

Neutron Diffraction Studies of Antiferromagnetism in CrF_2 and CrCl_2 J. W. CABLE, M. K. WILKINSON, AND E. O. WOLLAN
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Neutron diffraction observations have been made on powder samples of CrF_2 and CrCl_2 from 298° to 4.2°K. These materials, which have crystal structures similar to rutile but distorted from tetragonality, become antiferromagnetic at low temperatures with different magnetic structures. For CrF_2 the magnetic unit cell is identical with the chemical cell and the moments at the corner sites are directed oppositely to those at the center of the cell. The magnetic unit cell of CrCl_2 requires doubling of the b and c axes of the orthorhombic chemical cell and the structure consists of ferromagnetic (011) planes with adjacent planes antiparallel. In neither case were the intensities compatible with a magnetic axis directed along a simple crystallographic direction. Unique magnetic axes could not be definitely established but the data suggest that they lie parallel to the longest Cr-F and Cr-Cl bonds. Néel temperatures of 53° and 20°K were observed for CrF_2 and CrCl_2 , respectively.

INTRODUCTION

THIS investigation was undertaken to determine the existence of magnetic ordering in CrF_2 and CrCl_2 in which the magnetic ions have the $3d^4$ electronic configuration. This configuration appears to play a unique role in determining the antiferromagnetic structures observed in the cubic crystals MnF_2 ¹ and LaMnO_3 ² because of the simple overlap properties of the e_g orbitals with the intervening anion p orbitals.

In the chromous compounds which have distorted rutile structures the overlap of the cation d orbitals with the anion p orbitals is more complicated than in the manganese compounds and hence the $3d^4$ configuration may play a less significant role in magnetic coupling. Nevertheless, it was considered of interest to compare the magnetic structure properties of these two classes of compounds with the same d -shell occupation.

CRYSTAL STRUCTURES

Chromous fluoride and chromous chloride crystallize in distorted rutile-type structures as shown in Fig. 1. For CrF_2 Jack and Maitland³ report a bimolecular monoclinic unit cell of space group $P_{21/c}$, in which the chromium ions are located at 0,0,0 and $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ while the fluoride ions are at $\pm(x, y, z)$ and $\pm(\frac{1}{2} + x, y - \frac{1}{2}, \frac{1}{2} + z)$, with $x = y = 0.297$ and $z = 0.044$. The lattice constants are: $a = 4.732$, $b = 4.718$, $c = 3.505$, and $\beta = 96.52^\circ$. Recent x-ray results⁴ for chromous chloride show a bimolecular orthorhombic cell of space group P_{nnm} with the two chromium ions at 0,0,0 and $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ and the chloride ions at $\pm(u, v, 0)$ and $\pm(u + \frac{1}{2}, \frac{1}{2} - v, \frac{1}{2})$. The lattice constants are $a = 6.638$, $b = 5.984$, and $c = 3.476$ and the combined x-ray and neutron data yield the parameters $u = 0.36$ and $v = 0.27$. As expected from crystal field theory the distribution of anions about the cations in both compounds shows a large tetragonal distortion ($c/a \approx 1.20$) from cubic symmetry.

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

² E. O. Wollan and W. C. Koehler, Phys. Rev. **100**, 545 (1955).

³ K. H. Jack and R. Maitland, Proc. Chem. Soc. (London), 232 (August 1957).

⁴ H. Yakel and R. Steele (private communication).

EXPERIMENTAL

The chromous fluoride was prepared by B. J. Sturm of the Oak Ridge National Laboratory by the reaction of metallic chromium with molten stannous fluoride.⁵ The chromous chloride was a commercially available material further purified by vacuum sublimation. The samples were powdered to 100-mesh size, loaded in cylindrical aluminum cells and mounted in the low temperature cryostat of the neutron diffractometer. Temperature measurements were made with a calibrated copper-constantan thermocouple.

TABLE I. A comparison of the calculated and observed intensities for CrF_2 .

hkl	Intensities			
	Nuclear		Magnetic	
	Calculated ^a	Observed ^b	Calculated ^c	Observed
100 010 ^d			3888	4347
001 ^d			371	313
110	551	664		
10 $\bar{1}$	48	62		
011	0			
101				
11 $\bar{1}$ ^e	1666	1420	212	150
200 020				
111 ^e	1482	1517	356	392
120 210 ^e	821	1084	511	568
20 $\bar{1}$ ^d				
021 ^e			128	134
21 $\bar{1}$	578	537		
201 ^d			69	83
12 $\bar{1}$				
121				
002	1443	1372		
211				
220				
012 ^e	971	1077		
11 $\bar{2}$				

^a Using $f_{Cr} = 0.352$ and $f_F = 0.55 \times 10^{-12}$ cm and $x = y = 0.30$, $z = 0.03$.

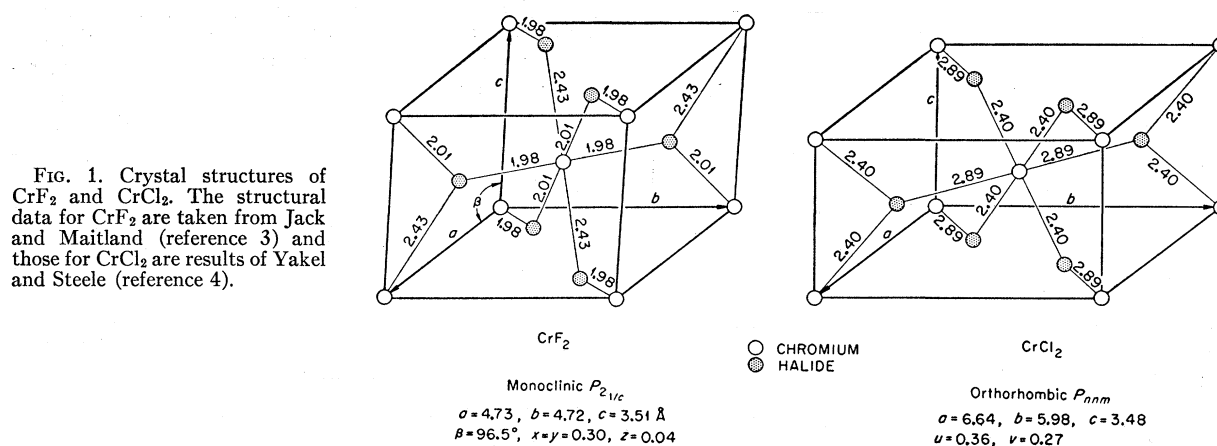
^b Average values of data taken at 298° and 78°K which have been corrected for thermal motion.

^c Assuming a spin only moment, the chromium form factor and the magnetic axis parallel to the longest Cr-F bond.

^d Magnetic only.

^e Nuclear and magnetic.

⁵ B. J. Sturm, Oak Ridge National Laboratory Report, ORNL-2681 (unpublished).

 **CrF_2**

The neutron powder diffraction patterns obtained from CrF_2 at sample temperatures of 298° and 4.2°K are shown in Fig. 2. The pattern at 298°K is typical of a paramagnetic material and consists of the nuclear Bragg reflections superimposed on an angularly dependent paramagnetic background. A comparison of the calculated and observed nuclear intensities is given in Table I. For the calculated intensities scattering amplitudes of 0.352 and 0.55×10^{-12} cm were used for chro-

mium and fluorine, respectively. The parameters $x = y = 0.30$ and $z = 0.03$ were found to give the best agreement with the neutron data and differ only slightly from the x-ray values reported by Jack and Maitland. The observed intensities in the table represent the average of the 298° and 78°K data which have been corrected for thermal motion of the atoms. A Debye characteristic temperature of $320^\circ \pm 25^\circ$ was determined from the neutron data and used in this correction. The major discrepancies between the calculated and observed values may be attributed to a preferred par-

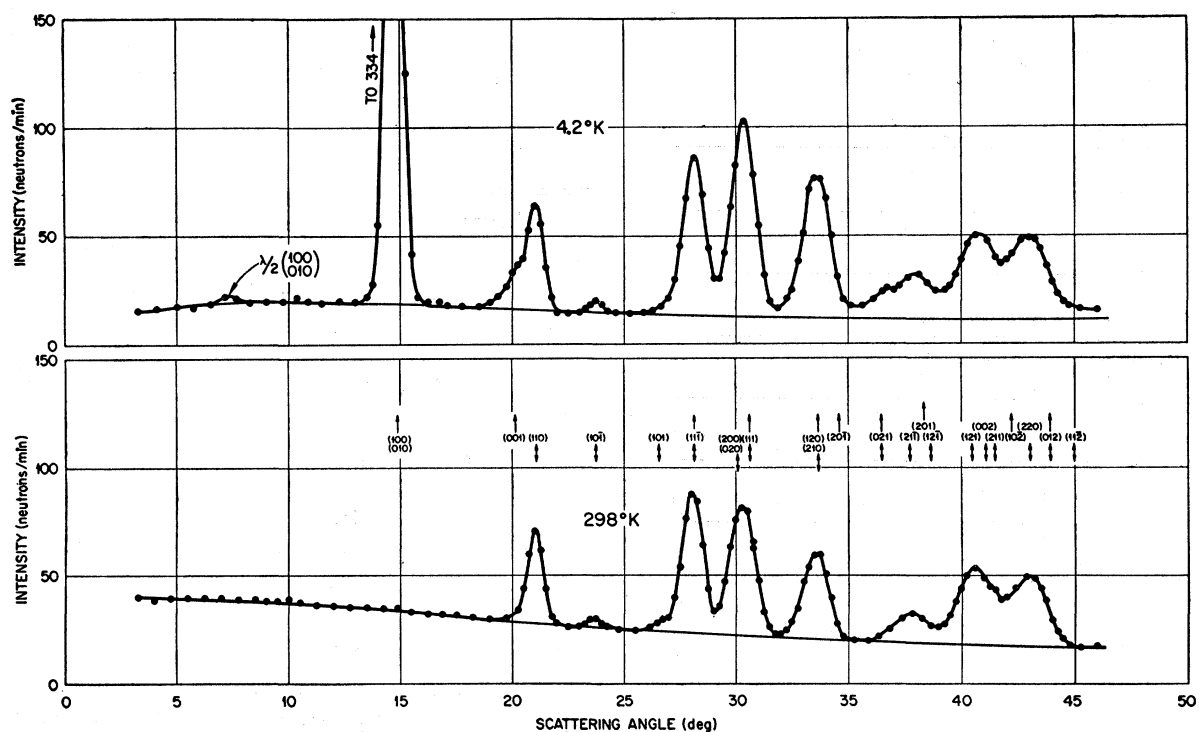


FIG. 2. Neutron powder diffraction patterns of CrF_2 at 298° and 4.2°K . The single-headed arrows refer to the magnetic reflections in the 4.2°K pattern while the double-headed arrows indicate the nuclear reflections which appear in both patterns.

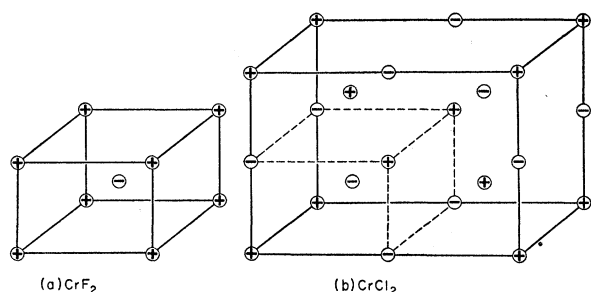


FIG. 3. (a) The antiferromagnetic structure of CrF_2 . (b) The antiferromagnetic structure of CrCl_2 . Only the phase relationships of the moments are shown; the axis of magnetization is discussed in the text.

title orientation which enhances the $(h k 0)$ reflections by about 20%.

In the 4.2°K pattern additional Bragg reflections are observed due to the development of long range antiferromagnetic order in the sample. These are apparent in Fig. 2 in which the double-headed arrows indicate the nuclear reflections present at both temperatures while the single arrows refer to the magnetic reflections in the 4.2°K pattern. The magnetic reflections are indexed on the same cell as the chemical cell and the condition for reflection is that the sum of the indices is odd. This corresponds to antiferromagnetic ordering in which the two magnetic ions of the unit cell are aligned antiparallel as shown in Fig. 3(a). This is the same magnetic structure as that reported by Erickson⁶ for the other iron group difluorides which have similar, but undistorted, rutile structures. The presence of the (001) magnetic reflection in CrF_2 shows that the axis of

magnetization cannot lie along the c axis of the crystal and calculations show that it does not coincide with any of the simple crystallographic directions. For the calculated intensities given in Table I the axis of magnetization has been taken parallel to the longest Cr-F bond. (There are two such bond directions and the corresponding axes yield equal intensities.) A spin-only magnetic moment and the chromium form factor as deduced from the paramagnetic scattering (this is discussed in a later section) have been used. The observed intensities are in satisfactory agreement when the preferred orientation is taken into account. The observed intensity of the $(11\bar{1})$ reflection is low, but this particular reflection has an unusually large experimental error because of the large nuclear component, and in addition, there is a 20% preferred orientation effect indicated in the nuclear intensity. Slightly better agreement can be obtained by reorienting the magnetic axis to directions which have less physical significance, e.g., the best agreement was obtained with the axis tilted 32° from the c axis in the (010) plane.

The Néel temperature of CrF_2 was obtained by studying the intensities of the magnetic reflections as a function of temperature, and Fig. 4 shows the temperature variation of the intensity of the $(100, 010)$ magnetic reflection. The curve exhibits the usual Brillouin-type dependence with a transition temperature of 53°K.

CrCl_2

The neutron powder diffraction patterns obtained from CrCl_2 at sample temperatures of 298° and 4.2°K are shown in Fig. 5. The nuclear reflections, indicated by the double-headed arrows, are consistent with the

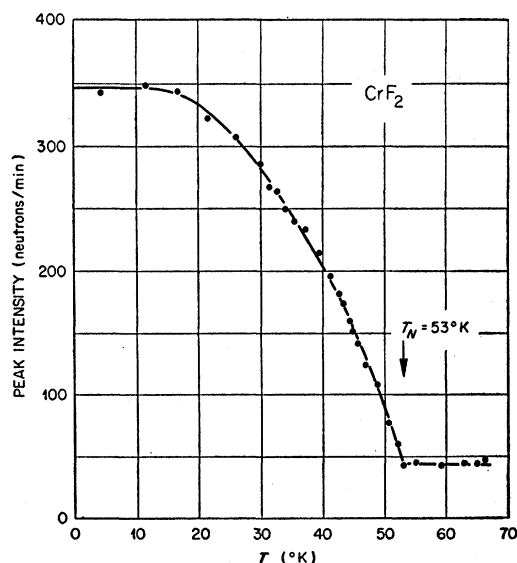


FIG. 4. Temperature variation of the $(100, 010)$ magnetic reflection from CrF_2 .

⁶ R. A. Erickson, Phys. Rev. **90**, 779 (1953).

TABLE II. A comparison of calculated and observed intensities from CrCl_2 .

Nuclear intensities			Magnetic intensities		
hkl	Calc. ^a	Obs. ^b	hkl	Calc. ^c	Obs.
110	174	169	011	589	543
200	0	0	11 $\bar{1}$	381	313
101			03 $\bar{1}$	108	120
011			131		
020	1669	1399	211	195	157
210			23 $\bar{1}$		
111			01 $\bar{3}$	87	114
120	1257	1286	051		
211			113		
220	145	169	15 $\bar{1}$	85	70
121			31 $\bar{1}$		
310	801	716			
130					
221	603	544			
301					

^a Using $f_{\text{Cr}} = 0.352$ and $f_{\text{Cl}} = 0.98 \times 10^{-12}$ cm; also $u = 0.36$ and $v = 0.27$.

^b Average values of data taken at 298° and 78°K which have been corrected for thermal motion.

^c Assuming a spin-only moment, the chromium form factor and the magnetic axis parallel to the longest Cr-Cl bond.

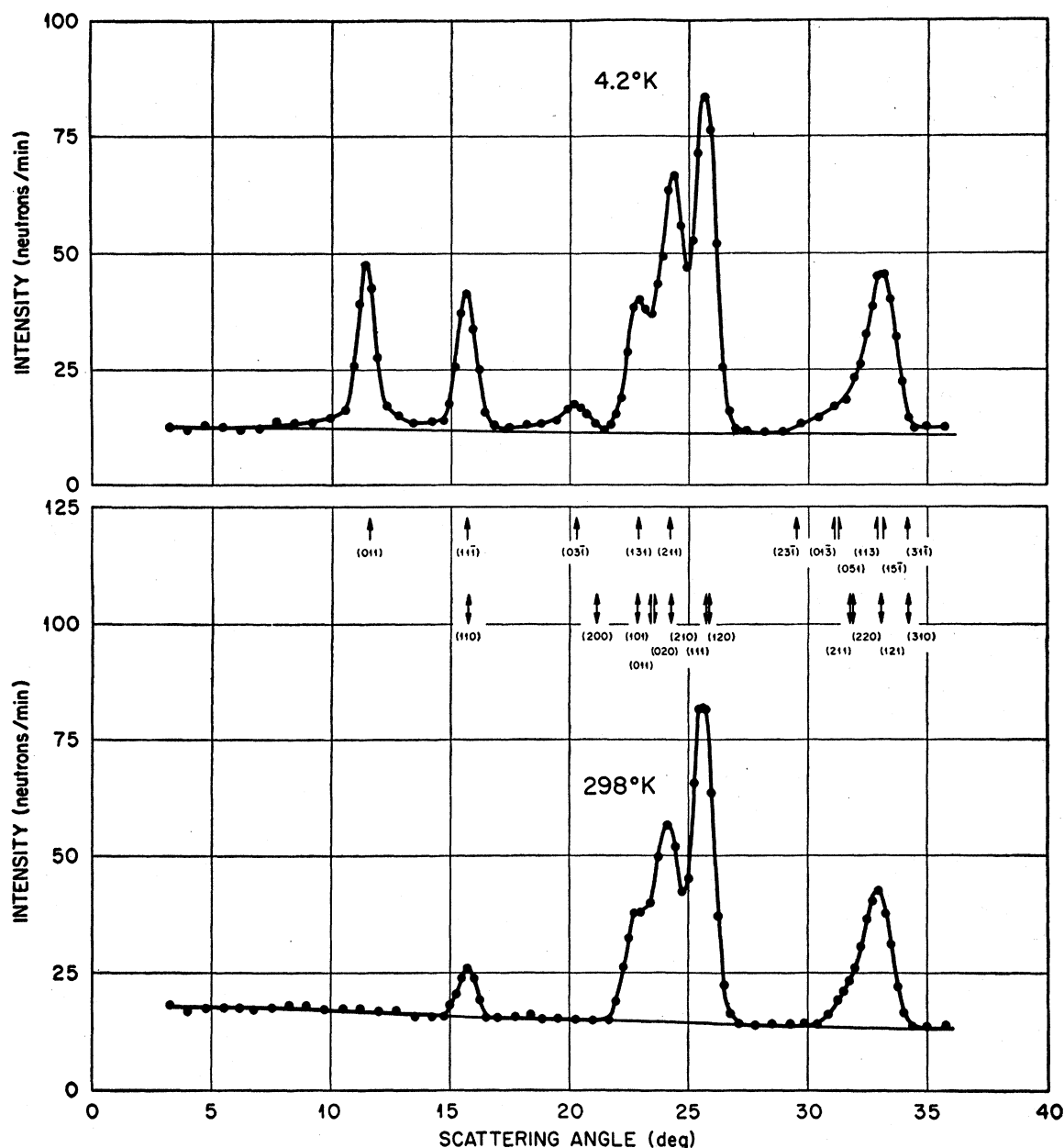


FIG. 5. Neutron powder diffraction patterns of CrCl_2 at 298° and 4.2°K . The single-headed arrows refer to the magnetic reflections in the 4.2°K pattern while the double-headed arrows indicate the nuclear reflections which appear in both patterns.

known structure, and a comparison of the calculated and observed nuclear intensities is given in Table II. Scattering amplitudes of 0.352 and 0.98×10^{-12} cm were used for chromium and chlorine, respectively, while the structure parameters were chosen as $u=0.36$ and $v=0.27$. The observed intensities represent the average of the 298° and 78°K data which have been corrected for thermal motion with a Debye characteristic temperature of $260 \pm 20^\circ$ that was determined from the neutron data. At 4.2°K , antiferromagnetic reflections were observed and these are indicated in Fig. 5 by the

single arrows. These reflections are indexed on the basis of a magnetic unit cell with the same a axis as the chemical cell but with the b axis and c axis of the chemical cell doubled. Reflections are observed for which k and l are odd and $2h+k+l=4n+2$ corresponding to the magnetic structure shown in Fig. 3(b).

The intensities of the first three magnetic reflections are not consistent with a magnetic axis directed along any of the simple crystallographic directions. The best agreement was obtained with the moments directed parallel to one or the other of the long Cr-Cl bonds.

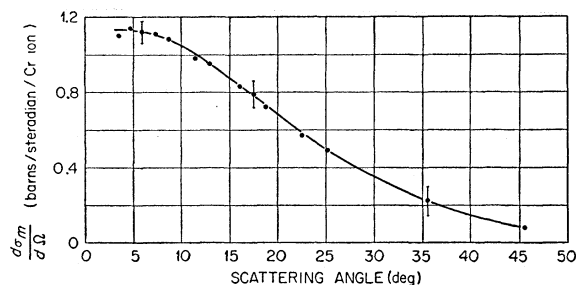


FIG. 6. Paramagnetic differential scattering cross section for CrF_2 at 298°K . The value at zero scattering angle for the orbitally quenched Cr^{+2} ion is 1.16 barns/steradian/ion.

This moment direction, a spin-only magnetic moment, and the Cr^{+2} form factor were used in calculating the intensities of the magnetic reflections given in Table II and the observed values are in satisfactory agreement with the model. The intensity of the (011) magnetic reflection showed a Brillouin-type thermal dependence with a Néel temperature of 20°K .

PARAMAGNETIC SCATTERING

The chromium form factor that was used in the intensity calculations of the magnetic reflections from these two compounds was determined from the paramagnetic scattering at room temperature. This analysis required a determination of the isotropic diffuse background and the thermal diffuse scattering. The former was established by a comparison of the 4.2° and 298°K data with the assumption that the magnetic diffuse

scattering was proportional to S at 4.2°K and to $S(S+1)$ at 298°K . The thermal diffuse scattering was calculated with the Debye characteristic temperatures determined from the coherent nuclear reflections. Subtraction of the isotropic and thermal diffuse scattering from the total diffuse scattering at room temperature gave the paramagnetic scattering. The extrapolated values in the forward direction correspond to atomic moment values of 3.96 ± 0.24 and 3.86 ± 0.20 for CrF_2 and CrCl_2 , respectively, in good agreement with the value expected for the Cr^{+2} ion with the orbital moment quenched. Figure 6 shows the paramagnetic differential scattering cross section which was obtained for CrF_2 . The errors, about one-half of which are due to the uncertainty in the determination of the isotropic background, are given for representative points. The points plotted in Fig. 7 represent the ratios of the magnetic scattering cross section at various angles to that in the forward direction. The solid dots refer to the CrF_2 data while the CrCl_2 data, which were analyzed in a similar manner, are represented by the open circles. The errors indicated for representative points become much greater at the higher angles due largely to the errors in the determination of the thermal diffuse scattering. The solid curve, drawn through the experimental points, represents the Cr^{+2} form factor while the dashed curve is the Mn^{+2} form factor.⁷ By comparison the Cr^{+2} form factor is slightly compressed, although barely outside of experimental error. Such a compression would correspond to a $3d$ electron distribution slightly expanded relative to that of Mn^{+2} .

DISCUSSION

The antiferromagnetic structure of CrF_2 is the same as that found for the other iron group difluorides. It would seem then that the $3d^4$ configuration does not assume as significant a role in the magnetic coupling in these structures as in the previously mentioned cubic systems. From a comparison of the magnetic structure of CrF_2 and CrCl_2 , however, a correlation of the magnetic coupling with electronic configuration is observed. This comparison requires an examination of the crystal structures with particular emphasis on the nearest neighbors of the individual ions. In both crystals the chromous ions are surrounded by a tetragonally distorted octahedral arrangement of halide ions. This tetragonal distortion is presumably of the Jahn-Teller type and removes the orbital degeneracy. Since $c/a > 1$ for the ionic distribution the energy of the $d_{x^2-y^2}$ orbital is lowered relative to that of the d_{z^2} orbital, and the $d_{x^2-y^2}$ orbital becomes preferentially occupied so that the outer electron configuration can be described as $(d_{xz}, d_{yz}, d_{xy})^3 (d_{z^2})^1$.

For the magnetic interactions it is convenient to consider the immediate surroundings of the halide ions.

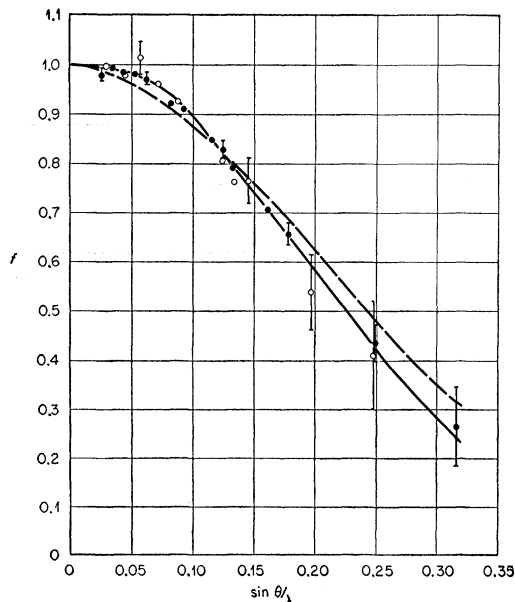


FIG. 7. The experimental Cr^{+2} form factor. These data are from the room temperature paramagnetic scattering of CrF_2 (solid circles) and CrCl_2 (open circles). The solid curve represents the experimental data and for comparison the dashed curve is the experimentally determined Mn^{+2} form factor.

⁷ C. G. Shull and E. O. Wollan, in *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1957), Vol. 2, p. 211.

This provides a relatively simple grouping of ions which includes the nearest and next nearest cation neighbors. Each anion is surrounded by three cations which lie nearly in a plane and of which two are equidistant and the other at a 20% greater distance from the anion. From the previous discussion it is apparent that the singly occupied d_{z^2} orbital is associated with the longer cation-anion separation while the unoccupied $d_{x^2-y^2}$ orbital is associated with the shorter ones. It is observed that the two cations with short cation-anion separations are coupled antiferromagnetically in both structures. In CrF_2 these cations are next nearest neighbors (corner and body center sites) while for CrCl_2 they are nearest neighbors (corner sites along c). In the former the Cr-F-Cr angle is large enough (132°) for indirect exchange involving σ -type overlap of the orbitals but in

the latter the relevant angle is so small (92°) that some other mechanism is probably required. One is forced then to consider such mechanisms as indirect exchange of the $t_{2g}-p_\pi$ type or direct exchange involving t_{2g} cation orbitals. An interpretation of these magnetic structures based on a comparison of the relative strengths of such interactions is at the present somewhat speculative and must await further developments of both theoretical and experimental nature.

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PHYSICAL REVIEW

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Atomic Heat of Sodium Metal from 0.4 to 2°K *

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The atomic heat of sodium metal was measured from 0.4 to 2°K using the magnetic refrigerator calorimeter. The experimental data is given by $C = 1.32T + 0.485 T^3$ millijoule/mole- $^\circ\text{K}$. No anomaly is observed in this temperature range. The experimental value of the electronic specific heat and the Pauli spin paramagnetism measured by Schumacher and Slichter are used for comparison with the electronic band theory of sodium and with those modifications introduced by electron-electron and lattice-electron interactions.

INTRODUCTION

THE alkali metals, having one valence electron per atom and simple crystal structures, are expected to agree rather well with the various theoretical models for their solid-state properties. The suggestion by Rayne¹ that an anomaly occurs in the specific heat of sodium metal near 0.7°K does not have an explanation in terms of these models. Since the magnetic refrigerator calorimeter² is well adapted for specific heat measurements on large samples in the temperature region below 1°K , an investigation of the specific heat of sodium metal under more favorable experimental conditions than used previously was undertaken below 1°K .

EXPERIMENTAL

In order to minimize spurious contributions to the apparent heat capacity of the sodium sample, considerable care was taken in the preparation of the sample. A.C.S. reagent grade sodium metal of stated purity 99.99% was vacuum distilled in order to remove

gaseous impurities and inclusions of the oxide. Since sodium metal readily attacks glass, the distillation was carried out in a stainless steel assembly which permitted the sodium to be deposited directly into a thin-walled copper vessel. After deposition of the liquid metal into the container, the temperature was gradually reduced to allow the sample to anneal. Further handling of the sample was done in an argon atmosphere. A large sodium metal sample of 2.71 moles was prepared in a 2.11-mole copper vessel in this manner.

Temperature measurements were made with a Speer 470 ohm-1/2 watt carbon resistor and heat was supplied electrically by a Manganin heater. The carbon resistor and heater coil were inserted in separate copper inserts which were a part of the copper vessel as shown by K and L in Fig. 1. Thermal bonding to the copper was provided by General Cement No. 56-2 varnish. Since the heat capacity of this assembly of heater, thermometer, and copper container was estimated as 20% of that of the sodium, a heat capacity measurement was made prior to filling. The sample assembly is rigidly mounted inside a copper shield as shown in Fig. 1, and the shield is cooled to 0.3°K by means of the magnetic refrigerator.² Over the temperature range in which heat capacity measurements were made the effects of the residual

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¹ J. Rayne, Phys. Rev. **95**, 1428 (1954).

² C. V. Heer and R. A. Erickson, Phys. Rev. **108**, 896 (1957).