

Synthesis, Structural Characterization, and Magnetic Properties of the Dimer Compounds $\text{Cs}_3\text{Cr}_2\text{X}_9$, $X = \text{Cl}, \text{Br}, \text{I}$

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The title compounds were prepared from the melt and powder neutron diffraction patterns were measured. The result of the Rietveld analysis of the chloride and the bromide data are in agreement with the known crystal structures. $\text{Cs}_3\text{Cr}_2\text{I}_9$ exists in two modifications, which are both present in the same sample. A two-phase Rietveld analysis showed that one modification is isostructural with the bromide and chloride, hexagonal space group $P6_3/mmc$: $a = 8.044(1) \text{ \AA}$, $c = 20.15(1) \text{ \AA}$, $Z = 2$. The other modification belongs to the hexagonal space group $R\bar{3}c$: $a = 14.07(1) \text{ \AA}$, $c = 20.82(1) \text{ \AA}$, $Z = 6$. The lattice and atomic position parameters were determined for both modifications. The two-phase analysis was confirmed by X-ray powder diffraction experiments. Both structures contain the dimeric unit $\text{Cr}_2\text{I}_9^{3-}$, but with different relative dispositions of neighboring dimers. Magnetic susceptibilities of the compounds $\text{Cs}_3\text{Cr}_2\text{X}_9$ ($P6_3/mmc$ modification) were measured and analyzed to give estimates of the intradimer exchange parameter J (singlet-triplet splitting): -16.9 K (Cl), -10.3 K (Br), and -9.2 K (I). © 1986 Academic Press, Inc.

Introduction

The ternary halides $\text{Cs}_3\text{Cr}_2\text{X}_9$ ($X = \text{Cl}, \text{Br}$) crystallize in the hexagonal space group $P6_3/mmc$ (1, 2). They contain the dimeric units $\text{Cr}_2\text{X}_9^{3-}$, shown in Fig. 1, and belong to a novel class of magnetic materials. Antiferromagnetic exchange between the Cr^{3+} ions of the dimer leads to a singlet ground state and triplet as first excited state. Besides this dominant magnetic interaction J , there are much weaker interactions be-

tween Cr^{3+} ions on neighboring dimers along $\text{Cr}-X \cdots X-\text{Cr}$ pathways. The interplay of intra- and interdimer exchange leads to some interesting and novel physical properties at low temperature (3). Intradimer exchange favors a nonmagnetic ground state, while the interdimer interactions, on the other hand, tend to drive the system to a magnetically ordered state at low temperatures. An experimental manifestation of this competitive situation is the energy dispersion of the singlet to triplet dimer excita-

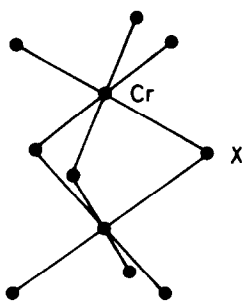


FIG. 1. The dimer $\text{Cr}_2\text{X}_9^{3-}$

tion, which was observed at 1.5 K for both $\text{Cs}_3\text{Cr}_2\text{Cl}_9$ and $\text{Cs}_3\text{Cr}_2\text{Br}_9$ by inelastic neutron scattering (3, 4). These measurements provided a detailed picture of the exciton dynamics and allowed an unambiguous determination of the exchange parameters. No transition to magnetic order was detected for either compound down to 1.5 K. But the bromide was found to be only slightly undercritical at this temperature, whereas the chloride is far from ordering magnetically. Based on these results the corresponding iodide was predicted to undergo a transition to magnetic order at finite temperature (4). Magnetic studies on the iodide would therefore be of high interest and could probably lead to an improvement of our understanding of phase transitions.

Since there was only a brief report with estimated lattice constants about $\text{Cs}_3\text{Cr}_2\text{I}_9$ in the literature (5), in which it was assumed to be isostructural with $\text{Cs}_3\text{Cr}_2\text{Br}_9$, we decided to synthesize and characterize it in detail. $\text{Cs}_3\text{Cr}_2\text{I}_9$ is extremely air and water sensitive and its synthesis is difficult. Since we are not able so far to grow good single crystals our main experimental techniques were powder neutron and X-ray diffraction. There are always problems of purity in polycrystalline samples of such air-sensitive materials. We found it necessary to include $\text{Cs}_3\text{Cr}_2\text{Cl}_9$ and $\text{Cs}_3\text{Cr}_2\text{Br}_9$ in the study, in order to appraise our experimental data. In this paper we present the synthetic technique, describe the crystal

structures of the two modifications of $\text{Cs}_3\text{Cr}_2\text{I}_9$, and discuss the structural properties with an emphasis on their relation to the low-temperature magnetic properties and interactions. We report, in addition, magnetic susceptibility experiments of all the three compounds and the intradimer exchange parameters resulting from their analysis.

Experimental

All three compounds $\text{Cs}_3\text{Cr}_2\text{X}_9$ ($X = \text{Cl}, \text{Br}, \text{I}$) were prepared from the melt by using stoichiometric mixtures of CsX and CrX_3 . CsX was obtained from Merck (suprapur) and CrX_3 from Cerac and Alfa Ventron (typically 99%). All manipulations were performed in a glove box containing less than 0.5% humidity under nitrogen. The quartz ampoules used for the synthesis were 12 cm in length and had a diameter of 1 cm. They were cleaned with 8% HF and dried at 700°C under vacuum. The ampoules were graphitated only for the growth of large single crystals of the bromide. To graphitate an ampoule, it is rinsed with acetone and heated over two big burners. This procedure produces a thin film of graphite on the quartz glass, which prevents the formation of a network between the crystal and the quartz. The loaded ampoules of the chloride and bromide were evacuated at 200°C to a pressure of 10^{-4} Torr. For the iodide the ampoules were quickly evacuated to 10^{-3} Torr at room temperature, then cooled to -40°C and kept at 10^{-4} Torr for 24 hr. All the ampoules were cooled to liquid nitrogen temperature, sealed with an acetylene/ O_2 burner and placed in a Bridgman apparatus (6). The Bridgman apparatus consists of a vertically moving furnace, while the ampoule is kept stationary. A two-zone furnace with a temperature difference of 200°C and a total length of 25 cm was used. The reaction temperatures for the chloride, bromide, and iodide were 920°C, 790 and 725°C, respectively. The

furnace was heated to the reaction temperature and moved downward within 24 hr to melt the powder mixture. After an additional 24 hr, the furnace was slowly moved upward within three weeks. By this technique large single crystals of 1–3 cm³ were obtained for the violet chloride and the green bromide. The crystals are of excellent quality and well suited for inelastic neutron scattering experiments (3, 4). The dark brown iodide boules were polycrystalline. They were found to be inhomogeneous under the microscope. No crystals bigger than approximately 1 mm³ have been obtained so far. X-ray precession showed that even these small crystals are of rather poor quality. Elemental analyses of several boules were found to be identical within experimental accuracy. They are in excellent agreement with the composition Cs₃Cr₂I₉: Cr, 6.34% (calc, 6.32%); and I, 69.0% (calc, 69.4%).

For the density determination individual crystals were picked from the boule and measured by displacement pycnometry with CH₂I₂.

For X-ray powder diffraction measurements the samples were covered with Scotch tape. An evacuated Guinier camera was used to obtain the diffraction patterns on films. The radiation was CuK α ₁.

Finely powdered samples of about 5 cm³ were sealed in vanadium cylinders for the neutron scattering experiments. The neutron diffraction was performed on the two-axis spectrometer DMC, which is equipped with a multidetector. The spectrometer is located at the reactor Saphir at Würenlingen, Switzerland. The wavelength of the graphite monochromator was fixed to 2.330 Å and a 20' beam-collimator was used in front of the sample. A cooled Si filter was placed in front of the monochromator to reduce the epithermic background. The samples were rotated during the measurements, which were all performed at room temperature. The diagrams were measured within a

2 θ range of 7 to 125° and with a step size of 0.1°. These scans therefore produced 1180 data points. The diffraction data were corrected for absorption on the basis of transmission experiments, performed on the same spectrometer by using a special transmission setup.

The data analysis was done on a CDC computer using one and two-phase Rietveld programs (7, 8). The following neutron scattering lengths were used (10⁻¹² cm): Cs, 0.542; Cr, 0.353; Cl, 0.958; Br, 0.677; I, 0.528.

Powder samples of about 50 mg were filled in plexiglass containers under helium gas for the susceptibility measurements. The measurements were performed with the moving sample technique by using a helium cryostat equipped with a superconducting magnet. The applied magnetic field was chosen to be so small that the magnetization depends linearly on the field. The susceptibility was obtained by dividing the magnetization by the applied magnetic field. For the chloride, bromide and iodide the magnetic field was 0.31, 0.56, and 1.02 T, respectively.

Structure Determination and Description

The Rietveld analysis of the chloride and the bromide data is straightforward because the X-ray structures are known (1, 2). The space group is hexagonal, *P*6₃/*mmc*. Calculated and observed diffraction patterns are shown in Fig. 2. The background was measured for 15 points, linearly interpolated between the points, and then subtracted from the measured profiles. It was not refined in the Rietveld fit. In addition to the atomic position parameters we refined the lattice constants, the zero point of the detector, the overall scale factor, and three half-width parameters of the Gaussian lineshapes, as defined in Ref. (7). No asymmetry of the lineshapes was taken into account. The whole measured profile was in-

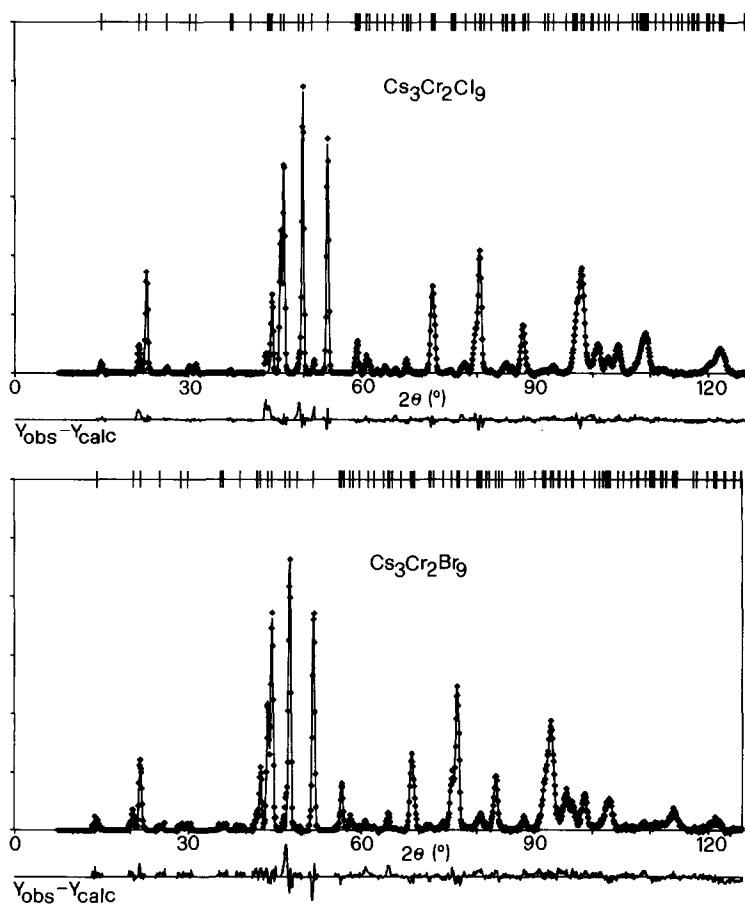


FIG. 2. Rietveld analysis of the neutron diffraction patterns of $\text{Cs}_3\text{Cr}_2\text{Cl}_9$ and $\text{Cs}_3\text{Cr}_2\text{Br}_9$ at room temperature. The wavelength was 2.330 Å. The squares correspond to the observed intensities and the full line represents the Rietveld fit. The tic marks on the top show the individual Bragg reflections.

cluded in the fit. A total of 137 Bragg reflections contribute to the observed diffraction pattern. The determined lattice and atomic position parameters are listed in Table I. For comparison the X-ray single-crystal data are included (1, 2). The agreement between our results and the X-ray results is better for $\text{Cs}_3\text{Cr}_2\text{Cl}_9$ than for $\text{Cs}_3\text{Cr}_2\text{Br}_9$. We obtain a Cr–Cr separation within the dimer of 3.19 Å for the bromide, while the X-ray data lead to 3.32 Å (2). If we trust the X-ray result, this discrepancy has to be mainly attributed to impurities in the powder sample used for neutron diffrac-

tion. In addition, Cr is the atom with the smallest neutron scattering length, accounting for only 8% of the total scattering power in $\text{Cs}_3\text{Cr}_2\text{Br}_9$. Its position is therefore not as accurately determined as that of Cs and Br. No changes in the fit were obtained when the Cr position was fixed to a constant Cr–Cr distance of 3.32 Å within the dimer.

For the iodide we obtained different neutron and X-ray diffraction patterns for different samples prepared by the same method and showing the correct chemical analysis for $\text{Cs}_3\text{Cr}_2\text{I}_9$. This was a strong indication that the iodide crystallizes in more

TABLE I
STRUCTURAL PARAMETERS OF $Cs_3Cr_2X_9$, $X = Cl, Br$
AT ROOM TEMPERATURE OBTAINED FROM A
RIETVELD ANALYSIS OF NEUTRON POWDER DATA^a

$Cs_3Cr_2Cl_9$	Neutron, powder	X-ray, crystal (1)
Space group	$P6_3/mmc$	$P6_3/mmc$
Z	2	2
a (Å)	7.217(2)	7.22(1)
c (Å)	17.91(1)	17.93(2)
Volume (Å ³)	807.8(2)	
Molar weight (g/mol)	821.8	
(4e) Cs (0, 0, $\frac{1}{2}$)		
(4f) Cs ($\frac{1}{3}, \frac{2}{3}, z$) z	0.0761(8)	0.077
(4f) Cr ($\frac{1}{3}, \frac{2}{3}, z$) z	0.8380(10)	0.837
(6h) Cl (x, 2x, $\frac{1}{2}$) x	-0.4817(5)	-0.492
(12h) Cl (x, 2x, z) x	-0.1809(4)	-0.176
	z	0.0933(2)
Temp. factor (Å ²)	1.7(5)	
R_i	0.082	
R_{wp}	0.133	
R_p	0.123	
$Cs_3Cr_2Br_9$	Neutron, powder	X-ray, crystal (2)
Space group	$P6_3/mmc$	$P6_3/mmc$
Z	2	2
a (Å)	7.508(1)	7.507(6)
c (Å)	18.70(1)	18.67(2)
Volume (Å ³)	912.9(3)	
Molar weight (g/mol)	1221.9	
(4e) Cs (0, 0, $\frac{1}{2}$)		
(4f) Cs ($\frac{1}{3}, \frac{2}{3}, z$) z	0.0739(8)	0.0756(3)
(4f) Cr ($\frac{1}{3}, \frac{2}{3}, z$) z	0.8354(9)	0.8388(6)
(6h) Br (x, 2x, $\frac{1}{2}$) x	-0.4919(9)	-0.4851(5)
(12h) Br (x, 2x, z) x	-0.1799(6)	-0.1767(4)
	z	0.0916(3)
Temp. factor (Å ²)	1.6(5)	
R_i	0.133	
R_{wp}	0.194	
R_p	0.180	

^a The structural data determined by single-crystal X-ray diffraction are included for comparison (from Refs. (1, 2)). The R values are defined in Ref. (8).

than one modification. The neutron diffraction diagrams of two samples are reproduced in Fig. 3a (sample *a*) and 3b (sample *b*). Attempts to fit a crystal structure model of space group $P6_3/mmc$ to diagram *a* by a

Rietveld analysis resulted in a weighted R_{wp} value of 0.42 with pronounced disagreement in the region of the most intense reflections. No reasonable analysis of diagram *b* was possible in this space group. Four types of structures are known with stoichiometry $A_3M_2X_9$, two of which contain $M_2X_9^{3-}$ dimers, whereas MX_6^{3-} units are present in the other two (9–11). All these structures were considered for diagram *b*. Reasonable results with $R_{wp} = 0.38$ were achieved only for space group $R\bar{3}c$, the other structure with dimer units. It was then assumed that the samples *a* and *b* consist of two modifications I ($P6_3/mmc$) and II ($R\bar{3}c$) of $Cs_3Cr_2I_9$ in different proportions. A two-phase Rietveld analysis was performed with the data of sample *a*, where we refined the proportion of the two modifications in addition to the above parameters. Introducing a parameter for preferred crystallite orientation, as defined in Ref. (7), was found unnecessary. 117 Bragg reflections of the $P6_3/mmc$ structure and 305 reflections from the $R\bar{3}c$ modification contribute to the observed profile. The result of a least-squares fit, corresponding to a weighted overall $R_{wp} = 0.209$ and individual integrated $R_i(\text{mod.I}) = 0.151$, $R_i(\text{mod.II}) = 0.200$ is given in Fig. 3a. The R values are defined in Ref. (8) and the parameters are listed in Table II. The largest correlation matrix element within the set of structural parameters is between the x and y coordinates of the $R\bar{3}c$ modification: 0.63. Even this value is quite small and proves the significance of the obtained structural parameters. A Rietveld fit was then applied to the data of sample *b*, thereby keeping the structural parameters of the fit of sample *a* constant and varying only the relative amounts of the two modifications in the sample. This fit led to an overall R_{wp} value of 0.310 and $R_i(\text{mod.I}) = 0.441$, $R_i(\text{mod.II}) = 0.306$. The R values are considerably larger than those of the fit *a*, mainly because we only refined the relative amounts of the two modifications and sam-

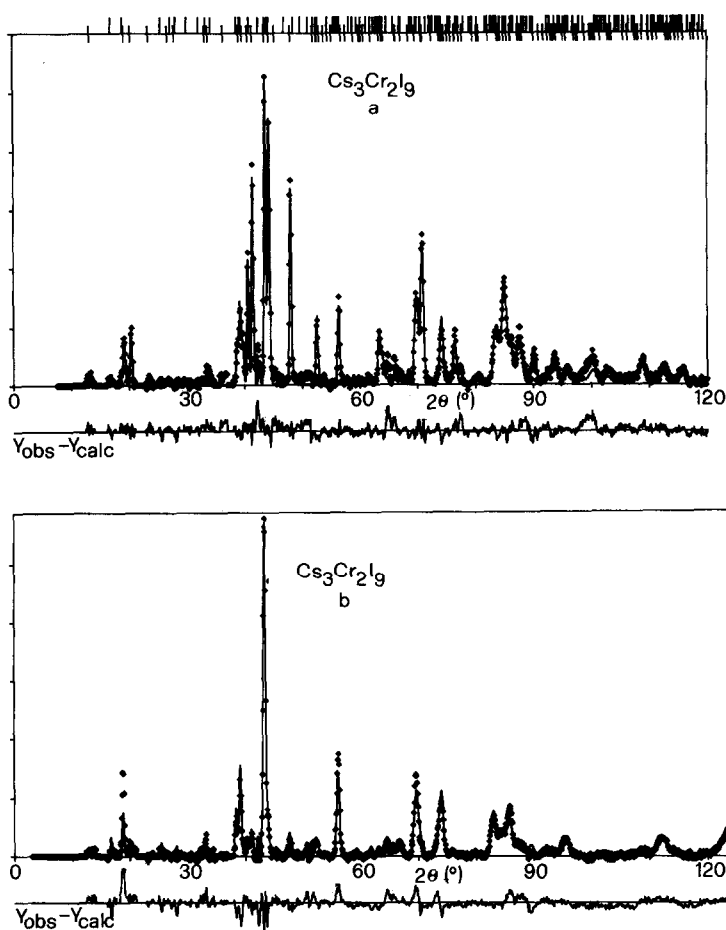


FIG. 3. Two-phase Rietveld analysis of the neutron diffraction patterns of samples *a* and *b* of $\text{Cs}_3\text{Cr}_2\text{I}_9$ at room temperature. The wavelength was 2.330 Å. The upper and lower tic marks indicate Bragg reflections of the $R\bar{3}c$ and $P6_3/mmc$ modifications, respectively.

sample *b* contains a larger amount of unidentified impurities. The result is shown in Fig. 3b. The ratio I/II of the two modifications was thus determined as 1/0.249(4) and 1/0.75(2) in the samples *a* and *b*, respectively.

The R values of the Rietveld fit increase in the series $\text{Cs}_3\text{Cr}_2\text{Cl}_9$ ($R_i = 0.082$), $\text{Cs}_3\text{Cr}_2\text{Br}_9$ ($R_i = 0.133$), and $\text{Cs}_3\text{Cr}_2\text{I}_9$ ($R_i = 0.151$ and 0.200 for modifications I and II, respectively, in sample *a*). We interpret this increase as a result of increasing amounts of impurities due to the increased air sensitivity. The atomic positions are thus least

defined in the iodide. This is particularly true for the Cr position. Cr–Cr distances in the $\text{Cr}_2\text{I}_9^{3-}$ dimer of 3.19 and 3.28 Å were obtained for the modifications I and II, respectively, in the fit of the sample *a*. These are likely to be too small, and indeed, no significant change of the fit was obtained when this distance was kept constant at 3.40 Å for both modifications. This is in good correspondence with our conclusions for $\text{Cs}_3\text{Cr}_2\text{Br}_9$ from a comparison of single crystal X-ray and powder neutron diffraction data.

TABLE II
LATTICE AND ATOMIC PARAMETERS OF THE TWO
MODIFICATIONS OF $\text{Cs}_3\text{Cr}_2\text{I}_9$ OBTAINED FROM A
TWO-PHASE RIETVELD ANALYSIS OF THE NEUTRON
POWDER DATA OF SAMPLE *a* AT ROOM
TEMPERATURE^a

$\text{Cs}_3\text{Cr}_2\text{I}_9$ Modification I			
Space group	$P6_3/mmc$		
Z	2		
<i>a</i> (Å)	8.044(1)		
<i>c</i> (Å)	20.15(1)		
Volume (Å ³)	1129.1(4)		
Molar weight	1644.8		
(4e) Cs	0	0	$\frac{1}{2}$
(4f) Cs	$\frac{1}{2}$	$\frac{1}{2}$	0.0704(10)
(4f) Cr	$\frac{1}{2}$	$\frac{1}{2}$	0.8292(13)
(6h) I	-0.4978(12)	2x	$\frac{1}{2}$
(12h) I	-0.1824(9)	2x	0.0896(4)
<i>R</i> _i	0.151		
<i>R</i> _f	0.149		
$\text{Cs}_3\text{Cr}_2\text{I}_9$ Modification II			
Space group	$R\bar{3}c$		
Z	6		
<i>a</i> (Å)	14.07(1)		
<i>c</i> (Å)	20.82(1)		
Volume (Å ³)	3569(2)		
Molar weight	1644.8		
(18e) Cs	0.6732(31)	0	$\frac{1}{2}$
(12c) Cr	0	0	0.8287(38)
(18e) I	0.1621(28)	0	$\frac{1}{2}$
(36f) I	0.4968(25)	0.3057(19)	0.4263(11)
<i>R</i> _i	0.201		
<i>R</i> _f	0.170		

^a The relative amounts of the two modifications I/II are refined to 1/0.249(4). The total weighted R_{wp} value is 0.209, while the R_p value is 0.225. The *R* values are defined in Ref. (8). The overall temperature factor is refined to 2.1(6) Å².

Unambiguous confirmation of the above two-phase analysis of the neutron diffraction data was obtained from X-ray diffraction. Even though we were so far not able to synthesize either modification of $\text{Cs}_3\text{Cr}_2\text{I}_9$ in pure form, it was possible to separate the two modifications under the microscope. They have different crystal habitus, with modification I exhibiting well defined hexagonal plates, whereas modification II

has no typical crystal shapes. The two X-ray diffraction patterns are shown in Fig. 4. A comparison immediately shows that the purity of the samples was remarkable. Included in Fig. 4 are the calculated powder patterns (calculated with the program LAZY (12)), obtained from the structural parameters determined by neutron diffraction (Table II). The agreement between experimental and calculated positions and relative intensities is impressive. It leaves no doubt that our analysis of the neutron diffraction data is essentially correct. The intensity distribution in the two modifications is very different, both for X-ray and neutron diffraction. In modification II ($R\bar{3}c$)

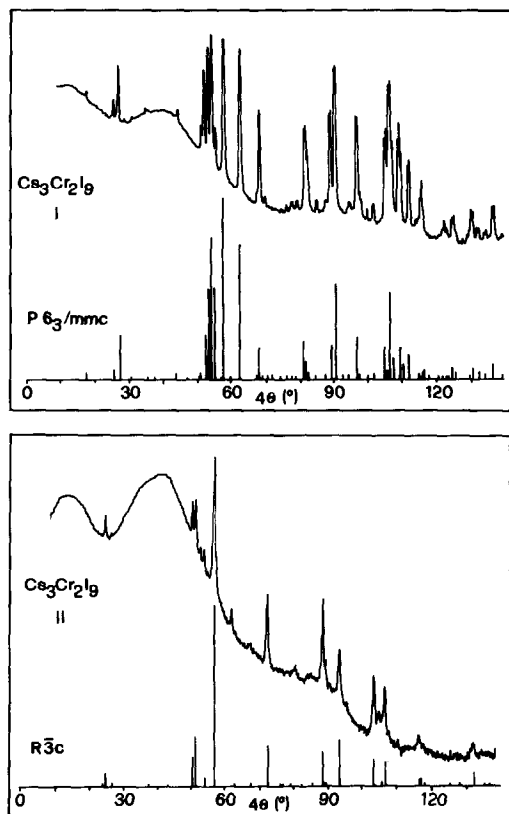


FIG. 4. Guinier X-ray diffraction pattern of modifications I and II of $\text{Cs}_3\text{Cr}_2\text{I}_9$ at room temperature. $\text{CuK}\alpha_1$ radiation was used for the measurements. The corresponding calculated patterns are included.

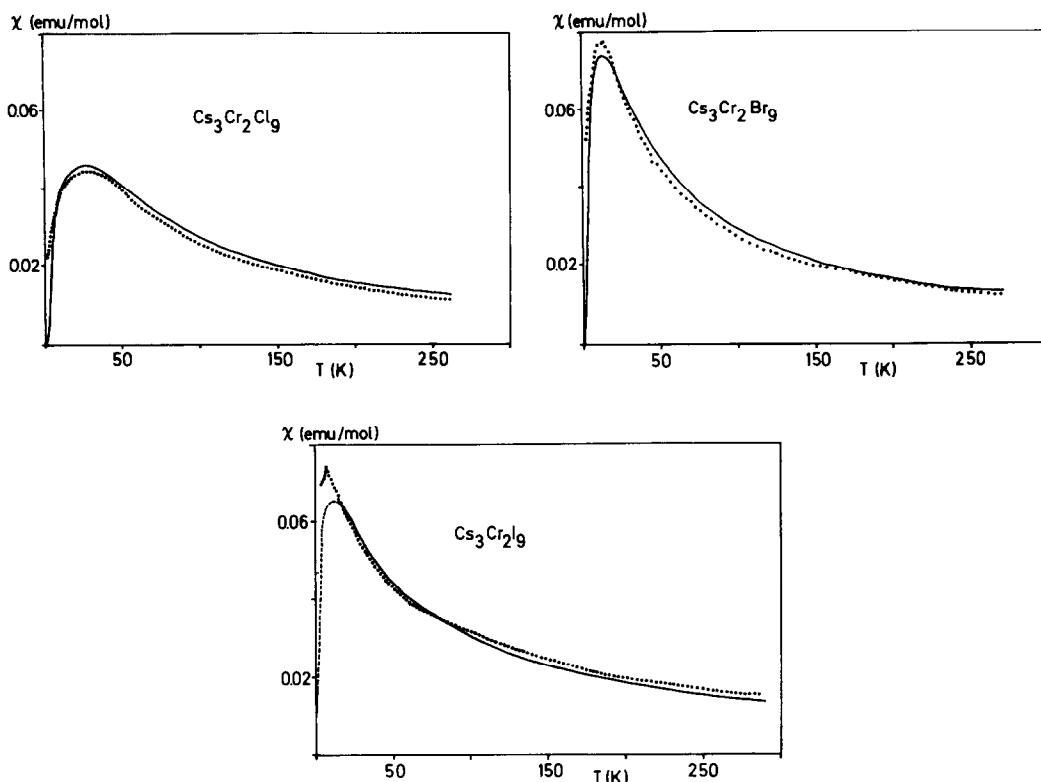


FIG. 5. Magnetic powder susceptibilities of $\text{Cs}_3\text{Cr}_2\text{X}_9$, $X = \text{Cl}, \text{Br}, \text{I}$ ($P6_3/mmc$ modification). The full lines correspond to the least-squares fit outlined in the text.

most of the intensity is distributed among a relatively small number of reflections, with one reflection dominating the others by a factor of at least three. In modification I ($P6_3/mmc$) there are several strong reflections with comparable intensity.

Crystals of modification I have an experimental density of 4.80 g/cm^3 , which compares well with the calculated density of 4.84 g/cm^3 . It was not possible to determine the density of modification II, because the sample decomposed before the completion of the experiment.

Magnetic Susceptibility

Figure 5 shows the magnetic susceptibilities of the dimer compounds $\text{Cs}_3\text{Cr}_2\text{X}_9$, $X =$

$\text{Cl}, \text{Br}, \text{I}$ ($P6_3/mmc$ modification). The susceptibility of the other iodide modification ($R3c$) could not be measured due to decomposition of the compound. The maximum in the susceptibility is broad for the chloride and sharper for the bromide. This reflects that the intradimer interaction is larger for the bromide than for the chloride (vide infra). For the iodide we find a sharp peak at 8.5 K which is attributed to a transition to magnetic order. This assignment is confirmed by neutron scattering experiments (13).

Cr^{3+} has a spin-only ground state, 4A_2 , and a Heisenberg Hamiltonian is therefore appropriate for the intradimer exchange:

$$H = -JS_1 \cdot S_2 \quad (1)$$

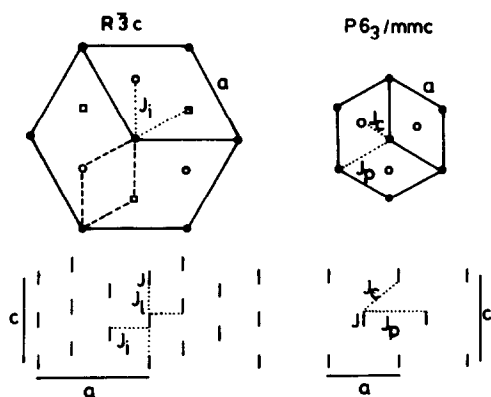


FIG. 6. Schematic structures of the two modifications of $\text{Cs}_3\text{Cr}_2\text{Cl}_9$ in the hexagonal basal plane and along the c axis. The structures are shown in the correct relative size. The dashed line in the $R\bar{3}c$ structure shows how the idealized unit cell of the $P6_3/mmc$ structure is derived. The $\text{Cr}_2\text{L}_9^{3-}$ dimers are represented by circles and squares in the upper part, and by lines in the lower part. The magnetic interactions J , J_p , J_c , and J_1 , J_1 , J_1 are indicated.

S_1 and S_2 are the spin operators of the two Cr^{3+} ions of the dimer. The magnetic susceptibility $\chi_0(T)$ is easily calculated from the Hamiltonian (1):

$$\chi_0(T) = [2N_1\mu_b^2g^2/kTZ][\exp(J/kT) + 5 \exp(3J/kT) + 14 \exp(6J/kT)] \quad (2)$$

with

$$Z = 1 + 3 \exp(J/kT) + 5 \exp(3J/kT) + 7 \exp(6J/kT). \quad (3)$$

However, the compounds $\text{Cs}_3\text{Cr}_2\text{X}_9$ do not consist of isolated dimers, but rather of interacting dimers. Interdimer interactions are treated within the random phase approximation (RPA) (3) and the susceptibility is given by

$$\chi(T) = \chi_0(T)/[1 - 3(J_p + J_c) \cdot \chi_0(T)/(g^2\mu_b^2N_1)]. \quad (4)$$

J_p and J_c are the two relevant interdimer exchange parameters. They are illustrated in Fig. 6 and discussed in more detail in the next section. The expression for the sus-

ceptibility contains three parameters, J , g , and $(J_p + J_c)$. Due to the high correlations between the parameters it is not meaningful to perform least-squares fits with all three parameters. Cr^{3+} compounds normally show g values which are very close to the spin-only value of 2 (14). g values of about 2 have been found for $\text{Cs}_3\text{Cr}_2\text{Cl}_9$ by EPR experiments (15) and for $\text{Cs}_3\text{Cr}_2\text{Br}_9$ by magneto-optical spectroscopy (16). In contrast, a g value of 1.4 was recently reported for $\text{Cs}_3\text{Cr}_2\text{Br}_9$ obtained from optical Zeeman absorption spectra at low temperatures (4.2 K) and very high magnetic fields (10 T) (17). Interdimer interactions, which were neglected in Ref. (17), are important in this temperature and field range where $\text{Cs}_3\text{Cr}_2\text{Br}_9$ is only slightly undercritical (3). Based on this as well as the fact that there is no precedent for a ground-state g value smaller than 1.9 in any known insulating Cr^{3+} compound we decided to use $g = 2$ for all the three compounds in our analysis. The interdimer interaction parameters ($J_p + J_c$) are known for the chloride and the bromide to be -0.73 and -1.1 K, respectively, from the analysis of the magnetic excitations (3, 4). For the iodide this parameter has been estimated to -1.7 K from neutron scattering experiments together with susceptibility measurements (13). We finally performed a least-squares fit with only one parameter, namely J . For the iodide the fit had to be restricted to temperatures above 10 K due to the ordering at lower temperatures.

The results of the fits are shown in Fig. 5 and the following intradimer exchange parameters J were obtained: -16.9 K (chloride), -10.3 K (bromide), and -9.2 K (iodide). The small systematic deviations between the fits and the experimental data in Fig. 5 could be due to modifications of the higher dimer levels by biquadratic exchange or due to a temperature dependence of the interaction parameters. The two dominant trends, however, emerge very

TABLE III
SINGLET-TRIPLET SEPARATIONS OBTAINED BY
DIFFERENT METHODS FOR $\text{Cs}_3\text{Cr}_2\text{X}_9$, $X = \text{Cl}, \text{Br}$

Method	Reference	$X = \text{Cl}$ (K)	$X = \text{Br}$ (K)
Optical spectroscopy (1.3-35 K)	22	-17.3(9)	
(5-50 K)	23	-18.0(7)	
(2-25 K)	16		-8.3(8)
(1.5-25 K)	17		-9.1(9)
EPR (2-5 K)*	15	-16.9(9)	
Powder susceptibility (90-300 K)	18	-18 (1)	-17 (1)
Crystal susceptibility (4.7-77 K)	19	-18.7	
Powder susceptibility (1.5-273 K)*	This work	-16.9(8)	-10.3(8)
Neutron scattering (1.5 K/2 K) RPA*	3, 4	-20.3(1)	-12.0(1)
Neutron scattering, correlation*	20, 21	-19.5	-6.7

* Indicates that interdimer exchange has been considered.

clearly from the analysis: The intradimer exchange decreases in the series chloride, bromide, iodide, while the interdimer interaction increases. The decrease of the intradimer exchange can be rationalized by a simple molecular orbital model (4), and the opposite trends of intra- and interdimer interactions are obviously responsible for the occurrence of magnetic order in the iodide.

Our work represents the first estimate of the exchange parameter J for $\text{Cs}_3\text{Cr}_2\text{I}_9$. On the other hand, J values have already been reported for $\text{Cs}_3\text{Cr}_2\text{Cl}_9$ and $\text{Cs}_3\text{Cr}_2\text{Br}_9$. Various J values obtained by different methods are collected in Table III together with our own values from the present study and from neutron scattering work (3, 4). Interdimer interaction has generally been neglected in the determination of the values listed in Table III. It has been included only in our own studies and, partially, in the EPR work of Ref. (15). In addition, biquadratic exchange has been included in Refs. (16, 17), and small deviations of the g values from 2 were used in Refs. (18, 19). The susceptibility of Ref. (18) was measured be-

tween 90 and 300 K. The obtained J values may therefore be less reliable. This seems to be especially true for the bromide. The agreement between the different J values in Table III is good, if we keep in mind that they were obtained by different theoretical models. The agreement is better for the chloride than for the bromide. This indicates that interdimer exchange, which is larger for the bromide than for the chloride, should be taken into account.

The rather large differences of parameter values obtained for $\text{Cs}_3\text{Cr}_2\text{Br}_9$ by different techniques and different theoretical models in our own work are illuminating and therefore worth a comment. In the inelastic neutron scattering studies the parameters were extracted from data measured at a given temperature, 1.5 K in Ref (3). The J value obtained by using the random phase approximation (3) is almost twice as large as that obtained by correlation theory (20) using the same set of data. Correlation theory is more sophisticated than RPA, and it predicts a temperature dependence of the RPA value. $|J|$ (RPA) is expected to decrease with increasing temperature and to approach the temperature independent correlation value. The analysis of the magnetic susceptibility in the present work is based on the random phase approximation (Eq. (4)). Using this expression to analyze the magnetic data over the whole temperature range should lead to a $|J|$ value which is smaller than the RPA value for 1.5 K, but larger than the correlation value, which indeed it does (Table III). In this procedure we have neglected the temperature dependence of the interdimer interaction parameters as well as a modification of the Boltzmann population factors, both predicted by correlation theory. We feel justified in this because the effects on the intradimer exchange parameter J are expected to be dominant.

To conclude, we have shown that interdimer interactions are important for the com-

pounds $\text{Cs}_3\text{Cr}_2\text{X}_9$, $X = \text{Cl, Br, I}$. They are most important for the iodide, where they lead to a spontaneous magnetic ordering. This ordering is expected from the trend of increasing interdimer interaction and decreasing intradimer exchange in the series chloride, bromide, iodide. In addition, we have shown that the J values obtained from susceptibility measurements represent some kind of temperature-averaged J values, in contrast to those obtained by neutron spectroscopy. Although susceptibility data are usually of moderate accuracy due to the presence of paramagnetic impurities, they lead to J values which describe the magnetic behavior of the compounds over the whole temperature range. Susceptibility measurements and neutron spectroscopy are therefore complementary in the sense that they provide a different focus on the magnetic properties.

Discussion

Compounds of the composition $A_3M_2X_9$ containing the $M_2X_9^{3-}$ dimeric units are known to crystallize either in space group $P6_3/mmc$ or in $R\bar{3}c$, or in closely related lower-symmetry space groups. The properties of both structure types have been elaborated in detail (9). The results of our least-squares fits strongly suggest that the two modifications I and II of $\text{Cs}_3\text{Cr}_2\text{I}_9$ belong to these two structure types. Within the chloride and bromide series of $\text{Cs}_3M_2X_9$ compounds it is possible to establish a trend of the structure type on the basis of molar volumes and ionic sizes (10, 11). Applying the same rules to iodides, a $P6_3/mmc$ structure is expected for $\text{Cs}_3\text{Cr}_2\text{I}_9$ (10, 11). The existence of modification I is therefore no surprise. The $R\bar{3}c$ structure of modification II, on the other hand, is not expected. Its coexistence with modification I demonstrates that empirical rules based on geometrical considerations may not be as valid for iodides as they are for chlorides and

bromides. There is usually more variety in the physical and chemical properties of iodides.

In the following we will discuss the two structure types as they relate to the magnetic properties of the compounds $\text{Cs}_3\text{Cr}_2\text{X}_9$. Both structures contain the Cr^{3+} ions as dimeric units $\text{Cr}_2\text{I}_9^{3-}$ of D_{3h} ($P6_3/mmc$) and D_3 ($R\bar{3}c$) symmetry, respectively, oriented along the c axis of the hexagonal lattice. This dimer unit is illustrated in Fig. 1. Modification I ($P6_3/mmc$) can be thought of as consisting of hexagonal planes built of these dimers with the interaction between the Cr^{3+} ions on neighboring dimers denoted by J_p . Each dimer has six equivalent neighbors in the same plane. The stacking of these planes is not such that linear chains of dimers are formed. Neighboring planes are displaced by $(\frac{1}{3}, \frac{1}{3})$ in the (a, b) directions. One unit cell comprises two planes which we consider as two sublattices. Each dimer has three neighboring dimers in the plane above and three in the plane below. The interaction between nearest Cr^{3+} ions on neighboring dimers in different planes is denoted by J_c . The structure is illustrated in Fig. 6. Only the three interactions J , J_p , and J_c were necessary to discuss the magnetic properties. The Cr–Cr distances corresponding to the interactions J , J_p , and J_c are 3.4, 8.0, and 8.1 Å for the iodide, if we fix the intradimer distance to 3.4 Å, as outlined in the discussion of crystal structures.

Ideally the unit cell of modification II ($R\bar{3}c$) is enlarged by $\sqrt{3}$ in the a direction compared to modification I, while the c axes are of equal length. The observed unit cell of modification II is enlarged by 1% in the a direction and by 3% in the c direction, compared to this idealized structure. The schematic structure is shown in Fig. 6. The hexagonal lattice consists of linear chains of dimers with each unit cell containing six dimers in three neighboring chains. We denote the interaction between Cr^{3+} ions on

neighboring dimers within and between chains as J_1 and J_i , respectively. The Cr–Cr distances corresponding to the interactions J , J_1 , and J_i are 3.4, 7.0, and 8.1 Å, respectively, if we use the fixed value of 3.4 Å for the intradimer separation. Due to the relatively large difference between nearest intrachain and interchain distances, it can be expected that the compound behaves magnetically as a dimerized linear chain, with a singlet dimer ground state.

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