

High-Pressure Nuclear Resonance Study of the Metal-Insulator Transition of V_2O_3

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 (Received 24 April 1970)

^{51}V nuclear magnetic resonance (NMR) has been observed in metallic V_2O_3 at pressures up to 65 kbar at 4.2 °K. Pressures greater than 26 kbar suppress the metal-to-antiferromagnetic insulator transition, leaving V_2O_3 a metal at 4.2 °K. ^{51}V NMR shows that the metallic phase, unlike the insulating phase, does not order magnetically down to 4.2 °K. The measurements are the highest-pressure resonance measurements which have been reported in the He temperature range. Knight shifts and relaxation times were measured, the Knight shift having an anomalously strong dependence on volume. The relaxation time allows an upper limit of 10^{-13} sec to be placed on the spin fluctuation lifetime of the d electrons.

INTRODUCTION

V_2O_3 is one of the few materials which are known to exhibit a temperature-induced insulator-metal transition.¹ The low-temperature insulating phase is antiferromagnetic,² but the magnetic character of the metallic phase is not clear. Recently it has been found that the addition of 1% Cr_2O_3 to V_2O_3 results in a first-order transition with no change in long-range order from metallic (M) to insulating (I) properties at room temperature.³ Pure V_2O_3 must then be considered as part of a more general phase diagram consisting of surfaces for a metal-paramagnetic insulator (M-I) transition and for a metal-antiferromagnetic insulator transition (M-AF) as a function of temperature, pressure, and composition. For $x \gtrsim 0.02$ in $(V_{1-x}\text{Cr}_x)_2\text{O}_3$, there is a purely magnetic (AF-I) transition as a function of temperature. The M-I transition has been interpreted as a Mott transition.⁴ In order to elucidate the mechanism of this transition a more complete characterization of the magnetic properties of the metallic phase is necessary.

At 1 atm it is not possible to study the metallic phase at very low temperatures because of the M-AF transition, but at pressures in excess of ≈ 26 kbar the AF phase of V_2O_3 is suppressed.⁵ If there were local moments in the metallic phase they should order magnetically at low temperatures. Studies of the electrical resistivity as a function of temperature at pressures above 26 kbar did not reveal any anomalies which could be associated with magnetic ordering.⁵ These are only indirect measurements of the magnetic character of metallic V_2O_3 , so it was decided to study the ^{51}V nuclear magnetic resonance (NMR) at high pressure and low temperature. These measurements detect the very sizable ($\sim 10^5$ Oe/ μ_B) hyperfine fields resulting from magnetic ordering and thus provide a direct and critical test of the magnetic character. In addition, it is possible with this technique to measure the effect of the imaginary parts of the electronic susceptibility on nuclear relaxation.

In the present paper, the techniques necessary to do nuclear magnetic measurements at 4.2 °K and pressures in excess of 26 kbar are described. Evi-

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dence will be presented to show that no magnetic order occurs in the metallic state down to 4.2 °K and that the material must thus be described from a band point of view. Nuclear relaxation measurements are used to estimate the lower limit on the bandwidths.

I. EXPERIMENTAL

For simultaneous low-temperature high-pressure experiments the pressure transmitting medium which is closest to true hydrostatic conditions is solid He. However, a practical pressure limit is set at ≈ 10 kbar by the occurrence of leaks in the pressure system. In order to reach the pressures of interest for the present experiment it was necessary to use a supported multianvil device and a solid pressure transmitting medium. A conventional girdle die employing AgCl as the pressure transmitting medium was used. The whole device was then mounted in a cryogenic press capable of delivering 300 tons to a chamber at 4.2 °K. Part of the experimental apparatus is shown in Fig. 1. The magnetic field is produced by a split-coil superconducting solenoid which is capable of reaching 10 kG. In order to produce a homogeneous magnetic field at the sample, the high-pressure die was constructed of nonmagnetic components. The support rings are made of Discaloy and the tungsten carbide was Kennametal 601 (anvils) and 602 (girdle). K 601 is a binderless carbide which is very difficult to use because of its brittle nature. To improve slightly the lifetime of the die, K 602 which contains 0.5% Cr binder was used in the girdle.

The powdered V_2O_3 was made from high-purity V_2O_5 supplied by Johnson Matthey. The total cation impurity content of the V_2O_3 was determined by emission spectrographic analysis to be less than 5 ppm. The powdered V_2O_3 was placed in a Pt boat in an atmosphere-controlled tube furnace. The temperature was slowly raised to 1000 °C in a

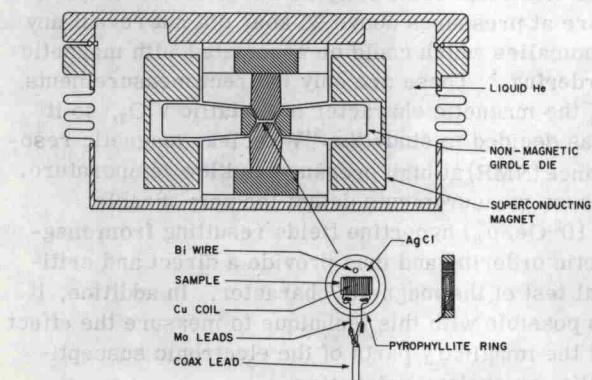


FIG. 1. Schematic diagram of the liquid-helium-cooled high-pressure press, superconducting magnet, and sample cell for nuclear resonance measurements.

stream of hydrogen over a period of 24 h. The furnace was maintained at 1000 °C for 16 h. The furnace power was turned off and the sample allowed to cool to room temperature. The resulting V_2O_3 was checked by powder x-ray diffraction analysis, and it was found to be single-phase material with lattice parameters in agreement with those found in other studies.⁶

The sample and coil arrangement are shown in the inset of Fig. 1. A description of the multianvil cryogenic high-pressure device has been given elsewhere.⁷ From the point of view of the NMR studies, one would like to have the largest possible sample. On the other hand, from the high-pressure point of view one would like a small sample immersed in a large volume of the pressure transmitting medium in order to minimize the pressure gradients and to obtain a reliable pressure calibration. As a compromise, a coil of 0.05 cm³ was used and encased in 0.22 cm³ of AgCl. The sample was slightly compacted in a mold and then GE 7031 adhesive was allowed to soak into the compact in order to give mechanical stability and to separate the sample particles. This procedure was found sufficient to keep enough of the V_2O_3 particles electrically insulated from one another to allow penetration of the rf field into the sample. The 25–30-turns coil of 0.13-mm-diam insulated copper wire was wound around the sample. After coating with GE 7031, the assembly was fitted between AgCl disks which were cut out to hold the sample. The axis of the coil was perpendicular to the magnetic field. The ends of the coil were wrapped around 0.13-mm gold-plated Mo wire leads which passed through the pyrophyllite gasket and were then soldered to a coaxial cable which came out of the cryostat.

In order to calibrate the pressure against the load applied to the high-pressure die, a bismuth wire was mounted axially in the cell next to the sample and a two-lead electrical resistivity measurement made across the anvils. The transition at 25.5 kbar⁷ was observed at room temperature and a linear calibration at all temperatures was assumed. It is known that AgCl becomes brittle at low temperatures, and it is not clear that the pressure calibration is the same at low temperature and at room temperature. Indirect evidence can be obtained from earlier work on the suppression of the transition in V_2O_3 . In the earlier studies, the phase diagram was determined by repeated cycling through the transition as the apparatus was cooled to 4.2 °K and warmed again.⁵ In a separate run the pressure was advanced at room temperature to just above the critical pressure (≈ 26 kbar), and then the apparatus was cooled to 4.2 °K and cycled through the transition. The transition was observed at similar applied loads in each experiment so the