

Neutron Diffraction Study of the Magnetic Structures for the Perovskite-Type Mixed Oxides $\text{La}(\text{Mn}, \text{Cr})\text{O}_3^{\dagger*}$

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A neutron diffraction study has been made of the magnetic properties of the series of perovskite-like compounds $\text{La}[(1-x)\text{Mn}, x\text{Cr}]\text{O}_3$. This series exhibits ferromagnetic and antiferromagnetic properties which depend on the composition of the sample. The antiferromagnetic structure of pure LaMnO_3 persists only for very small concentrations of Cr^{+3} ; the antiferromagnetic structure characteristic of pure LaCrO_3 is found over a large composition range. For samples of intermediate composition a ferromagnetic moment is observed, the maximum occurring at about 20% Cr^{+3} . In contrast to the mixed oxides $[(1-x)\text{La}, x\text{Ca}]\text{MnO}_3$ which for certain compositions were truly ferromagnetic, the maximum ferromagnetic moment in this series is very much less than that expected if all the spins were contributing to the moments. A complex ferrimagnetic structure is suggested for the intermediate composition range.

INTRODUCTION

THE techniques of neutron diffraction have previously been applied by Wollan and Koehler¹ to the study of the magnetic structure properties of the perovskite-type mixed oxide system $(\text{La}, \text{Ca})\text{MnO}_3$. In addition to the ferromagnetic ordering which had previously been observed over part of the range of composition by Jonker and Van Santen² on the basis of macroscopic magnetic measurements, a variety of antiferromagnetic structures was observed, the amount and type of which depended upon the relative content of trivalent and tetravalent manganese and on their ordering on lattice sites.

The present investigation is concerned with the similar series of perovskite-type mixed compounds $\text{La}[x\text{Mn}, (1-x)\text{Cr}]\text{O}_3$. This series, which for convenience will be referred to as the (Mn, Cr) series, starts with the same compound LaMnO_3 as the previously studied one which will be referred to as the (Mn) series and ends with the compound LaCrO_3 in which the Cr^{+3} ions have the same number of $3d$ electrons as the Mn^{+4} ions in the compound $\text{Ca}^{+2}\text{Mn}^{+4}\text{O}_3$ at the end of the (Mn) series. It is also known from the work of Koehler and Wollan³ that the magnetic structure of LaCrO_3 is identical to that of CaMnO_3 . The two series do, however, have one distinct difference which is associated with the possibility of ion ordering. In the (Mn) series, ordering of the Mn^{+3} and Mn^{+4} ions may occur merely by electron transfer, the conductivity being relatively high, and there was evidence that such ordering did take place. In the (Mn, Cr) system on the

other hand, the Mn^{+3} and Cr^{+3} ions, being of different atomic types, are fixed to lattice sites at the time of sample preparation, and the compounds have a relatively low conductivity. It was hoped that the study of the effect of this difference in these otherwise similar series of compounds might lead to a better understanding of the magnetic interactions between these ions.

SAMPLE PREPARATION

The method of preparing the mixed oxides has been outlined by Jonker and Van Santen^{2,4} and was essentially the same as that used in the production of the (Mn) series. For the (Mn, Cr) mixtures, where it was desired to keep the Mn^{+4} content at a minimum, an atmosphere of pure nitrogen was used in the production. Because the valence state of the sample is partially determined by the maximum temperature, a final temperature of 1400°C was used for low tetravalent ion content. Wollan and Koehler found that quenching had no apparent effect on the structure of the manganites; however, since a magnetic field study requiring the briquet form was to be made on some of the samples, they were cooled slowly to prevent possible cracking.

In order to check the purity and determine the valence state of the metallic ions, a chemical analysis was made⁵ of all samples. X-ray powder diffraction studies were made⁶ to check the homogeneity of the samples, to determine the lattice parameters and to ascertain the distortions from cubic symmetry. Crystallographically, all compounds were some modification of the perovskite structure which is ideally cubic. Samples which showed the presence of unfused starting chemicals or crystallographic inhomogeneity were not used for magnetic analysis.

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¹ E. O. Wollan and W. C. Koehler, *Phys. Rev.* **100**, 545 (1955).

² G. H. Jonker and J. H. Van Santen, *Physica* **16**, 337 (1950).

³ W. C. Koehler and E. O. Wollan, *J. Phys. and Chem. Solids* (to be published).

⁴ G. H. Jonker and J. H. Van Santen, *Physica* **19**, 129 (1953).

⁵ These analyses were made by A. D. Horton of the Analytical Chemistry Division.

⁶ H. L. Yakel and R. M. Steele of the Metallurgy Division produced the x-ray diffraction patterns and aided in the analyses.

APPARATUS AND PROCEDURE

The neutron spectrometer with cryostat and magnet developed by Wollan and Koehler¹ during the course of their investigations and described in their report was used for this entire series. Diffraction patterns were obtained at room temperature or above the critical temperature and at one or more temperatures below the critical temperature at which diffraction peaks characteristic of the magnetic ordering were observed. Curves presented here are point by point difference curves for data taken above the critical temperature and well below the critical temperature. These curves display only the scattering resulting from temperature-dependent phenomena. The nuclear contributions to the scattering are subtracted out, by this procedure, leaving only temperature-dependent phenomena of which the magnetic scattering is the most important. Corrections can be made for the Debye temperature effect on the nuclear scattering. If crystallographic changes occur, there may also result shifts of position and changes of intensity of some diffraction peaks. Since magnetic coupling is largely determined by atomic arrangement, the difficulty of separating the effect of crystallographic changes and true magnetic effects limit the utility of the difference curves.

Since the intensity of the Bragg peaks resulting from coherent magnetic scattering depends upon the degree of temperature saturation, it was desirable to obtain data at more than one temperature below the critical point. By fitting the data to an appropriate Brillouin curve, the ordering temperatures for the samples were determined. When two magnetic phases are present, the transition temperatures are generally not equal.

CRYSTALLOGRAPHIC DATA

The room temperature x-ray diffraction data obtained for samples of the (Mn, Cr) series are given in Table I and in Fig. 1(a). The apparent symmetries of these compounds, as determined from x-ray powder data are represented as monoclinic to display the distortions of these structures from ideal cubic symmetry in a convenient manner. It is obvious that an orthorhombic

description could equally well have been given, and in fact such a description correctly characterizes many of the compounds of this series. From the recent work of Geller,⁷ Geller and Wood,⁸ and Gilleo⁹ it is known that many perovskite-like compounds including LaCrO_3 and the mixed oxides $\text{La}[(1-x)\text{Mn}, x\text{Cr}]\text{O}_3$ for $0.33 < x \leq 1$ are isostructural with orthorhombic GdFeO_3 with varying degrees of distortion. It is highly possible that except for compositions close to LaMnO_3 , for which the correct structure has still not been definitely established that all the compounds of the series are GdFeO_3 -type perovskites.

For these compounds the (Mn, Cr) ions are in special positions of the space group and hence the interpretation of the magnetic scattering is not complicated by unknown magnetic ion parameters and the difference pattern technique eliminates to a great extent uncertainties introduced by the lack of a precise knowledge of the lanthanum and oxygen parameters.

The data shown in Fig. 1(a) are similar to those obtained for the (Mn) series for which apparent cubic symmetry was attained with about 25% Mn^{+4} ; in this case the apparent monoclinic splitting comes up to a minimum value at about 20% Cr. The magnitude of the average lattice parameter changes only slightly with increasing Cr^{+3} content in contrast with the behavior of the lattice parameters in the (Mn) series.

A- AND G-TYPE MAGNETIC STRUCTURES

The terminology used here is the same as that introduced for the magnetic structures in the paper on the (Mn) series.¹ The *A*-type structure for pure LaMnO_3 has been described previously. In this structure the direction of the antiferromagnetic coupling is presumed to be that of the unique shorter axis represented in Fig. 1(a). The *G*-type structure, which represents the magnetic moment arrangement of the Cr^{+3} ions in LaCrO_3 , is an antiferromagnetic one in which each metallic ion is antiferromagnetically coupled (via the oxygen ions) with all six nearest neighbors.

The *A*- and *G*-type magnetic structures characteristic of the pure Mn and Cr compounds persist into the

TABLE I. Summary of sample data.

No.	Sample Composition	% of ions with spin 3/2	Apparent symmetry	Lattice parameters		
				$a_1 = a_3(\text{Å})$	$a_2(\text{Å})$	β
16	LaCrO_3	100	Monoclinic	7.778	7.735	90°23'
15	$\text{La}(0.2 \text{ Mn}, 0.8 \text{ Cr})\text{O}_3$	80	Monoclinic	7.778	7.754	90°15'
13	$\text{La}(0.4 \text{ Mn}, 0.6 \text{ Cr})\text{O}_3$	60	Monoclinic	7.783	7.778	90°18'
6	$\text{La}(0.6 \text{ Mn}, 0.4 \text{ Cr})\text{O}_3$	44	Monoclinic	7.789	7.788	90°11'
7	$\text{La}(0.8 \text{ Mn}, 0.2 \text{ Cr})\text{O}_3$	33	Monoclinic	7.816	7.809	90°12'
8	$\text{La}(0.9 \text{ Mn}, 0.1 \text{ Cr})\text{O}_3$	12	Monoclinic	7.883	7.762	91° 1'
9	$\text{La}(0.95 \text{ Mn}, 0.05 \text{ Cr})\text{O}_3$	6.9	Monoclinic	7.958	7.723	91°30'
12	LaMnO_3	2.0	Monoclinic	7.973	7.693	92° 7'

⁷ S. Geller, J. Chem. Phys. 24, 1236 (1956).⁸ S. Geller and E. Wood, Acta Cryst. (to be published).⁹ M. A. Gilleo, Acta Cryst. (to be published).

region of the mixed (Mn, Cr) compounds. The *A*-type structure [which is characterized by an (010) reflection] disappears rapidly with increase of chromium content as shown by the line connecting solid circles in Fig. 1(c). This phase disappears completely at about 15% chromium content; this roughly corresponds to the destruction of the *A* phase by an average replacement of one of the six nearest Mn neighbors of each Mn ion by a Cr ion. The rate of destruction of the *A* phase by the introduction of Cr³⁺ ions in the (Mn, Cr) system is quite comparable to that observed in the (Mn) system when Mn³⁺ ions are replaced by Mn⁴⁺ ions.

On the chromium side of the (Mn, Cr) system, the *G*-type magnetic structure [as measured by its characteristic (111) reflection] persists over a large composition range; the apparent destruction of this magnetic phase requires the addition of about 60% Mn³⁺ ions [Fig. 1(c)]. This contrasts with the results obtained on the calcium rich side of the (Mn) system. One must, however, recognize that the (111) reflection does not necessarily identify a discrete *G* phase but does nevertheless characterize the type of antiferromagnetic coupling associated with this structure.

INTERMEDIATE COMPOSITIONS

In the (Mn) system, the disappearance of one magnetic phase was accompanied by the simultaneous growth of other phases to the extent that essentially all of the ions were ordered in one or another structure below a critical temperature. In the (Mn, Cr) system also, there is evidence for a more or less supplementary growth of other magnetic structures but these are of entirely different character than those exhibited by the related (Mn) system. In order to discuss these phases it is convenient to refer to the $\bar{\mu}^2$ curve supplementary to that associated with the *A* and *G* structures. The $\bar{\mu}_{\text{theory}}^2 - (\bar{\mu}_A^2 + \bar{\mu}_G^2)$ values are indicated by the light line in Fig. 1(c). An uncertainty in the presentation of the data for sample No. 7 (20% Cr) is to be noted. We were unable to produce a stoichiometric sample for this composition; chemical analysis indicated the presence of Mn⁴⁺ ions which have spin 3/2 as do the Cr ions. Whether the sensitive parameter in this composition region of the (Mn, Cr) series is the ionic spin or the atomic species cannot be determined and hence the values for this sample represented in Fig. 1 could be shifted to the right as indicated by the arrows. The dotted alternate sections of the curve in Fig. 1(c) indicate this indeterminacy.

In the next paragraphs the magnetic structure properties of the intermediate region will be discussed.

a. Antiferromagnetic Properties

In addition to the antiferromagnetic *A* and *G* structures characteristic of the pure compounds, still other magnetic structures are indicated for intermediate com-

positions. Figure 2 shows temperature difference diffraction patterns for samples having 5%, 10%, and 20% chromium content, respectively. They show the decrease of the intensity of the (010) line characteristic of the *A*-type structure and the development of a prominent temperature dependent superlattice line at $2\theta \sim 12^\circ$. This line can be accounted for on the basis of a magnetic structure consisting of antiferromagnetic layers of the type shown in Fig. 3 with ferromagnetic coupling between layers. The 12° line corresponds to the planes shown. They are indexed in Fig. 2 on a cubic cell having edges twice that of the chemical cell as (3/2, 1/2, 0). The basal plane of the unit cell shown in the figure is twice that required for this structure; it is chosen this way, however, for convenience in later considerations. For this cell $a=b=2\sqrt{2}a_0$ and $c=a_0$, where a_0 is the edge of the ideal chemical cell. The 12° superlattice line is found to persist for this (Mn, Cr) system for a large range of composition. For convenience, the structure characterized by this line will be designated as the *X*-type.

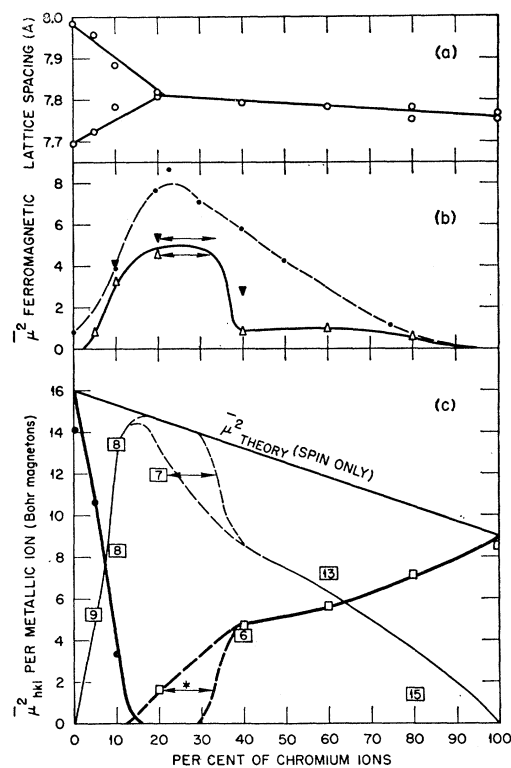


Fig. 1. Magnetic moments and lattice spacing as a function of sample composition. (a) Room temperature lattice constants from x-ray measurements. (b) Ferromagnetic moments. Closed triangles refer to ferromagnetic saturation measurement, open triangles to neutron diffraction measurement. Curve represents Jonker's data. (c) Solid circles represent *A* structure; solid squares represent *G* structure; open squares represent hypothetical antiferromagnetic structure; thin curve represents supplemental $\bar{\mu}_{\text{theory}}^2 - (\bar{\mu}_A^2 + \bar{\mu}_G^2)$. Sample No. 7 nonstoichiometric; 16% of Mn is +4.

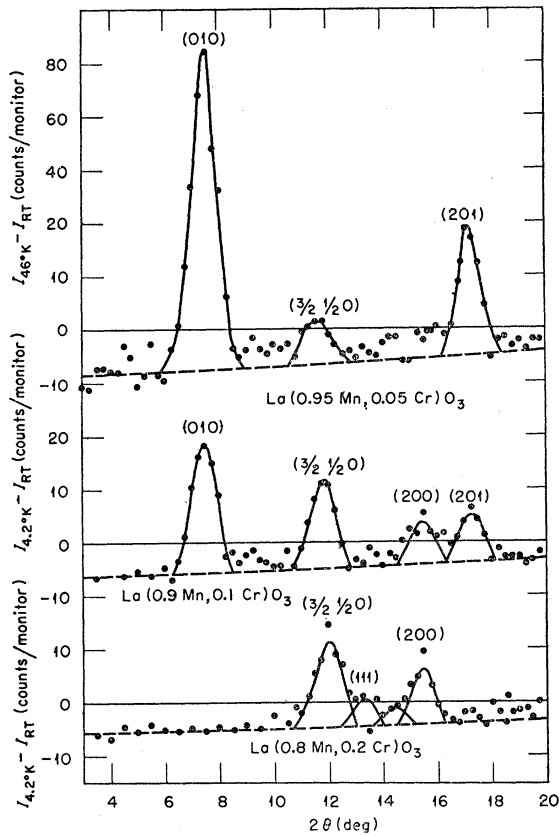


FIG. 2. Soller-slit temperature-difference patterns for samples of intermediate composition, showing presence of X-type structure. Indices on basis of simplest cubic magnetic cell whose dimensions are double that of chemical unit cell.

b. Ferromagnetic Properties

It is to be noted from Fig. 2 that the difference patterns involve, in addition to the superlattice line at 12° , an appreciable temperature dependent intensity for the (200) reflection. These lines indicate that there is also a ferromagnetic contribution to the scattering. The ferromagnetic aspect of all the samples was studied by observing the (200) line intensities and the results are represented by the open triangles in Fig. 1(b). The saturation magnetization was also measured for some samples by the induced magnetization method described in the paper on the (Mn) series. These results are represented in the figure by the solid triangles. Measurements of this latter type have also been made for the (Mn, Cr) system by Jonker¹⁰ whose results are given in the same figure by the dotted line. Although the quantitative agreement is not good and some ambiguity is apparent in the interpretation of the magnetic moment as determined by the intensity of the (200) line, the curves do agree in character.

¹⁰ G. H. Jonker, *Physica* (to be published).

c. Ferrimagnetic Properties

The data discussed thus far have shown that samples in the region of intermediate composition possess both ferromagnetic and antiferromagnetic properties. In order to determine whether these properties are to be associated with separate magnetic phases or are to be associated with a ferrimagnetic structure, a study of the field sensitivity of the 12° superlattice line was made. The results for the (0.4 Mn, 0.6 Cr) sample are shown in Fig. 4. Curve (a) shows the low-temperature pattern, curve (b) shows the temperature difference pattern and curve (c) shows the magnetic field difference pattern. Curves (a) and (b) show that for this composition not all of the 12° line is temperature dependent. This line must have some nuclear contribution since the Néel point is well below room temperature (180°K). Curves (b) and (c) show that the temperature-dependent part of this 12° reflection is, within experimental error, entirely erased by a magnetic field. The (111) line, which is identified with the G structure, is seen to be essentially unaffected by the field and hence not related to the new phase. There is, however, a small negative field effect on the (111) line which cannot easily be accounted for.

It appears then that the intermediate compositions possess, in addition to the A- and G-type structures, a ferrimagnetic phase in which the ferromagnetic moment and the intensity of the most prominent superlattice reflection ($2\theta = 12^\circ$) vary with sample composition. The similarity between the ferromagnetic properties as represented in Fig. 1(b), and the supplementary curve in Fig. 1(c) and also the fact that the 12° superlattice line persists throughout the entire intermediate region suggests a common type ferrimagnetic structure for this region. The structure must basically have the unit cell characteristics shown in Fig. 3 in order to account for the 12° superlattice line and yet have more spins oriented in one direction than in the opposite direction to produce the ferromagnetic moment. Moreover, this unbalance of spins must change with composition to account for the changing ferromagnetic moment. In addition there are some additional weak reflections present in some patterns indicating particular geo-

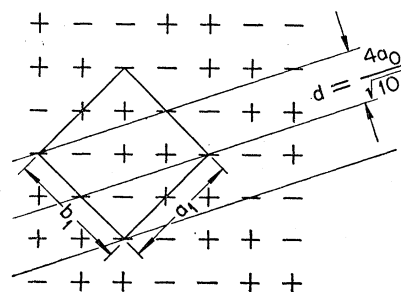


FIG. 3. A single layer of the X-type antiferromagnetic structure. One set of the 120 planes are indicated. On the basis of the simplest cubic cell these are the $\frac{3}{2}, \frac{1}{2}, 0$ planes.

metrical arrangements of moments which must be accounted for in developing a satisfactory scheme for the intermediate phase region.

Some success was achieved in accounting for these data on the basis of ferrimagnetic modifications of the antiferromagnetic structure shown in Fig. 3 for which different moment arrangements are introduced into successive layers of the basal cell shown. A four-layered cell is necessary to allow indexing of all observed peaks. A characteristic feature of a given structure is the direction of the spin relative to a crystallographic axis. For the proposed ferrimagnetic structures the best correlation is found when the direction chosen is parallel to the unique axis; for some samples a direction perpendicular to the unique axis allows better correlation with observed intensities. In no case were structures found which satisfactorily correlated the ferromagnetic moments and all superlattice line intensities; a qualitative accounting of the general trend of the data can, however, be given. Values of $\bar{\mu}^2$ for the samples of the intermediate region determined on the basis of the antiferromagnetic cell of Fig. 3 and the observed intensity of the 12° line are entered in Fig. 1(c) as the numbered open squares. Modifying the X structure to include the unbalanced moments of a ferrimagnetic cell has the effect of raising the $\bar{\mu}^2$ values. This results from the fact that the intensity of the 12° reflections is then lower for the same total spin moment of the sample. As an example, the value of $\bar{\mu}^2$ calculated for sample No. 8 (10% Cr) with the ferromagnetic moment produced by randomly flipping the proper number of spins of the X structure leads to the $\bar{\mu}^2$ value represented by the numbered open circle in the figure. The agreement with the supplementary curve is thus seen to be improved.

DISCUSSION

The magnetic properties of the (Mn, Cr) systems described here and the previously reported (Mn) system have several features in common, and several distinct differences. In each case the magnetic ions for the end point compositions have the same electronic configurations and LaCrO_3 and CaMnO_3 have the same antiferromagnetic spin configuration. Both systems involve mixtures of $3d^3$ and $3d^4$ ions but the magnetic structures of the intermediate compositions in the two cases are entirely different. These differences are undoubtedly to some extent associated with the fact that the Cr^{+3} ions take their positions, presumably at random, at the time the compound is formed. In the (Mn) series only electron transfers are necessary to produce ordering of Mn^{+3} and Mn^{+4} ions.

For both systems there is a rapid destruction of the antiferromagnetic A-type structure with increasing Mn^{+4} or Mn^{+3} concentration, and this is accompanied by the buildup of a ferromagnetic or ferrimagnetic phase. Observations in the (Mn) series are consistent with the assumption of a strong positive $\text{Mn}^{+3}-\text{Mn}^{+4}$

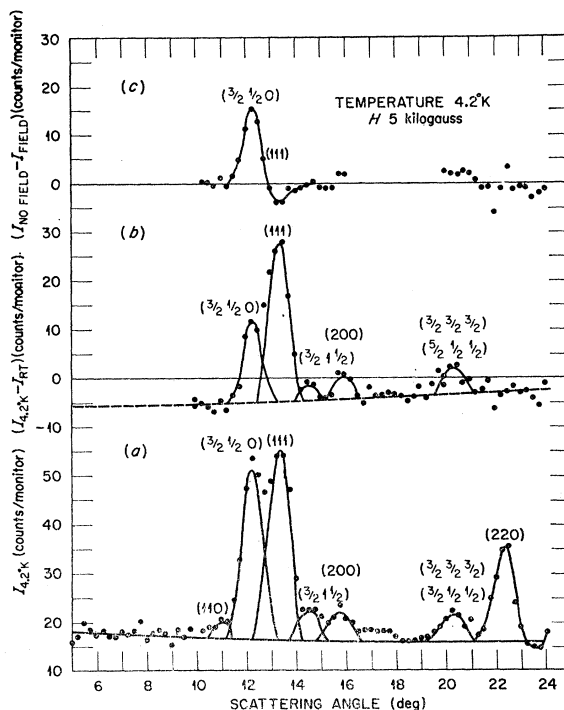


FIG. 4. Soller-slit patterns showing temperature and field dependence for $\text{La}(0.4 \text{ Mn}, 0.6 \text{ Cr})\text{O}_3$, sample No. 13.

exchange, which because of the ease of ordering, leads to a clustering of the Mn^{+4} ions in a localized ferromagnetic region within a given crystallite. A similar mechanism may also be operative in the (Mn, Cr) series as indicated by the coexistence of antiferromagnetic and ferrimagnetic phases, but to a lesser extent.

Qualitatively one may argue that the ferrimagnetic properties of the series for low Cr^{+3} (e.g., up to about 20%) are consistent with a strong positive $\text{Mn}^{+3}-\text{Cr}^{+3}$ interaction. For in such a case the introduction of an occasional Cr^{+3} ion into the A-type antiferromagnetic structure could cause a spin reversal of one or more of its nearest Mn^{+3} neighbors leading to a ferromagnetic moment. This can neither be a completely random nor completely ordered process, however, and be consistent with the data.

On the high- Cr^{+3} -content side of the present series, the G-type structure is seen to fall off less rapidly with composition change than was the case in the (Mn) system. This may be related in part to the small change in spacing value in the high-Cr-content range of this series. In any case one must conclude that the introduction of Mn^{+3} into LaCrO_3 does not have a strong tendency to alter the type of coupling and hence the Mn-O-Cr neighbor relations are compatible with antiferromagnetic exchange in this composition range.

Crystallographically the two systems are very similar. Both systems develop cubic symmetry in the same composition range and the ferromagnetic properties,

although developing differently in the two systems, do reach a maximum at this point. Jonker has shown that the Curie temperatures for the two systems have maxima for similar ranges of composition, with the maximum corresponding to the composition with highest ferromagnetic moment.

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Thermal Inelastic Scattering of Cold Neutrons in Polycrystalline Graphite

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The temperature variation of the thermal inelastic scattering cross section of cold neutrons in graphite, calculated on the assumption of a Debye frequency spectrum, is in disagreement with experiments. This is not surprising in view of the highly anisotropic nature of its lattice. In this paper we have modified the formulas of the scattering cross section obtained earlier by us, for the case of an anisotropic layer lattice. Using the Krumhansl and Brooks model of graphite with the values of the parameters occurring in their theory as fixed by Keesom and Pearlman on the basis of their specific heat measurements at low temperatures, we have calculated the inelastic scattering cross section for 10 Å neutrons as a function of temperature. The calculated values are in reasonably good agreement with the experimental results of the Brookhaven group. For room temperature we have also calculated the variation of the scattering cross section with neutron wavelength, and we find that it is in disagreement with the observed variation. This discrepancy may partly be due to small-angle scattering arising from the finite grain size of carbon.

I. INTRODUCTION

RECENT attempts to explain the observed temperature dependence of the thermal inelastic scattering cross section of cold¹ neutrons in solids characterized by high lattice symmetry have been fairly successful.²⁻⁴ These attempts are based on the assumption of a Debye frequency spectrum for the lattice vibrations. Assuming a similar lattice spectrum for graphite, Kleinman⁵ (quoted by Hughes⁶) has calculated the scattering cross section for 7 Å neutrons, as a function of temperature. His calculations are in complete disagreement with the observed values. This is not surprising in

view of the highly anisotropic nature of the graphite lattice. As is well known, the anomalous behavior of the specific heat of graphite is also a consequence of this anisotropy.

Recently Krumhansl and Brooks⁷ have made a theoretical analysis of the normal modes of graphite. They divide the lattice vibrations into two types: (i) modes with atomic displacements normal to the layer planes, and characterized by a Debye temperature Θ_z , and (ii) modes with atomic displacements in the layer planes, and characterized by a Debye temperature Θ_{xy} . Their theory involves certain parameters the values of which can now be fixed with a fair degree of certainty from the more recent experimental data of Keesom and Pearlman⁸ on the specific heat of graphite between 1° and 20°K. With the parameters so chosen, the theory of Krumhansl and Brooks is able to explain the variation of the specific heat from 1° to 1000°K.

¹ The word "cold" is used here to denote neutrons which have wavelength greater than that corresponding to the Bragg cutoff.

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