

Neutron Diffraction Investigation of Magnetic Ordering in the Trifluorides of 4d-Transition Elements

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MoF₃ becomes antiferromagnetic below 185°K with a spin-only magnetic moment corresponding to $S=\frac{3}{2}$ and a magnetic structure which can be correlated with coupling rules applicable to the iron-group trifluorides. These results, together with the absence of observable magnetic neutron scattering from PdF₃ and RuF₃, suggest that Hund's rule does not apply to ions in the 4d-transition series.

INTRODUCTION

THE magnetic properties of compounds containing ions of the 4d- and 5d-transition series are of considerable interest, because they appear to be quite different from those of similar compounds containing ions of the 3d series. The values of the atomic magnetic moments obtained from susceptibility measurements on 4d and 5d compounds are generally quite small, and they do not correspond to the spin-only values characteristic of the iron group. Furthermore, there has previously been no direct experimental confirmation of ordering of the atomic magnetic moments in these higher transition series.

In a recent neutron diffraction investigation of the iron group trifluorides¹ it was shown that the magnetic structures which develop at low temperatures can be accounted for in terms of the orbitals which result from the splitting of the *d* levels by the crystal field. The crystal field splits the 3*d* levels of an iron-group ion in an octahedral site into a lower triplet (*t_{2g}*) and an upper doublet (*e_g*), the latter orbitals being of a type which point toward and overlap the *p* orbitals of the anions located between adjacent metal ions. The indirect magnetic coupling which results from this overlap depends on the electron occupation of the *e_g* orbitals of the particular cations involved.

Since the magnetic ordering properties of the iron group trifluorides could be correlated with their *d*-electron configurations, it was felt that a study of the trifluorides of the second transition group elements might give information on the electron configuration of the 4*d* shell. This report contains the results which were obtained on PdF₃, RuF₃, and MoF₃.

CRYSTAL STRUCTURES

Both PdF₃ and RuF₃ have been reported by Hepworth, Jack, Peacock, and Westland² to crystallize with a bimolecular rhombohedral unit cell of space group $R\bar{3}c$ containing two metal atoms at (0,0,0) and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and six fluorine atoms at $\pm(x, \frac{1}{2}-x, \frac{1}{4})$, $\pm(\frac{1}{2}-x, \frac{1}{4}, x)$, and $\pm(\frac{1}{4}, x, \frac{1}{2}-x)$, where values of *x* were given as

−0.10 for RuF₃ and −0.083 for PdF₃. However, MoF₃ was reported by Gutman and Jack³ to have the cubic ReO₃ structure. The samples of PdF₃ and RuF₃ used in this investigation were found to have crystal structures in agreement with those reported, but the samples of MoF₃ were also found to have the bimolecular rhombohedral unit cell of the $R\bar{3}c$ space group,⁴ and the value of *x* was determined to be -0.12 ± 0.01 .

EXPERIMENTAL RESULTS

PdF₃ and RuF₃

Neutron diffraction patterns were obtained on powdered specimens of PdF₃ and RuF₃ at sample temperatures of 298°K and 4.2°K. There was no evidence of magnetic ordering in either compound. Furthermore, the diffuse scattering at room temperature showed little or no angularly dependent paramagnetic diffuse scattering. Unfortunately, the diffraction patterns for the samples which were studied showed a considerable line broadening of the nuclear reflections so that background measurements were difficult and an accurate analysis of the angular variation of the diffuse scattering was not possible.

MoF₃

Powder diffraction patterns were obtained on MoF₃ at temperatures ranging from 425°K to 4.2°K, and as shown in Fig. 1, antiferromagnetic ordering was observed at 4.2°K. The two cross-hatched reflections represent magnetic reflections which occurred at low temperatures, and these are the only two magnetic reflections which are observable in the pattern. This pattern closely resembles that which was reported¹ for the corresponding iron group compound, CrF₃, and the magnetic structures appear to be identical. They are *G*-type antiferromagnetic lattices⁵ in which each metal atom is antiferromagnetically coupled through the intervening fluorine atoms to each of its six nearest neighbors. Furthermore, the relative intensities of the two reflections show that the magnetic moments are oriented

¹ E. O. Wollan, H. R. Child, W. C. Koehler, and M. K. Wilkinson, Phys. Rev. **112**, 1132 (1958).

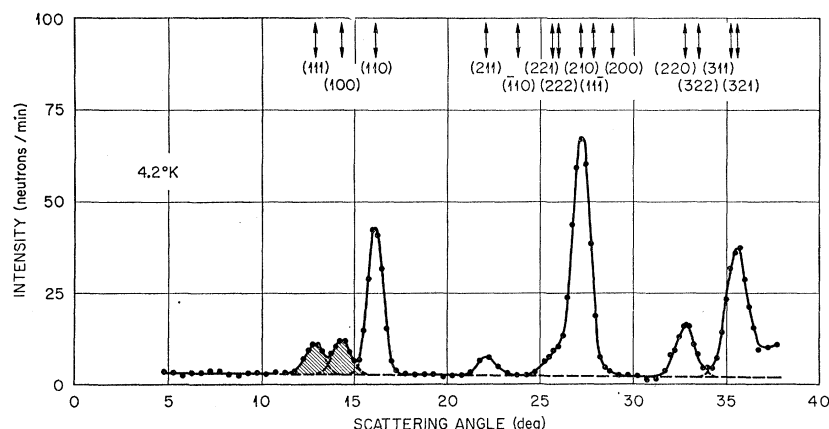
² M. A. Hepworth, K. H. Jack, R. D. Peacock, and G. J. Westland, Acta. Cryst. **10**, 63 (1957).

³ V. Gutman and K. H. Jack, Acta. Cryst. **4**, 244 (1951).

⁴ D. E. LaValle, R. M. Steele, M. K. Wilkinson, and H. L. Yakel, J. Am. Chem. Soc. **82**, 2433 (1960).

⁵ E. O. Wollan and W. C. Koehler, Phys. Rev. **100**, 545 (1955).

FIG. 1. Neutron diffraction powder patterns for MoF_3 at 4.2°K ($\lambda=1.08 \text{ \AA}$). The antiferromagnetic reflections are cross-hatched.



in a direction closely perpendicular to the unique axis of the rhombohedral unit cell.

The value of the antiferromagnetic transition in MoF_3 was determined by the variation of the (111) magnetic reflection with temperature, and the intensity of this reflection has a Brillouin-type dependence with a Néel temperature near 185°K . This value is considerably higher than that of 80°K observed for antiferromagnetic ordering in CrF_3 , thereby indicating that the magnetic coupling in MoF_3 is stronger than it is in the corresponding compound of the $3d$ series.

In addition to establishing the antiferromagnetic structure of MoF_3 , it was of interest to determine the value of the atomic magnetic moments and the magnetic form factor associated with the scattering. The latter determination was particularly interesting since no such experimental data had previously been obtained for electrons in the $4d$ shell. Furthermore, a comparison of the experimental form factor to that obtained from theoretical calculations would indicate whether or not there was a contribution to the atomic moments from the orbital currents. Since there were only two magnetic reflections and these occurred at comparable scattering angles, very little form factor information could be obtained from the coherent scattering, and it was necessary to determine this form factor from the paramagnetic diffuse scattering. Two types of diffuse scattering analyses are possible, and both were performed as shown in Fig. 2.

The points in Fig. 2(a) represent average values of many determinations of the diffuse scattering from MoF_3 at 425°K , a temperature well above the Néel transition so that short-range-order effects should be negligible. These points have been corrected for background scattering, and corrections have also been made for the thermal motion of the atoms on the basis of the Debye theory of independent oscillators. A Debye temperature of 280°K was determined from intensity changes of the (110), (210), and (321) nuclear reflections at a series of temperatures from 425°K to 4.2°K , and the estimated error of 25° in this determination is primarily responsible for the long feet on the points at

large scattering angles. The angle-dependent scattering in this plot corresponds to the paramagnetic diffuse scattering, and the differential cross section of this scattering is proportional to $\mu_p^2 f^2$, where μ_p is the effective moment per atom in the paramagnetic state and f is the magnetic form factor. An extrapolation of the data to zero scattering angle gives a cross-section value which corresponds to a spin-only paramagnetic moment with $S=1.38$. Since the relatively large errors in the points do not permit a good determination of the nuclear scattering level, this moment value is consistent with a spin-only moment for $S=\frac{3}{2}$ corresponding to three unpaired electrons.

Figure 2(b) gives points which represent average values of several determinations of the difference in the diffuse scattering from MoF_3 at 425°K and 4.2°K , and these points have been corrected for thermal effects by the method previously stated. Since these two temperatures are well above and well below the Néel transition, to a first approximation the difference in diffuse scattering is proportional to $\mu^2 f^2$, where μ is the average atomic magnetic moment in the ordered lattice. This difference method has the advantages of eliminating temperature independent nuclear scattering effects and of establishing the zero position on the scale for magnetic scattering. In this analysis of the MoF_3 data, the extrapolation to zero scattering angle is in excellent agreement with the value calculated for a spin-only moment with $S=\frac{3}{2}$. It is interesting to note the two points representing the (111) and (100) magnetic reflections that are plotted in Fig. 2(b). The intensities of these reflections are also proportional to $\mu^2 f^2$, and the agreement with the diffuse scattering data is additional evidence that the stated antiferromagnetic structure is correct and that the moment is equal to 3 Bohr magnetons. Analysis of the coherent magnetic scattering requires a knowledge of the ordered lattice, whereas the diffuse scattering analysis is independent of the type of magnetic ordering.

The data in Fig. 2 were converted to magnetic form factors by taking ratios of the plotted values of magnetic scattering to the extrapolated values in the forward direction, and the results are shown in Fig. 3. The esti-

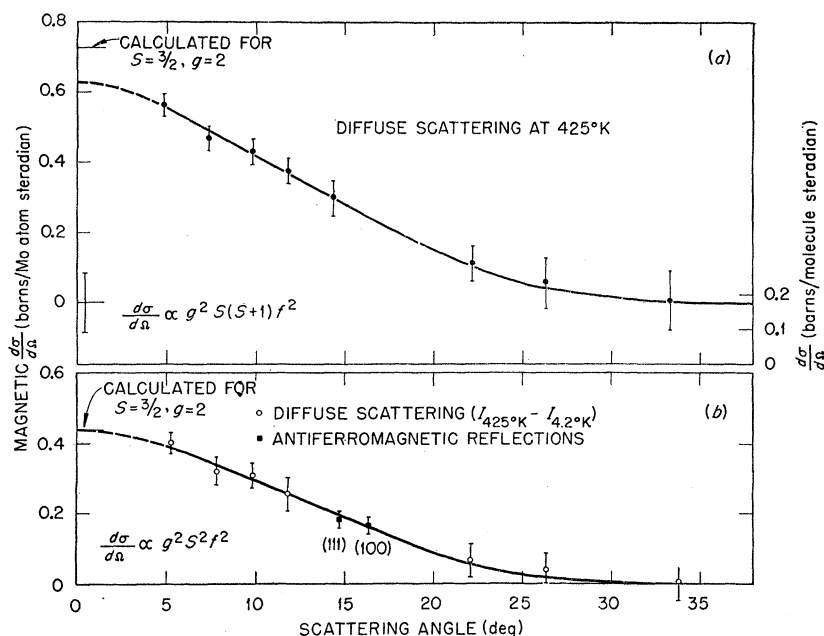


FIG. 2. Magnetic scattering from MoF₃ powder ($\lambda = 1.22$ Å).

rated accuracy of the points is indicated for the results obtained from Fig. 2(b), and the points obtained from the diffuse scattering at 425°K are less significant because of the uncertainty in the nuclear scattering level. The solid curve in this figure is the calculated form factor for Mo³⁺ as determined by the method of Pauling and Sherman⁶ using their recommended screening constant corresponding to $(Z-S)=10$. More accurate form factor calculations are not yet available for the 4d series, but the agreement between experiment and theory shown in Fig. 3 is certainly indicative that the atomic magnetic moments in MoF₃ have little or no orbital contribution. The rapid decrease of the Mo³⁺ form factor with scattering angle is seen from a comparison with the experimental Mn²⁺ form factor shown by the dotted curve. It

is this form factor behavior which is primarily responsible for the observation of only two magnetic reflections from the antiferromagnetic lattice in MoF₃.

CONCLUSIONS

The results of this investigation indicate that the magnetic properties of the 4d compound, MoF₃, are very similar to those of the corresponding 3d compound, CrF₃. MoF₃ becomes antiferromagnetic at temperatures below 185°K with a structure identical with that of CrF₃, and the atomic magnetic moment value is consistent with the expected spin-only value for a magnetic ion with three unpaired *d* electrons. Any theoretical considerations regarding the behavior of Cr³⁺ ions in octahedral sites might therefore be expected to apply also to Mo³⁺ ions in similar surroundings. However, neither PdF₃ nor RuF₃ showed magnetic properties similar to the corresponding iron-group trifluorides. No magnetic ordering was observed in these compounds at low temperatures, and any paramagnetic scattering from them was below the limit of detection.

The behavior of these three compounds can be qualitatively explained if it is assumed that Hund's rule does not apply to ions in the 4d transition series. The failure of this rule for ions of the higher transition series was originally suggested by Van Vleck⁷ as a possible explanation for the results of the magnetic susceptibility measurements, and more recently, Orgel⁸ has pointed out that the splitting of the levels in 4d transition-metal complexes is in line with this hypothesis. Under these conditions, the lower *t*_{2g} triplet would presumably be filled with six electrons before any elec-

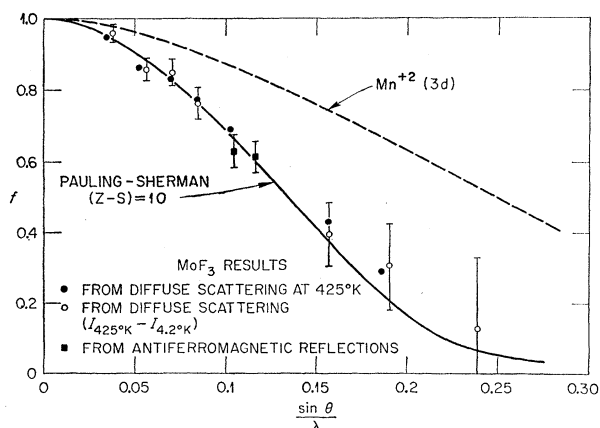


FIG. 3. Comparison of observed and calculated magnetic form factors for MoF₃(4d).

⁶ L. Pauling and J. Sherman, *Z. Krist.* **81**, 1 (1932).

⁷ J. H. Van Vleck, *Electric and Magnetic Susceptibilities* (Oxford University Press, London, 1932), p. 311.

⁸ L. E. Orgel, *J. Chem. Phys.* **23**, 1819 (1955).

trons occupied the e_g orbitals. Since Mo^{+3} contains only three $4d$ electrons, all would be in the t_{2g} levels with parallel spins, and there would be no difference between this ion and the corresponding ion, Cr^{+3} , of the iron-group series. However, both Pd^{+3} and Ru^{+3} would have only one unpaired electron instead of three and five, respectively, which would be expected if Hund's rule were applicable. In the current investigations, the sensitivity of the measurements was insufficient to observe paramagnetic scattering from ions with a spin-only magnetic moment from a single electron, and the rapid decrease of the $4d$ -magnetic form factor would have

prevented the detection of magnetic ordering unless the antiferromagnetic structure produced reflections at small scattering angles. It would be of considerable interest to obtain the magnetic moment values in these two compounds from paramagnetic susceptibility measurements.

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Effect of High Pressure on Electrical Properties of NiO , CoO , CuO , and Cu_2O †

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The effect of pressure on electrical resistance and Seebeck coefficient at or near room temperature in NiO , CoO , CuO , and Cu_2O has been determined. Equations relating the Seebeck coefficient to hole concentration have been used to calculate the effect of pressure on hole mobility. In all materials examined, hole mobility was decreased by pressures to 60 000 atm. It has been proposed that NiO charge transport occurs by the motion of holes trapped at local sites by polarization of the surrounding lattice. The effect of pressure on the diffusion of self-trapped holes has been considered. Motion of self-trapped holes in an ionic crystal and of vacancies in a metal may be similar to the extent

that the motion of either probably involves cooperative movements of surrounding ions or atoms. Some inward relaxation probably occurs around either a hole trapped at a local site in an ionic crystal or around a vacancy in a metal. In either case pressure would be expected to decrease the jump frequency for motion of the defect. It is proposed that in NiO , CoO , and CuO , the decreased hole mobility with pressure was due to a decrease in diffusion rate of self-trapped holes. The explanation for pressure effects in Cu_2O may be more complicated since Cu_2O is generally regarded as a wide-band semiconductor.

INTRODUCTION

THE band model of solids predicts that materials such as NiO , CoO , and CuO with incompletely filled $3d$ shells should be expected to exhibit metallic conductivity. However, NiO , CoO , and CuO in pure stoichiometric condition are as good insulators as Cu_2O , which has a completely filled $3d$ shell. Mott¹ and Verwey² have proposed that materials such as NiO are insulators because the Ni^{++} ions are too far apart for appreciable overlap of $3d$ orbitals. Room temperature electrical conductivity in both NiO and Cu_2O may be increased several orders of magnitude by the presence of excess oxygen or by addition of certain impurities such as Li to NiO .

According to Verwey,³ in excess-oxygen or Li-doped NiO , hole transfer between localized sites occurs by a chain of transitions $\text{Ni}^{++} + \text{Ni}^{+++} \rightarrow \text{Ni}^{+++} + \text{Ni}^{++}$. It has been suggested,⁴ on the basis of effects of oxygen

pressure on electrical conductivity, that charge transfer in either NiO or Cu_2O occurs to the Verwey model, that is, by electron exchange between divalent and trivalent nickel ions or monovalent and divalent copper ions, respectively. In NiO , the lack of a detectable Hall effect at room temperature and an apparent increase in hole mobility with temperature are in accord with the Verwey model.⁵ Cu_2O , however, exhibits a measurable Hall effect at room temperature and an apparent decrease in hole mobility with temperature, suggesting hole transport in a wide valence band.⁶ It should be mentioned, however, that the temperature dependence of hole mobility in Cu_2O may be reversed in some ranges of temperature and oxygen pressure.⁷ Interpretation of electrical data from sintered Cu_2O samples is complicated by the presence of surface layers, which may under some conditions carry most of the current.⁸

The purpose of this work was to determine the effects of pressure on electrical properties of excess-oxygen or doped NiO , CoO , CuO , and Cu_2O . The effects of pressure on resistivity and Seebeck coefficients of these materials were measured on powder compacts at or

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⁴ O. Kubaschewski and B. E. Hopkins, *Oxidation of Metals and Alloys* (Butterworths Scientific Publications Ltd., London, 1953), p. 30.

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⁷ P. Schmidt, *Ann. Physik* **14**, 265 (1954).

⁸ J. Bloem, *Philips Research Rept.* **13**, 167 (1958).