resonance was observed to disappear, which Jones correctly attributed to antiferromagnetism. At temperatures above 300 °K [E. D. Jones, J. Phys. Soc. Japan 27, 1692 (1969)] an anomaly was noted in that the resonance frequency shifts no longer varied proportionally with the susceptibility. We believe [A. Menth and A. C. Gossard, Proceedings of 1970 Grenoble Internation Conference on Magnetism, Grenoble, France (unpublished)] that this anomaly resulted from hyperfine coupling changes associated with the gradual supercritical change toward insulating behavior at high temperatures and thus is not directly related to the present investigation of the high-pressure metallic state.

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Observation of Nuclear Specific Heat in V_2O_3

K. Andres
Bell Telephone Laboratories, Murray Hill, New Jersey 07974

(Received 12 November 1969)

In an attempt to determine the magnetic moment of vanadium in the proposed antiferromagnetic state in insulating V_2O_3, the nuclear specific heat has been measured in the temperature range below 0.5°K. A nuclear Schottky anomaly varying with T^{-2} is observed which indicates an over-all hyperfine splitting of 74 m °K and a hyperfine field of 168 kOe. Using a hyperfine coupling constant deduced by Jones from Knight-shift measurements in the metallic state of V_2O_3, this hyperfine field is consistent with an ordered moment of $1.2\,\mu_B$ per vanadium ion.

INTRODUCTION

Recent additional experimental information[1-3] on the metal-insulator transition of V_2O_3 has renewed the interest in this material and called for a reexamination of theoretical models regarding the driving force of this transition. Due to lack of evidence from magnetic susceptibility and neutron diffraction data, V_2O_3 has been considered for a long time to be nonmagnetic in its insulating state below the phase transition temperature of 150 °K. Jones[4] first suggested an antiferromagnetic state since he observed the disappearance of the ^{51}V NMR signal below 150 °K. Recent neutron scattering data now seem to indicate local moments of $1.2\mu_B$ on the vanadium sites.[5] To provide an independent determination of the ordered moment, we have measured the specific heat of V_2O_3 down to a temperature of 0.1 °K in order to search for a nuclear Shottky anomaly of the ^{51}V nucleus ($I=\frac{7}{2}$, $g_n=1.47$). We do indeed observe a nuclear Schottky anomaly which is consistent with an over-all hyperfine splitting of $k\cdot 74$ m°K, which would correspond to a nuclear-resonance frequency of 192 MHz. A splitting of the same order of magnitude has recently also been observed by inelastic neutron scattering between the hyperfine levels of ^{51}V in V_2O_3.[6] In Sec. I we briefly describe the experimental arrangement which we have used and in Sec. II we compare the result to other existing data on the magnetic properties of V_2O_3.

I. EXPERIMENTAL DETAILS

The measurements were carried out in an adiabatic demagnetization cryostat in which powdered chromium potassium alum mixed with Apiezon grease and about 10^3 No. 42 H. F. copper wires was used as a cooling salt. This salt, as well as a shield around it, is demagnetized from 30 kOe after it has been precooled to 0.5 °K through superconducting lead thermal switches by means of liquid He^3. After demagnetization, the temperature of the salt (~12 m°K) can be maintained for about 1.5 h, the average stray heat leak during this time being about 2 erg/min. The sample consisted of 1.7 g of powdered (100 mesh) V_2O_3 which was in Apiezon grease contact with 800 No. 42 H. F. copper wires. These Cu wires were connected to the Cu wires of the salt pill through a superconducting tin thermal switch

(Fig. 1). Arsenic-doped germanium resistors calibrated against a cerium magnesium nitrate magnetic thermometer are used for thermometry. One of the major difficulties of this experiment is the long thermal relaxation time of the sample at these temperatures, partly due to the low thermal conductivity of Apiezon grease and partly due to the long nuclear spin-lattice relaxation time T_1. Long T_1's are to be expected, since V_2O_3 is an insulator at low temperatures. Although one might argue that spin-wave excitations from the antiferromagnetic ground state would shorten this relaxation time, we can anticipate a gap in the spin-wave spectrum at $k=0$ due to finite anisotropy energy which will lead to a vanishingly small excitation probability of spin waves below 0.5 °K. An anisotropy energy is to be expected since the crystal symmetry of V_2O_3 in the antiferromagnetic state below 150 °K is monoclinic. The total apparent thermal relaxation time of the sample is about 20 sec at 0.4 °K, rising to 1 min at 0.1 °K. Unfortunately, we are not able to extract T_1 out of our data, since we cannot distinguish the thermal resistance of the Apiezon grease from the thermal resistance between the phonons and the nuclear spin system in the crystal.

The procedure for taking specific-heat data in the temperature range below 0.5 °K is the following:

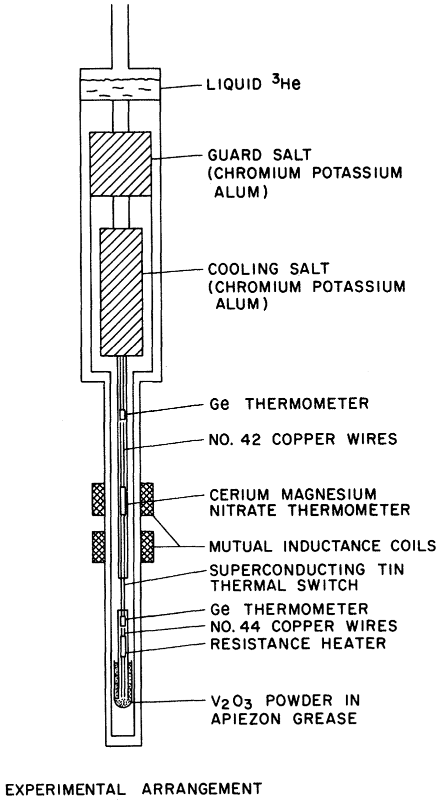

FIG. 1. Experimental arrangement.

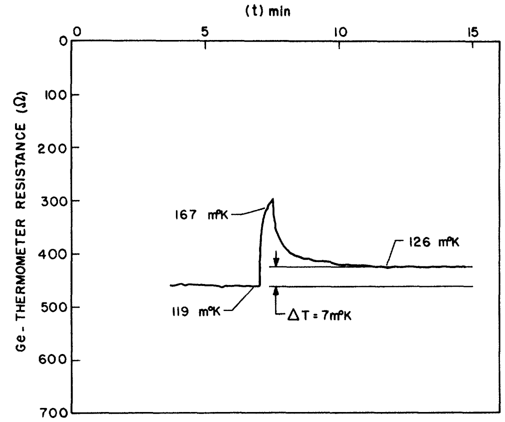

FIG. 2. Typical temperature recording during a heat pulse of 177.5 erg at 119 m °K.

After the salt pill has been cooled to about 17 m °K, the superconducting tin switch is opened by an external magnetic field. It then takes the sample about 30 min to cool from 0.5 to 0.1 °K. Meanwhile, the salt pill warms up to about 22 m °K because of the nuclear entropy coming out of the V_2O_3 sample. The tin switch is then closed and heat pulses of the order of 200 erg are applied to the sample by means of a resistance heater, resulting in temperature increments of the order of 10 m °K. A typical temperature recording during a heat pulse is shown in Fig. 2, illustrating the difficulties arising from the relatively poor thermal contacts and the associated long relaxation times which limit the accuracy of the data. The results are shown in Fig. 3, where the specific heat in units of R per mole of vanadium is plotted against temperature. Results of different runs using different thermometers with different calibrations agree, and the specific heat between 0.2 and 0.4 °K can, within the experimental uncertainty, be fitted to a T^{-2} law. The high-temperature expan-

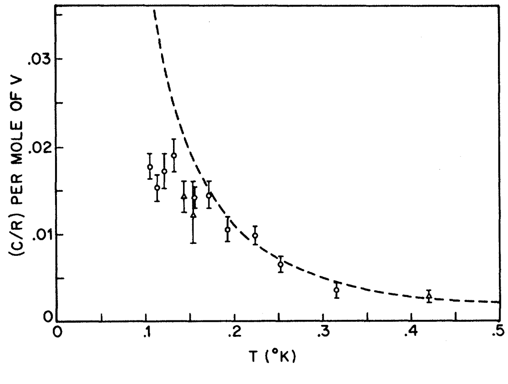

FIG. 3. Specific heat per mole of vanadium of V_2O_3 below 0.5 °K. Triangle and circle points are from different runs with different thermometer calibrations.

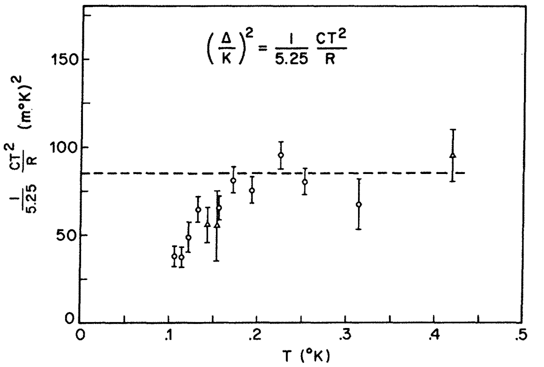

FIG. 4. Plot of $CT^2/5.25\,R$ versus T for V_2O_3 below 0.5 °K. The departure from the T^{-2} law below 0.2 °K is due to lack of thermal contact between the thermometer and the vanadium nuclear spins.

sion of the nuclear Schottky anomaly is given by

$$\frac{c}{R}=\frac{\Delta^2}{k^2T^2}\left(\frac{1}{8}\sum_1^8 n^2-\frac{1}{64}\left(\sum_1^8 n\right)^2\right)=5.25\left(\frac{\Delta}{kT}\right)^2 ,$$

where Δ is the adjacent splitting between the eight nuclear levels of ^{51}V. The peak of the Schottky anomaly actually occurs at about 10 m °K, well below the present range of measurements. Figure 4 is a plot of $(1/5.25)cT^2/R$ against T, which should yield a straight horizontal line. The points above 0.17 °K do scatter around a mean value of Δ^2/k^2 of 85 (m °K)^2, while those below 0.17 °K fall considerably below this value. We must, however, assume that these latter points no longer represent the true nuclear specific heat, since the thermometer may lose contact with the nuclear spin system. Below 0.17 °K, the lower the nuclear spin temperature, the more the the temperature of the thermometer will deviate towards the salt temperature (~ 22 m°K), since the thermal resistance between it and the spin system becomes comparable with the thermal resistance of the superconducting tin switch. The thermometer will thus indicate a quasisteady temperature less than the spin temperature, and the deviation will be larger for lower spin temperatures. During a heat pulse generated by the resistance heater, the thermometer temperature is above the spin temperature of the V_2O_3 sample. After the heat pulse, the thermometer indicates again a temperature lower than the spin temperature, but the difference between the two temperatures will be smaller than before the pulse. The temperature increment indicated by the thermometer will thus be larger than the temperature increment in the spin system. Therefore, below 0.17 °K, the true specific heat and also the true spin temperature will be larger than the values measured with the Ge thermometer. The dotted lines in Figs. 3 and 4 correspond to a value of Δ/k of 9.2 m°K or a nuclear-resonance frequency of 192 MHz. With a g value of 1.47 for ^{51}V this corresponds to a hyperfine field of 168 kOe. The estimated accuracy of this result is ± 15%.

II. DISCUSSION

In what follows, we try to determine the magnitude of the ordered moment in V_2O_3 from the observed hyperfine splitting. We define a hyperfine coupling parameter A by writing

$$E_n=H_{\mathrm{hf}}\,g_nI_{z,n}=A\langle\mu_z\rangle g_nI_{z,n}, \quad n=-I,\ldots,+I \quad (1)$$

where $\langle\mu_z\rangle$ is the expectation value of the ordered moment and A is measured in units of kOe per Bohr magneton. Experimental information on the magnitude of A is available from two sources: (a) A has been measured for V^{3+} in Al_2O_3, and (b) A has been inferred from Knight-shift measurements on ^{51}V in the metallic state of V_2O_3 (i.e., above 150 °K). In the first case, the $^3F_2$ state of the free vanadium ion is crystal field split into a low-lying orbital singlet which is threefold spin degenerate ($S=1$). Spin-orbit coupling splits this triplet into a singlet ($S_z=0$) and a doublet ($S_z=\pm 1$). EPR measurements[7,8] yield a g value of 1.910 and a hyperfine coupling constant of 0.959×10^{-2} cm^{-1} for this doublet, from which we compute a value for the parameter A defined in (a) of 133 kOe per Bohr magneton. In the second case, Jones[4] deduces A by comparing the temperature dependence of the Knight shift with the temperature dependence of the magnetic susceptibility in the metallic state of V_2O_3. He obtains a value for A of 140 koe per Bohr magneton. Using this latter value, our observed hyperfine field of 168 kOe would indicate an ordered moment of 1.2 μ_B per vanadium ion. This is a surprisingly low value. One would assume the orbital momentum in V_2O_3 to be quenched at least as much as for V^{3+} in Al_2O_3 and expect the ordered moment to be closer to the spin-only value of $2\mu_B$ for two d electrons per vanadium ion. It should be pointed out that our value of 1.2 μ_B for the ordered moment agrees well with the number of 1.2 μ_B which is suggested by recent neutron diffraction data[5] on antiferromagnetic V_2O_3. However, our above estimate is very tentative and has to be treated with caution for the following reason: We do not know the exact ratio of spin and orbital contribution to the ordered moment, since we have no knowledge of its g value in either the metallic or the insulating state. The hyperfine coupling parameter A is very critically dependent on g. According to an estimate by Jones[4] the hyperfine field per unit spin angular momentum is − 280 kOe, whereas a unit of orbital momentum produces + 790 kOe for V^{3+}. A 10% change in g thus results in about a 40% change in A. For that reason, the agreement between the two estimates given above for the value of of A (133 and 140 kOe/μ_B) may, in fact, be fortuitous. Moreover, the value of A for V^{3+} in the metallic state of V_2O_3 may differ from its value in the insulating state because of a different degree of covalency of the vanadium ion in the two states.

Recent experiments by Gossard, McWhan, and Remeika[3] have shown that no magnetic order occurs in the metallic state of V_2O_3 (under pressure) down to a temperature of 4.2 °K. It is, therefore, tempting to associate the moment reduction from the expected value of 2 to 1.2 μ_B with the fact that insulating V_2O_3 is close to being a metal, with large overlap between d states on neighboring vanadium ions by way of the intervening oxygen ions. This would imply that there is an increased probability of finding a d electron on its neighboring V site to which it is antiferromagnetically coupled so that it reduces the net moment of the ion pair involved. However, before such speculations can be made, an experimental determination of the g value of the ordered moment seems necessary in order to substantiate the above estimate.

ACKNOWLEDGMENTS

I would like to thank A. M. Clogston, who initiated this work, for many stimulating and illuminating discussions. My thanks also go to J. P. Remeika, who kindly furnished the V_2O_3 crystals and to S. Geschwind, D. B. McWhan, and A. C. Gossard for interesting discussions and for letting me use some of their results prior to publication.

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Crystal Structure of the Low-Temperature Antiferromagnetic Phase of V_2O_3

P. D. Dernier and M. Marezio
Bell Telephone Laboratories, Murray Hill, New Jersey 07974

(Received 26 May 1970)

At ~155 °K, the metallic corundum structure of V_2O_3 distorts to an insulating monoclinic one. Structural refinements of this low-temperature phase by x-ray diffraction techniques show an increase in the nearest-neighbor vanadium – vanadium distances at the transition. This is in direct contrast to previously reported distortion models. In the a-c plane of the monoclinic structure, the vanadium – vanadium distance across the shared octahedral face increases from 2.697 to 2.745 Å, while the vanadium – vanadium distance across the shared octahedral edge increases from 2.882 to 2.987 Å when proceeding from the corundum structure to the monoclinic one. The oxygen octahedra become skewed about the central vanadium atom, while the average vanadium – oxygen distance remains essentially constant. The expansion of the vanadium – vanadium distances associated with this transition is similar to the Mott transition observed in the Cr_2O_3-V_2O_3 system in which the conduction electrons localize on their ionic sites when proceeding from the metal phase, α-V_2O_3, to the insulating one, α-$(V_{0.962}Cr_{0.038})_2O_3$.

INTRODUCTION

At room temperature V_2O_3 has the corundum structure, space group $R\bar{3}c$, with approximate hexagonal close packing of the oxygen atoms and the vanadium atoms occupying $\frac{2}{3}$ of the octahedral sites. The compound is unique among the isostructural sesquioxides with respect to its unusually high c/a ratio and metallic conductivity. Recently, one of us has reported the structural refinements of single crystals of V_2O_3 and $(V_{0.962}Cr_{0.038})_2O_3$ near the metal-insulator (M-I) transition.[1] It has been observed that this M-I transition in the Cr_2O_3-V_2O_3 system[2] is accompanied by a discontinuous change in the c/a ratio while the nearest-neighbor vanadium – vanadium distances increase, and the vanadium – oxygen distances remain essentially unchanged.

At low temperature, 150–160 °K, the corundum V_2O_3 distorts to a structure with monoclinic symmetry,[3] which has been reported as insulating and