ANTIFERROMAGNETISM IN V_2O_3[†]

R. M. Moon
Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830

(Received 27 July 1970)

The existence of antiferromagnetic order in the monoclinic phase of V_2O_3 has been confirmed by a neutron polarization analysis experiment. Conventional neutron-diffraction experiments on powders and single crystals have been performed to determine the magnetic structure. The observations are in accord with a model in which the V moments are ferromagnetically coupled in monoclinic (010) layers, or hexagonal (110) layers, with a reversal between adjacent layers. The ordered moment is $(1.2 \pm 0.1)\mu_B$ per V atom.

The question of antiferromagnetic order in V_2O_3 has been clouded for many years by apparently conflicting experimental evidence. Early powder susceptibility measurements by Wucher[1] were interpreted as indicating antiferromagnetic order, but the opposite conclusion was reached by Carr and Foner[2] after making single-crystal susceptibility measurements. Various neutron-diffraction experiments failed to show definite evidence in favor of magnetic order.[3-4] However, convincing positive evidence was supplied by the NMR work of Jones[5] and the Mössbauer work of Shinjo and Kosuge.[6] These experiments seemed to put the existence of long-range magnetic order beyond doubt, but why had not magnetic peaks been detected by neutron diffraction?

In conventional neutron diffraction it is not possible to definitely identify magnetic peaks when the magnetic transition occurs simultaneously with a structural transition. In V_2O_3 the suspected magnetic transition occurs at about 170°K when the crystal transforms from a high-temperature rhombohedral phase (Al_2O_3) to a low-temperature monoclinic phase. Paoletti and Pickart[3] describe a low-angle peak in the monoclinic phase which showed no temperature dependence between 4.2 and 77°K but which was not present at 295°K. They argued that this was probably a nuclear line associated with the monoclinic phase. In view of the later evidence showing some sort of magnetic order, it seemed likely to us that this was a magnetic peak.

We have recently developed a new experimental technique[7] which allows positive identification of a coherent neutron peak as either nuclear or magnetic. We use a polarized neutron beam and detect separately those neutrons which have flipped their spin on scattering and those which have not. Coherent nuclear scattering will always be of the spin-nonflip variety and in our arrangement magnetically scattered neutrons will always flip their spins. Our initial effort was to use this technique to identify the peak observed by Paoletti and Pickart. The data obtained at 77°K with this polarization analysis technique are displayed in Fig. 1. The large peak in the spin-flip pattern is the one reported by Paoletti and Pickart and is seen to be magnetic in origin. There are two much smaller magnetic peaks also visible in this pattern. The

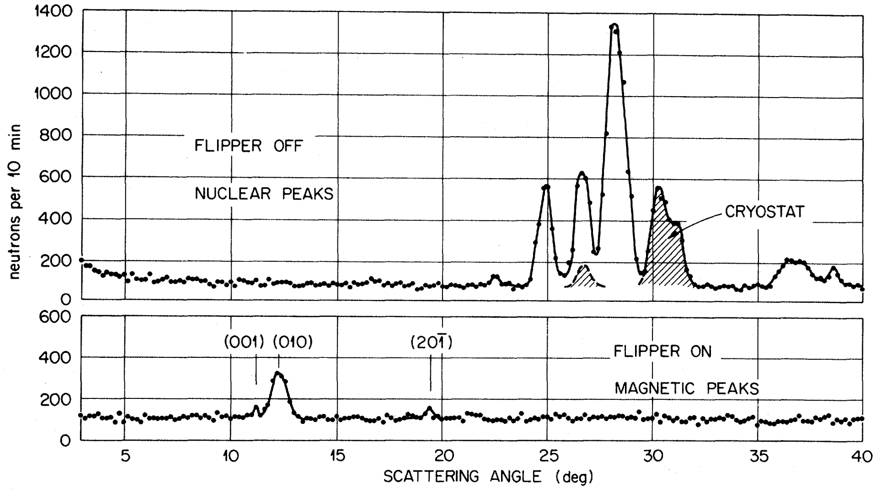

FIG. 1. Neutron polarization analysis of V_2O_3 powder at 77°K. The lower pattern is the spin-flip scattering. $\lambda = 1.07$ Å.

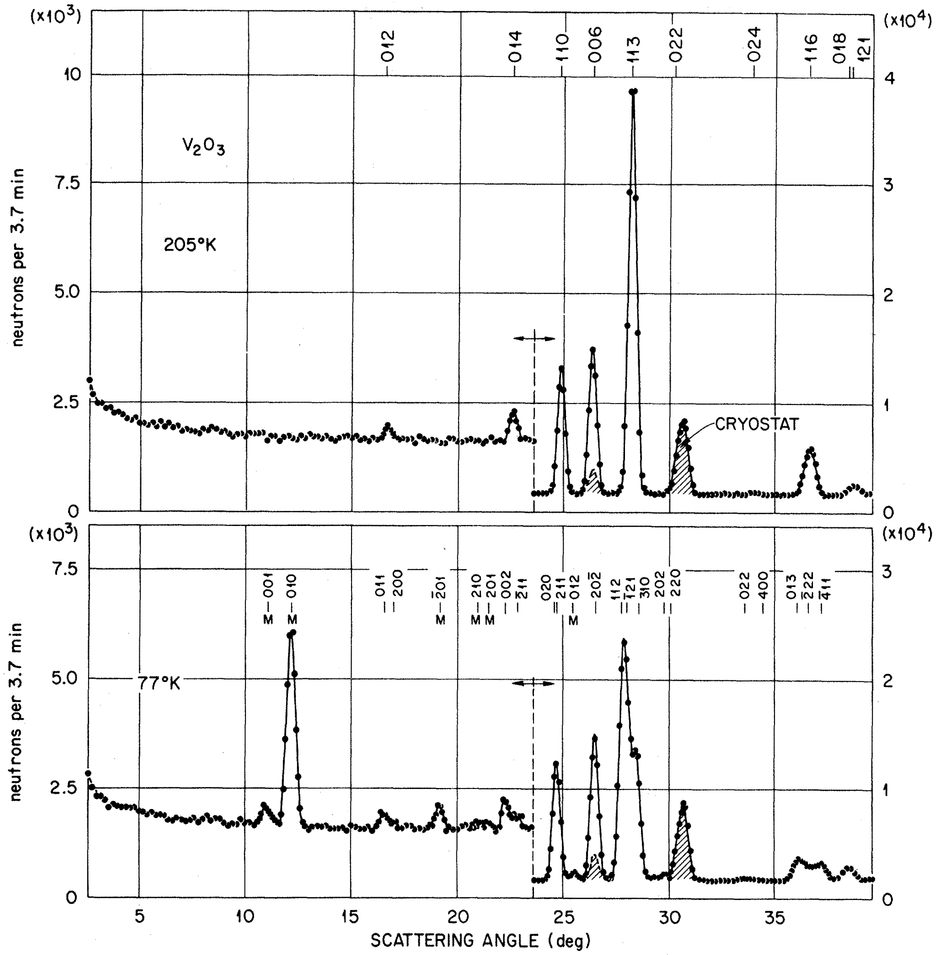

FIG. 2. Unpolarized neutron powder patterns of V_2O_3 above and below the transition temperature. Note the change of scale at about 24°. The magnetic peaks are indicated by the letter M. The 205°K pattern is indexed on a hexagonal cell and the 77°K pattern on a monoclinic cell. The changes in the nuclear peaks result from the monoclinic distortion. $\lambda = 1.068$ Å.

magnetic peaks index on the monoclinic cell of McWhan and Remeika[8] with the condition that $h+k+l=2n+1$. This is a body-centered cell so that the nuclear peaks have the condition $h+k+l=2n$. This means that in a conventional powder pattern, which would look like the superposition of the two patterns in Fig. 1, the magnetic peaks would not fall on top of nuclear peaks. Accordingly, the spectrometer was switched to unpolarized operation to take advantage of the much higher intensities that would be observed. The results of unpolarized experiments above and below the transition temperature are shown in Fig. 2. Additional magnetic peaks are evident in the low-temperature pattern. There is a small but definite difference in the diffuse scattering level in the two patterns of Fig. 2, indicating the presence of paramagnetic scattering in the high-temperature phase. In the hope of learning more about the state of the 3*d* electrons in the high-temperature phase, this paramagnetic scattering is the subject of a continuing investigation.

Unpolarized beam experiments have also been performed on several small single crystals.[9] A total of thirteen independent magnetic peaks have been observed. The temperature dependence of the (010) magnetic peak is shown in Fig. 3 together with the $(006)_{\mathrm{hex}}$ nuclear peak. The magnetic and crystallographic transformations occur simultaneously. An extrapolation of the temperature dependence of the magnetic peak yields an apparent Néel temperature of (285 ± 10)°K.

The indexing condition on the magnetic peaks immediately reveals an important feature of the magnetic structure. Atoms related by the body-center translation must have their moments in opposite directions. The other salient feature of the diffraction pattern is that the (010) line is

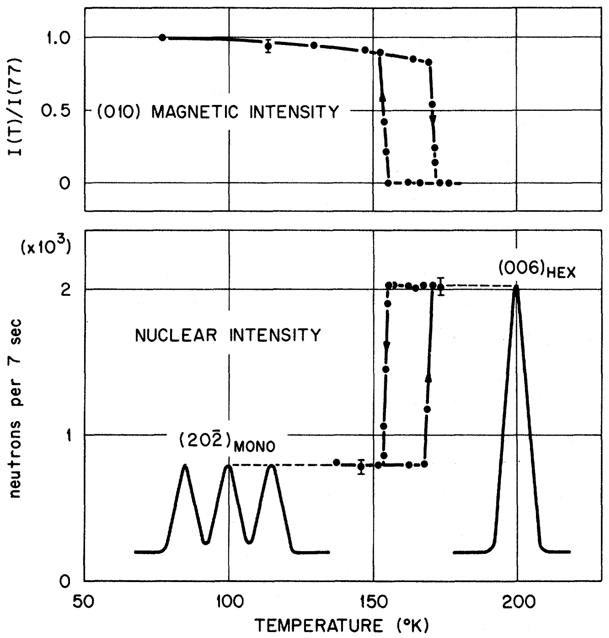

FIG. 3. Temperature dependence of magnetic and nuclear single-crystal intensities. When the system enters the monoclinic phase, the (006) nuclear peak splits into three separate peaks.

the only strong magnetic peak. This prompted us to consider models which maximized the (010) intensity. We want all the V atoms to scatter in phase for the (010) with the largest possible magnetic amplitude. This leads immediately to a structure with ferromagnetic coupling in (010) layers, or hexagonal (110) layers, and moment reversal between adjacent layers. The moments are oriented along some direction in these layers. Using this model, we obtain reasonable agreement with the observed single-crystal intensities with a moment of $1.2\mu_B$ per V atom oriented about 71° from the hexagonal c axis. These same parameters give good agreement with the powder intensities.

Because of the interest in the system $(V_{1-x}\cdot Cr_x)_2O_3$ generated by the work of McWhan and Remeika,[8] we have performed experiments on a single crystal with $x = 0.014$ and a powder sample with $x = 0.04$. In both of these samples we find the same magnetic structure and the same value for the ordered moment as in the pure material. The addition of Cr leads to a decrease in the apparent Néel temperature as determined by an extrapolation of the magnetic intensities. At $x = 0.4$ this temperature is (242 ± 6)°K. The change in the total diffuse scattering above and below the transition is strongly dependent on the Cr concentration. In the pure material, where the transition is between a metallic state and a magnetically ordered insulator, this change in the total diffuse cross section, extrapolated to zero scattering angle, is 47 mb per V atom at $\lambda = 0.978$ Å. With $x = 0.04$, where the high-temperature state is a magnetically disordered insulator, the change in cross section increases to 134 mb. Further work on the concentration and energy dependence of the diffuse scattering is planned.

We have recently generalized the model somewhat by allowing the moments to tip out of the (010) planes and allowing the total ordered moment to be made up of spin and orbital contributions. The orbital admixture has the effect of introducing a variable form factor into the analysis. Significantly better fits are obtained with the single-crystal intensities with this more general model. The moment deviates slightly from the (010) plane and the total moment is made up of opposed spin and orbital contributions, as would be expected for a less than half-filled $3d$ shell. However, we feel that the quality and extent of the present data are insufficient to justify conclusions on the exact moment direction and the spin-orbit admixture. We hope to acquire much better data with larger crystals. As a preliminary step to the final refinement of the magnetic structure, we have recently measured the single-crystal nuclear peaks in the monoclinic phase and determined the structural parameters. These neutron results are in reasonable agreement with the recent x-ray work of Dernier and Marezio.[10]

It is anticipated that the acquisition of new data will not change our conclusions about the basic type of structure or the value of the ordered moment, $(1.2 \pm 0.1)\mu_B$.

[†] Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corp.

[1] J. Wucher, J. Rech. Cent. Nat. Rech. Sci. 21, 254 (1952).

[2] P. H. Carr and S. Foner, J. Appl. Phys. 31, 344S (1960).

[3] A. Paoletti and S. J. Pickart, J. Chem. Phys. 32, 308 (1960).

[4] H. Kendrick, A. Arrott, and S. A. Werner, J. Appl. Phys. 39, 585 (1968).

[5] E. D. Jones, Phys. Rev. A 137, 978 (1965).

[6] T. Shinjo and K. Kosuge, J. Phys. Soc. Jap. 21, 2622 (1966).

[7] R. M. Moon, T. Riste, and W. C. Koehler, Phys. Rev. 181, 920 (1969).

[8] D. B. McWhan and J. P. Remeika, to be published.

[9] We are indebted to J. P. Remeika of the Bell Telephone Laboratories for supplying the single crystals.

[10] P. D. Dernier and M. Marezio, to be published.