mJK/mole V_2O_3 and $\gamma=0$, within the experimental error. (Because the 1- and 25-kbar heat capacities of the empty cell diverge below approximately 0.5 K, as shown in Fig. 3, we have less confidence in the accuracy of the heat capacity of the cell in that region. The three lowest temperature points in Fig. 4 have therefore been given somewhat lower weight than the others.) At 25 kbar (Fig. 5) there is a clear appearance of a large γ value and a reduction in A : $A=5.0$ mJ/K mole V_2O_3 and $\gamma=18.2$ mJ/K² mole V_2O_3 . It is known that there is no magnetic ordering in the metallic phase to 4.2 K,¹⁵ and the nonzero value of A at 25 kbar suggests, in agreement with the resistivity measurements, that only part of the sample is in the metallic phase. This probably results both from the marked anisotropy in the stress dependence of the metal-insulator transition temperature, and from the fact that in-

sufficient pressure was retained on the sample after tightening the locking nut. A pressure of 25 kbar will probably have a negligible effect on the nuclear hyperfine term A , so that the ratio of A at high and low pressure can be taken as a measure of the fraction of the total sample remaining in the insulating phase. This gives a value of $\gamma=\frac{7}{2}18.2=63.7$ mJ/K² mole V_2O_3 , or $\gamma=31.9$ mJ/K² mole V. The uncertainty in γ is obviously high ($\approx 20\%$), but it is clear that γ is very large and of the order of the values reported^{1,4} for $(V_{0.92}Ti_{0.08})_2O_3$ and $V_{1.97}O_3$, 40.2 and 54.4 mJ/K² mole V, respectively. These results show that the metallic phase of pure V_2O_3 , as well as that of the doped samples, has a very high electronic heat capacity although γ is probably somewhat larger in the doped samples. As suggested previously, this is evidence of spin-fluctuation enhancement in a highly correlated metal near a Mott transition from a band to a localized state.¹

The hyperfine heat capacity of V_2O_3 in the insulating phase was measured previously by Andres.¹⁶ The internal field has also been measured by observation of the ⁵¹V zero-field nuclear resonance¹⁷ and by the inelastic spin-flip scattering of neutrons.¹⁸ The resulting coefficients, in mJ/K mole V_2O_3 , are $A=7.0\pm 0.4$ (this work), 7.4 ± 2.2 (heat capacity, Ref. 16), 9.035 ± 0.008 (NMR, Ref. 17), and 8.0 ± 1.4 (inelastic neutron scattering, Ref. 18). Our value is substantially below the NMR result, which should be the most accurate, but it agrees with the other measurements within the combined experimental errors. The reason for the discrepancy with the NMR measurements is not clear. It seems improbable that it could arise from sample-to-sample variation of the internal field, and there was no indication in the heat-capacity measurements of long relaxation times that would lead to an underestimate of A .

In conclusion, we have shown that γ for pure metallic V_2O_3 is large, and also that it is feasible to extend low-temperature heat-capacity measurements to the 20-kbar range.

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[†]Present address: Department of Physics, Stanford University, Stanford, Calif. 94305.

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¹³We are grateful to H. Tracy Hall, Jr., for suggesting the use of powdered diamond.

¹⁴The approximate values of the coefficients are $A_{-1} = 0.450$, $A_0 = 0.552$, $A_1 = 3.44$, $A_3 = 0.185$, $A_5 = 6.13 \times 10^{-5}$, $A_7 = 2.42 \times 10^{-7}$, and $A_9 = -3.09 \times 10^{-10}$, in mJ units. The T^{-1} and T^0 terms are very probably associated with the

of beryllium copper in the cell. Heat-capacity measurements on two other Berylco 25 samples [J. C. Ho and N. E. Phillips (unpublished)] have shown T^{-1} and T^0 terms of similar magnitude but differing from each other by approximately a factor of 2.

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Effect of Pressure on the Order-Disorder Transition Temperature of Vacancies in NiVTi₂S₄[†]

S. Anzai

Japan Atomic Energy Research Institute, Tokai-mura, 319-11, Japan

K. Ozawa

Solid State Physics Laboratory, Japan Atomic Energy Research Institute, Tokai-mura, 319-11, Japan

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The order-disorder transition of vacancies in NiVTi₂S₄ has been studied by electrical-resistivity measurements at hydrostatic pressures up to 7 kbar. The measured resistivity values indicate that the order-disorder transition is first order. The transition temperature as a function of pressure can be expressed by the empirical relations $T_c^h = (348.5 + 9.2P - 0.31P^2)$ K in heating and $T_c^c = (343.5 + 9.7P - 0.32P^2)$ K in cooling runs, where P is the applied pressure in kbar. Application of the Bean-Rodbell method gives the ordering energy $\Xi_0 = -0.030$ eV/Ni atom, its volume dependence $(V/\Xi) \times (d\Xi/dV) = -40$, and the compressibility $\kappa = 7 \times 10^{-4}$ kbar⁻¹ at the transition temperature at 0 kbar. The critical pressure for the first-order-to-second-order transition is estimated to be 14 kbar which nearly agrees with the value 12 kbar obtained from linear extrapolation of experimental $(T_c^h - T_c^c)$ values. The initial pressure slopes of the transition temperature are considerably larger than those of the order-disorder systems without vacancies. The pressure effect can be explained by the volume-dependent differences in the following terms: (i) the Madelung energy of the Ni ions screened by the conduction electrons, (ii) the core-core interaction energy between Ni atoms, and (iii) the self-energy of e^T orbital electrons split from t_{2g} states in Ni Wigner-Seitz cell, between the ordered and the disordered states.

I. INTRODUCTION

NiS (NiAs structure) undergoes a first-order electronic phase transition with a sharp change in electrical resistivity when it is cooled below a transition temperature.^{1,2} A band-structure calculation of this compound has been made by Tyler and Fry,³ and electronic screening of the Ni atom in NiS has been discussed by White and Mott.⁴ In NiVTi₂S₄ derived by partially substituting vacancies and Ti atoms for Ni atoms in NiS, Plovnick *et al.*⁵ have found an anomalous increase in electrical resistivity at a transition temperature $T_c = 345$ K when the compound is heated. By observing the temperature dependence of x-ray intensities for superlattice reflections, they showed that Ni atoms and vacancies are in an ordered state below T_c . The system becomes disordered above T_c . The ordered and the disordered structures are shown in Figs. 1(a) and 1(b), respectively.

The present work is the first attempt to obtain knowledge of the effect of pressure on the order-disorder transition temperature of vacancies. The purpose of this study is to investigate the electronic properties of Ni atoms in this type of crystal. The ordering energy Ξ and its volume dependence $\beta = (V/\Xi) (d\Xi/dV)$ are evaluated by the thermodynamical method of Bean and Rodbell⁶ through measurements of the transition temperature as a function of pressure. The effects of pressure and the screened character of Ni²⁺ are discussed by considering the differences between the ordered and the disordered states, in the core-core interactions,⁷ in the polar interactions,⁸ and in the self-energy of electrons in the Ni cell.

II. EXPERIMENTAL

Little is known about the magnetic properties near T_c in NiVTi₂S₄. The magnetic susceptibility χ of a powdered specimen was measured at 7 kOe