

# Lawrence Berkeley National Laboratory

## Recent Work

### Title

HEAT CAPACITY OF METALLIC V2O3 AT HIGH PRESSURE

### Permalink

<https://escholarship.org/uc/item/77j428tn>

### Authors

McWhan, D.B.

Remeika, J.P.

Bader, S.D.

et al.

### Publication Date

1972-09-01

Submitted to  
Physical Review

LBL-1467  
Preprint c.1

HEAT CAPACITY OF METALLIC  $V_2O_3$  AT HIGH PRESSURE

D. B. McWhan, J. P. Remeika,  
S. D. Bader, B. B. Triplett, and N. E. Phillips

September 1972

Prepared for the U.S. Atomic Energy Commission  
under Contract W-7405-ENG-48

**For Reference**

Not to be taken from this room



LBL-1467  
c.1

## **DISCLAIMER**

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

HEAT CAPACITY OF METALLIC  $V_2O_3$  AT HIGH PRESSURE\*

D. B. McWhan and J. P. Remeika  
Bell Laboratories  
Murray Hill, New Jersey 07974

and

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

Abstract

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  $x \approx 0.05$ <sup>1</sup> or by changing the stoichiometry  $[V_{2-x}O_3]$  with  $x \approx 0.03$ <sup>2</sup> or by pressure.<sup>3</sup> In the first two cases, heat capacity studies at low temperatures on the metallic phases have revealed very large linear contributions.<sup>1,4</sup> These have been attributed to the highly correlated nature of a metallic state on the verge of localizing to form a Mott insulator. The heat capacity and magnetic susceptibilities<sup>1,4</sup> are in qualitative agreement with the spin fluctuation model of Brinkman and Rice.<sup>5</sup> 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.<sup>6</sup> 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 cerium<sup>7</sup> and uranium<sup>8</sup> 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 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<sup>9</sup> and the mushroom shaped piston was made of tungsten carbide.<sup>10</sup> 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,<sup>11</sup> 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 tightened. The resistance of the sample was measured as a function of temperature down to 4.2 K, where the pressure locked in was estimated<sup>12</sup> 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 measured. A second heat capacity measurement was then made after the pressure was released to an estimated 1 to 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.<sup>13</sup>

The heat capacity of the cell is shown as the deviation from

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

in Fig. 3. The coefficients 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 kbar 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  $A = 7.0$  mJ-K/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 0.5K, 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  $\gamma$  value and a reduction in A:  $A = 5.0$  mJ-K/mole  $V_2O_3$  and  $\gamma = 18.2$  mJ/K<sup>2</sup>-mole  $V_2O_3$ . It is known that there is no magnetic ordering in the metallic phase to 4.2 K,<sup>15</sup> 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 insufficient 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  $\gamma = (7/2) 18.2 = 63.7 \text{ mJ/K}^2 \text{ mole V}_2\text{O}_3$  or  $\gamma = 31.9 \text{ mJ/K}^2 \text{ mole V}$ . The uncertainty in  $\gamma$  is obviously high ( $\approx 20\%$ ), but it is clear that  $\gamma$  is very large and of the order of the values reported<sup>1,4</sup> for  $(\text{V}_{0.92}\text{Ti}_{0.08})_2\text{O}_3$  and  $\text{V}_{1.97}\text{O}_3$ , 40.2 and 54.4  $\text{mJ/K}^2 \text{ mole V}$ , respectively. These results show that the metallic phase of pure  $\text{V}_2\text{O}_3$ , as well as that of the doped samples, has a very high electronic heat capacity although  $\gamma$  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.<sup>1</sup>

The hyperfine heat capacity of  $\text{V}_2\text{O}_3$  in the insulating phase was measured previously by Andres.<sup>16</sup> The internal field has also been measured by observation of the  $^{51}\text{V}$  zero field nuclear resonance<sup>17</sup> and by the inelastic spin-flip-scattering of neutrons.<sup>18</sup> The resulting coefficients, in  $\text{mJ K/mole V}_2\text{O}_3$ , are  $A = 7.0 \pm 0.4$  (this work),  $7.4 \pm 2.2$  (heat capacity, Ref. 16),  $9.035 \pm 0.008$  (NMR, Ref. 17),  $8.0 \pm 1.4$  (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  $\gamma$  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.

We thank T. F. Smith for helpful discussions and A. L. Stevens and D. Newhart for technical assistance.

REFERENCES

\* Work at Berkeley supported by the U. S. Atomic Energy Commission.

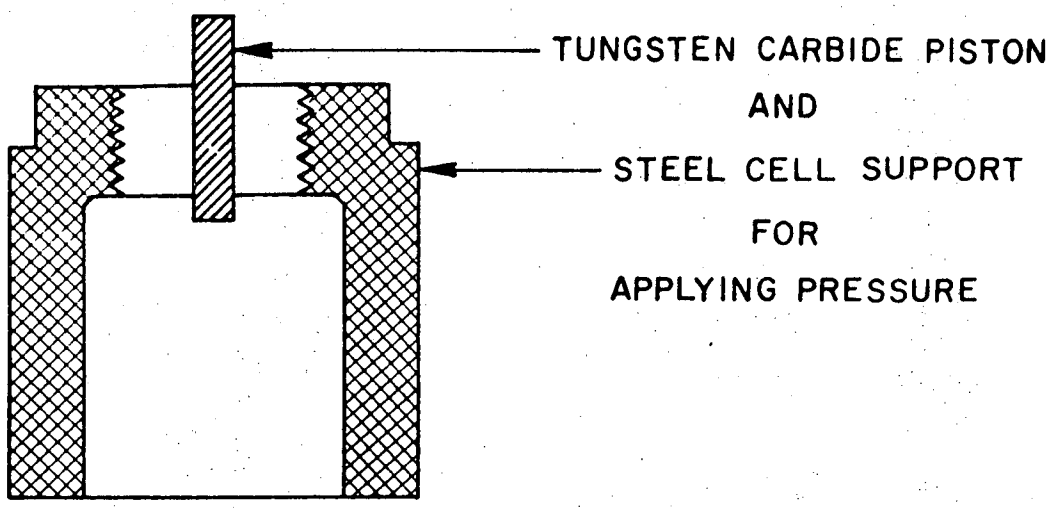
† Present address: Department of Physics, Stanford University, Stanford, California 94305.

1. D. B. McWhan, J. P. Remeika, T. M. Rice, W. F. Brinkman, J. P. Maita and A. Menth, Phys. Rev. Letters 27, 941 (1971).
2. D. B. McWhan, A. Menth, J. P. Remeika, J. Phys. (Paris) 32, C1-1079 (1971).
3. D. B. McWhan and T. M. Rice, Phys. Rev. Letters 22, 887 (1969).
4. D. B. McWhan, J. P. Remeika, J. P. Maita, H. Okinaka, K. Kosuge and S. Kachi, Phys. Rev. (B 1 Jan., ~~1973~~ ).
5. W. F. Brinkman and T. M. Rice, Phys. Rev. B2, 4302 (1970).
6. D. B. McWhan, A. Menth, J. P. Remeika, W. F. Brinkman and T. M. Rice, Phys. Rev. (B 1 Feb., ~~1973~~ ).
7. N. E. Phillips, J. C. Ho and T. F. Smith, Phys. Letters 27A, 49 (1968).
8. N. E. Phillips, J. C. Ho and T. F. Smith, Phys. Rev. Letters 17, 694 (1967).
9. Kaweck-Berylco Industries, P.O. Box 1462, Reading, Pa. 19603.
10. W. Paul, G. B. Benedek and D. M. Warschauer, Rev. Sci. Inst. 30, 874 (1959).
11. D. B. McWhan and J. P. Remeika, Phys. Rev. B2, 3734 (1970).
12. We are grateful to H. Tracy Hall, Jr., for suggesting the use of powdered diamond.

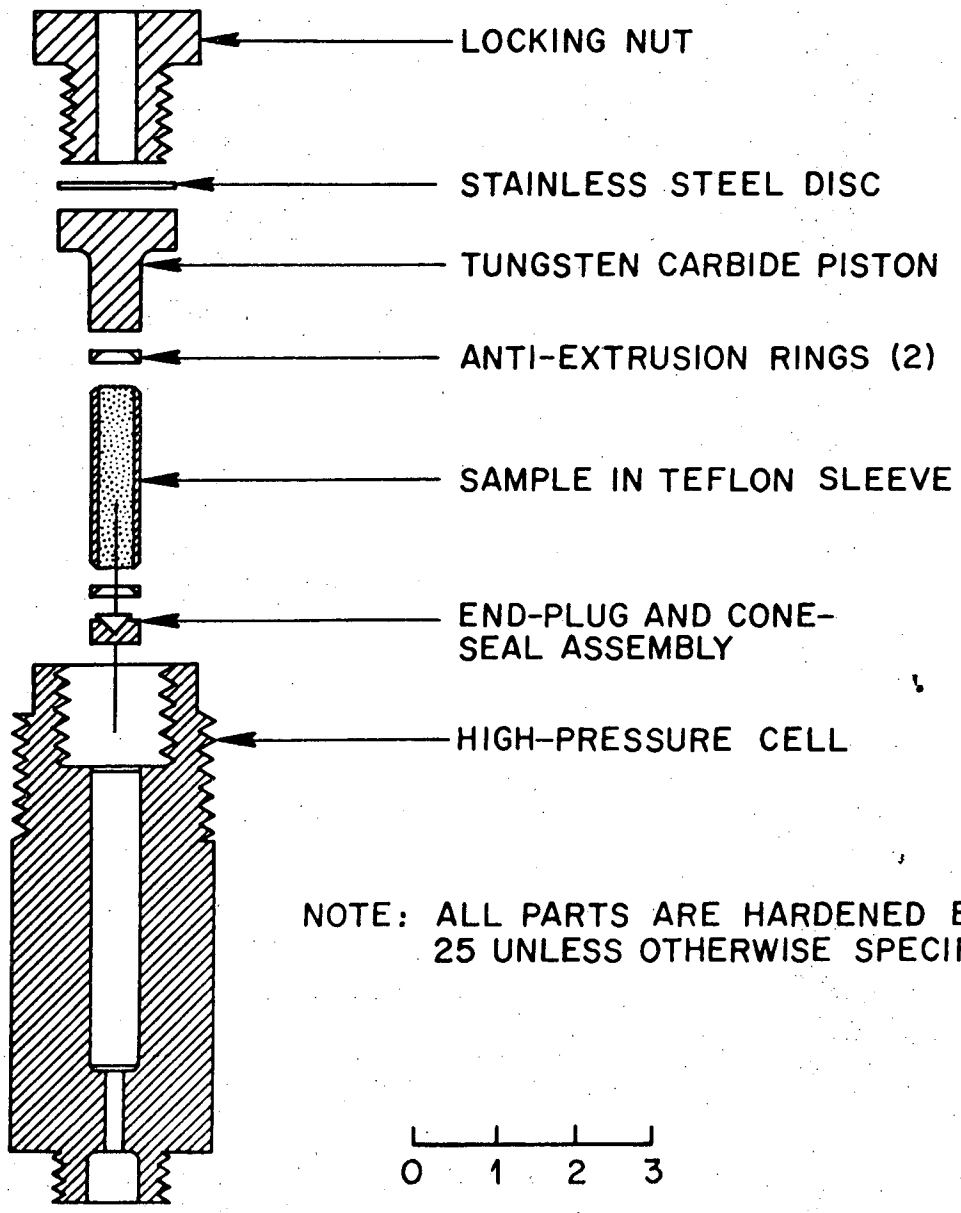
12. By comparison with strain-gauge measurements on similar cells by T. F. Smith (private communication), it was estimated that 90% of the load was retained by the locking nut at room temperature. The thermal expansions of the materials suggest there should be no further pressure loss on cooling.
13. We are grateful to H. Tracy Hall, Jr., for suggesting the use of powdered diamond.
14. The 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 241 g 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 two.
15. A. C. Gossard, D. B. McWhan and J. P. Remeika, Phys. Rev. B2, 3762 (1970).
16. K. Andres, Phys. Rev. B2, 3768 (1970).
17. H. Yasuoka, H. Nishihara, Y. Nakamura and J. P. Remeika, Phys. Letters 37A, 299 (1971).
18. A. Heidemann, Z. Physik 238, 208 (1970).

FIGURE CAPTIONS

- Fig. 1 Schematic drawing of high pressure heat capacity cell and related parts.
- Fig. 2 Resistance versus temperature showing partial suppression of the insulating phase.
- Fig. 3 The 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.
- Fig. 4 The heat capacity of  $V_2O_3$  at 1 kbar.
- Fig. 5 The heat capacity of  $V_2O_3$  at 25 kbar.



TUNGSTEN CARBIDE PISTON  
AND  
STEEL CELL SUPPORT  
FOR  
APPLYING PRESSURE



LOCKING NUT  
STAINLESS STEEL DISC  
TUNGSTEN CARBIDE PISTON  
ANTI-EXTRUSION RINGS (2)  
SAMPLE IN TEFLON SLEEVE  
END-PLUG AND CONE-  
SEAL ASSEMBLY  
HIGH-PRESSURE CELL

NOTE: ALL PARTS ARE HARDENED BERYLCO 25 UNLESS OTHERWISE SPECIFIED

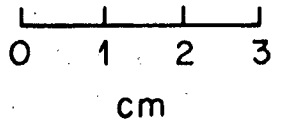


Fig. 1

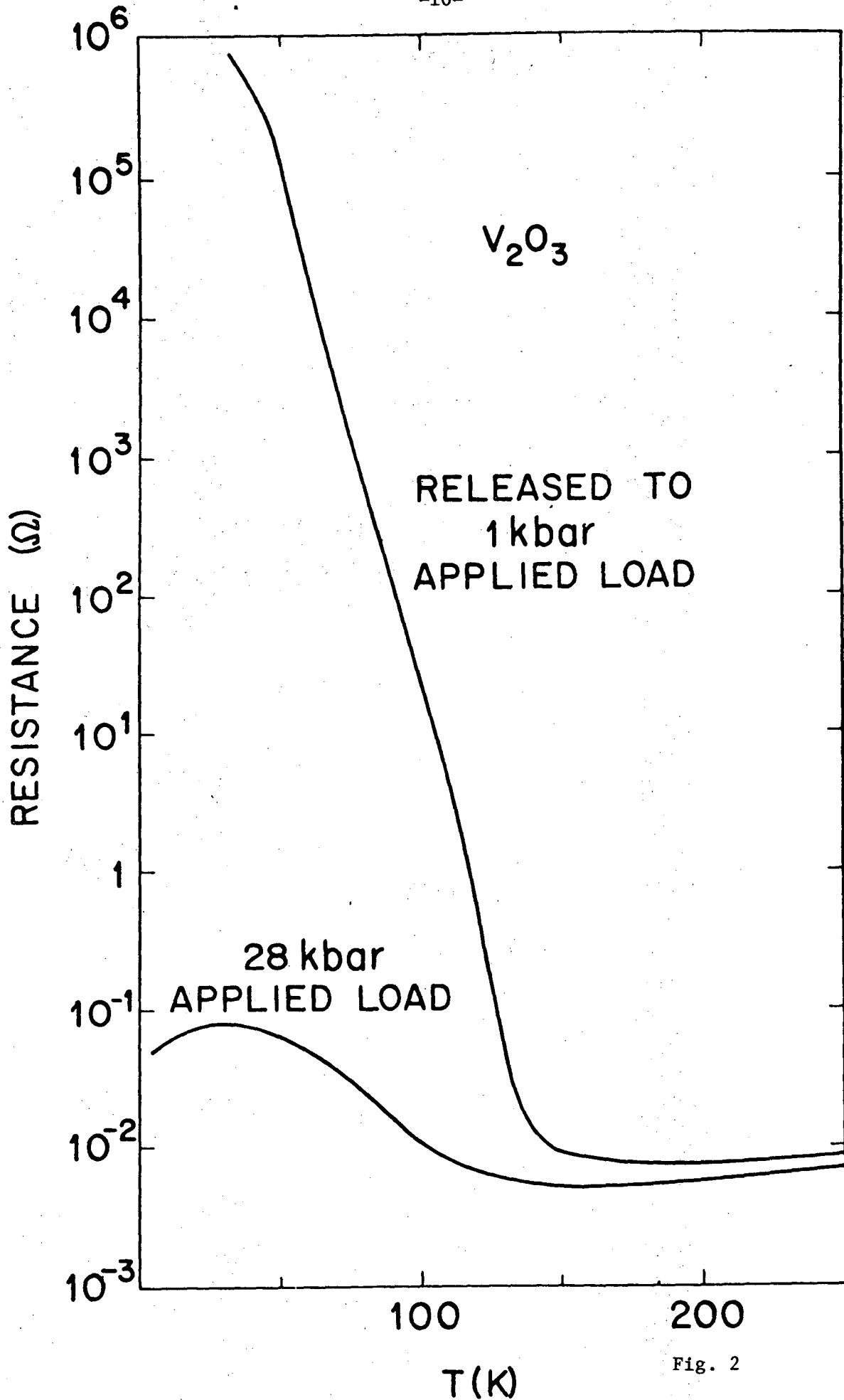
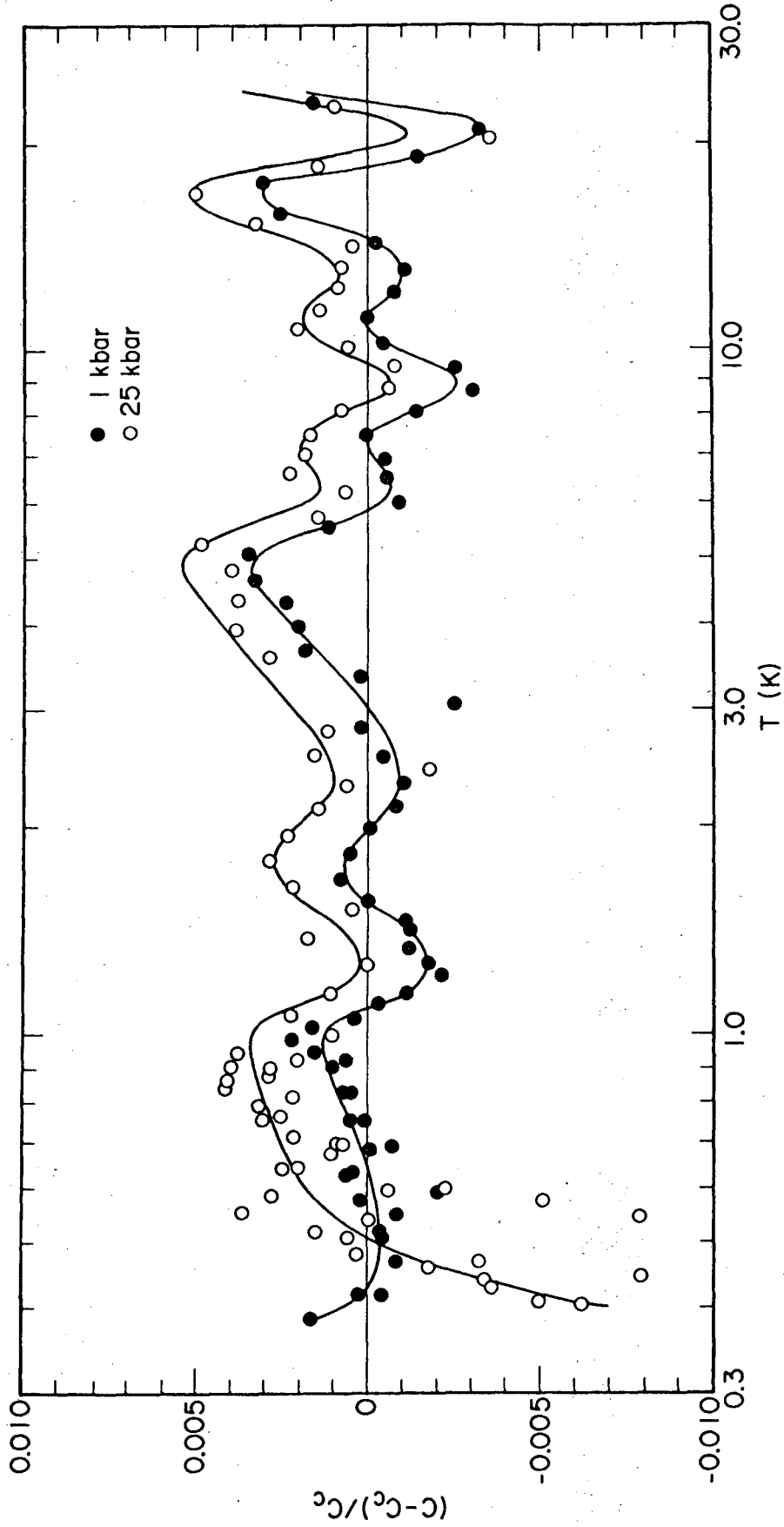
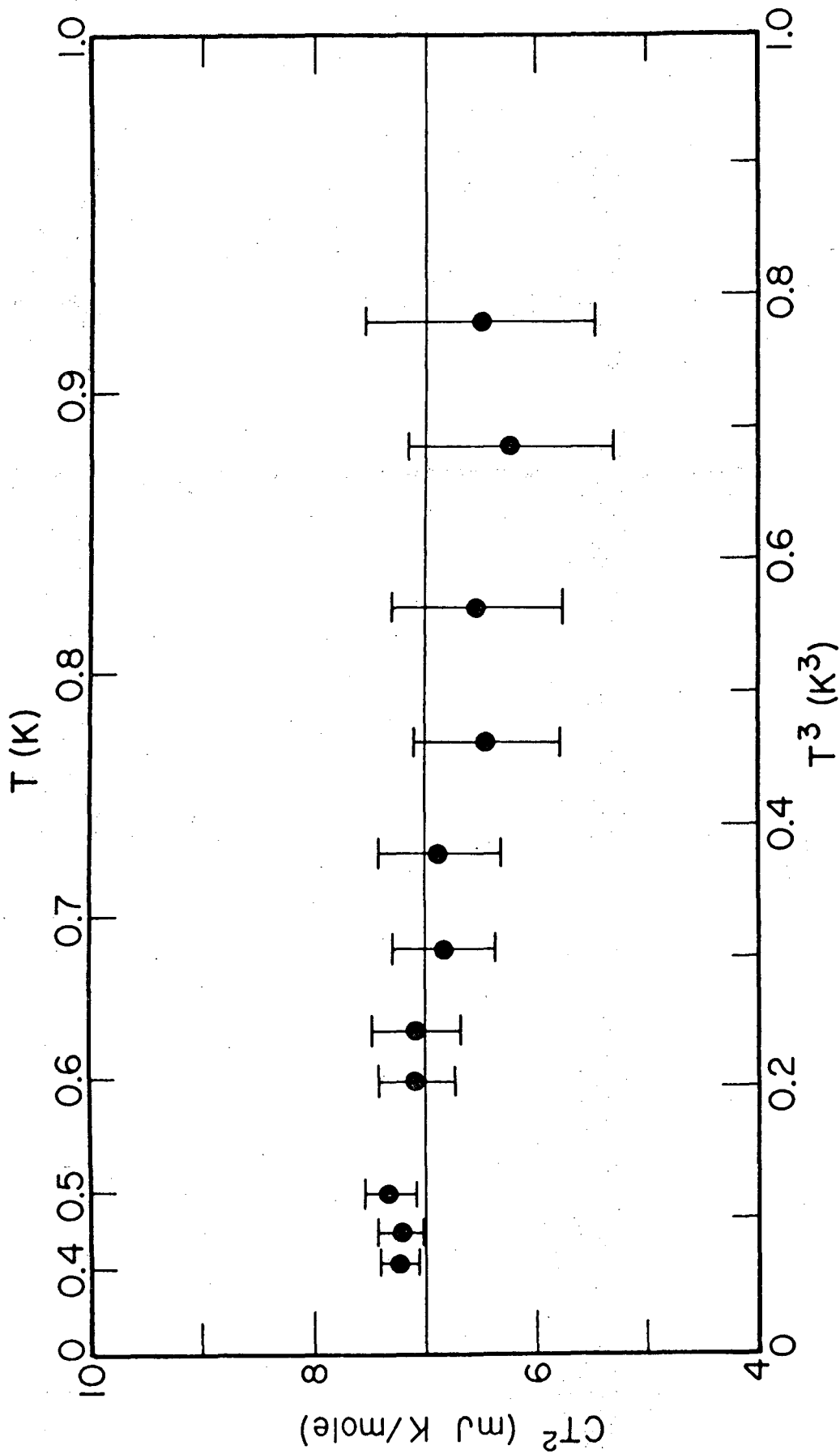


Fig. 2



XBL 726-3676

Fig. 3



XBL 726-3677

FIG. 4



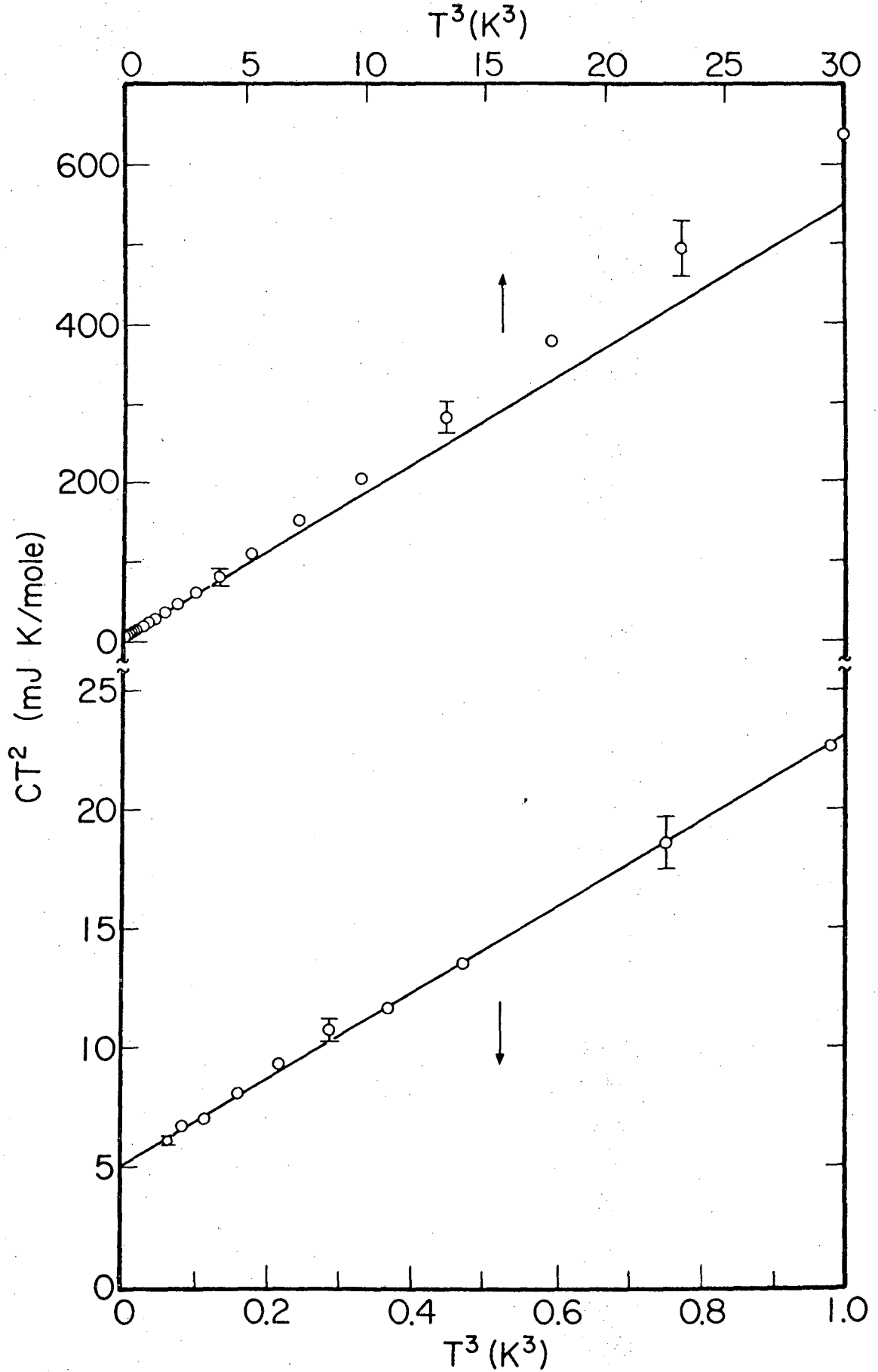


Fig.5

LEGAL NOTICE

*This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.*

TECHNICAL INFORMATION DIVISION  
LAWRENCE BERKELEY LABORATORY  
UNIVERSITY OF CALIFORNIA  
BERKELEY, CALIFORNIA 94720