JOURNAL OF SOLID STATE CHEMISTRY 13, 77–83 (1975)

Magnetic Ordering in Ba_2MnReO_6*

C. P. KHATTAK

Department of Materials Science, SUNY at Sony Brook, New York 11790 and Brookhaven National Laboratory,† Upton, New York 11973

D. E. COX

Brookhaven National Laboratory,† Upton, New York 11973

AND

F. F. Y. WANG

Department of Materials Science, SUNY at Stony Brook, Nev York 11790

Received February 25, 1974

The ordered perovskite Ba_2MnReO_6 has been reported to be ferrimagnetic with a Curie temperature of 105°K and a saturation moment of 3.9 μ_B, consistent with antiparallel coupling of spin-only moments of the combination Mn^{2+}–Re^{6+}. Neutron diffraction studies on polycrystalline material have confirmed that the Mn and Re ions are completely ordered chemically. At 4.6°K, two sets of magnetic peaks were observed, the stronger consistent with the ferrimagnetic model, and the weaker characteristic of antiferromagnetic ordering of the first kind, indicative of some canting of the moments in adjacent (001) planes. The moment on the Mn ion was found to be 4.8μ_B, but that on the Re ion was found to be less than 0.2 μ_B if a localized free-ion form factor is assumed. These results can be interpreted in terms of an extended spin density distribution due to covalent bonding in the ReO_6 clusters.

Introduction

Simple perovskites have the general formula ABO_3 where the large A cation is in twelvefold coordination with oxygen and the smaller B cation has sixfold coordination. If equiatomic proportions of two types of B cations are introduced, mixed perovskites, $A_2BB'O_6$ are formed, and, if the two types of B cations have sufficiently large differences in charge or size, an ordered structure results in which alternate (111) layers are occupied by B and B′ cations, respectively (Fig. 1). In such a case the unit cell is doubled along all three axes as compared to the simple perovskite, and the structure of the material has face-centered cubic symmetry. There is a slight shift in the oxygen positions, but the octahedral symmetry of the B and B′ cations is retained.

Magnetic measurements have revealed that many of these compounds in which B is a paramagnetic ion and B′ is diamagnetic order antiferromagnetically at low temperatures (*1*). In the case of Ba_2CoWO_6 and Ba_2NiWO_6, there is ordering of the second kind, in which next-nearest-neighbor moments are coupled antiparallel (*2*). However, when B′ is also paramagnetic a spontaneous moment is often observed (*3–5*). This may be interpreted in terms of a ferrimagnetic structure in which there is antiparallel coupling of the unequal B and B′ moments, analogous to the antiferromagnetic G type of structure found in the simple perovskites where B and B′ are

---

* A brief account of this work was given at the International Conference on Magnetism, Moscow (1973).

† Work performed under the auspices of the U.S. Atomic Energy Commission.

Printed in Great Britain

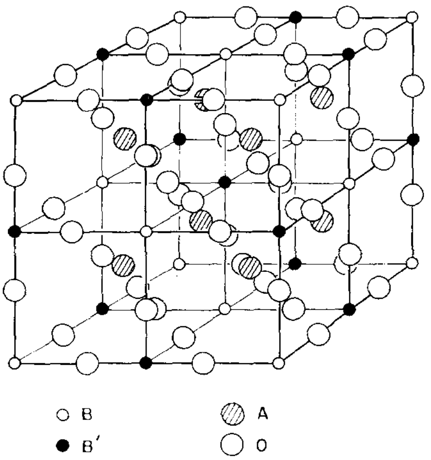

FIG. 1. Ordered perovskite structure $A_2BB'O_6$. The displacement of the anions towards the more highly charged B′ ion has been exaggerated for illustrative purposes.

identical. It should be noted, however, that in many cases the magnitude of the observed moment appears to be much too low to be accounted for in this way, and more complex structures may in fact exist. For example, Ba_2CoReO_6 has been found to have a spiral arrangement which is a modulation of the ferrimagnetic structure (*6*).

The present paper describes a neutron diffraction study on polycrystalline Ba_2MnReO_6 in which a spontaneous moment of about 4 μ_B has been reported at 4.2°K (*7*). This has been explained in terms of a ferrimagnetic structure in which there is antiparallel coupling of Mn^{2+} and Re^{6+} moments of 5 and 1 μ_B, respectively. The latter would correspond to the spin-only value for a $5d^1$ configuration, although one might have expected spin-orbit coupling to have modified this considerably in an octahedral field (*8*). The neutron data show that the Mn moments are coupled parallel with the expected value of about 5 μ_B, but that no magnetic scattering from the Re ion can be detected. This is interpreted in terms of an extended spin density distribution due to covalent bonding in the ReO_6 clusters.

Sample Preparation and Magnetic Measurements

Polycrystalline samples of Ba_2MnReO_6 were prepared by heating "Baker analyzed" grade carbonates and Re metal at 975°C in a nitrogen atmosphere. The compound thus obtained was ground and heated to 1000°C in a sealed evacuated quartz capsule, and then annealed at 800°C for three days. An X-ray powder pattern of the material was obtained in an IRD–Guinier camera using $CuK\alpha_1$ radiation. The material was found to be face-centered cubic with a lattice parameter of 8.16_6 Å, slightly smaller than the reported value of 8.181 Å (*7*). There was no evidence of distortion from cubic symmetry. One weak impurity line was also observed which could not be identified.

Magnetic susceptibility measurements were made on a PAR vibrating sample magnetometer in the temperature region between 4.2 and 300°K. The compound was found to develop a spontaneous moment below a Curie temperature of 109 ± 3°K. A plot of the magnetization data as a function of field at 4.2°K

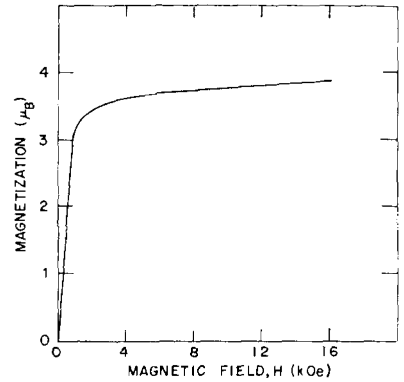

FIG. 2a. Variation of magnetization with magnetic field at 4.2°K for Ba_2MnReO_6.

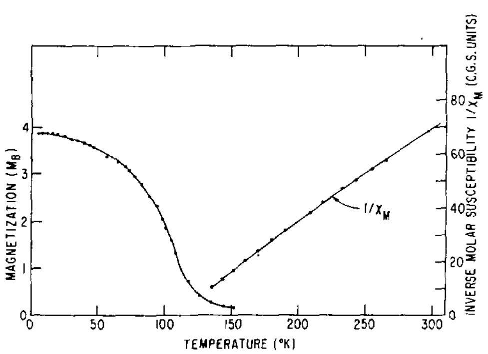

FIG. 2b. Variation of inverse molar susceptibility and magnetization at 16 kOe with temperature for Ba_2MnReO_6.

is given in Fig. 2a, and shows that the material is not saturated at 16 kOe. The magnetization vs temperature plot is shown in Fig. 2b, and the moment extrapolated to infinite field and 0°K is 4.1 ± 0.1 μ_B. In the paramagnetic region, the inverse susceptibility shows a non-linear behavior characteristic of a ferrimagnet. These results agree very closely with those of Sleight and Weiher (*7*).

Magnetic Structure Determination

Neutron diffraction data were obtained at room temperature on a powder sample of Ba_2MnReO_6 in the form of a pressed pellet using long wavelength neutrons ($\lambda = 2.369$ Å) for high resolution. These data revealed the presence of small traces of MnO and Re impurities. The relative amounts of MnO, Re, and Ba_2MnReO_6 were estimated from the intensities of their stronger peaks according to the relationship

$$I = KV\frac{\rho'}{\rho} j \frac{N_c{}^2 F^2}{\sin\theta \sin 2\theta},$$

where K is an instrumental scale constant, V is the volume fraction, ρ'/ρ is the packing density ratio and is assumed to be constant for all three phases, and the remaining quantities have their usual crystallographic significance. In this way, the atomic ratios were determined to be 0.003:0.005:1.000 for MnO:Re:Ba_2MnReO_6. This could indicate either a small departure from stoichiometry in the perovskite or a slight compositional uncertainty in the starting materials.

The intensity data for Ba_2MnReO_6 were used for refinement of the crystal structure, which can be described by the space group $Fm\,3m$ ($O_h{}^5$), with Ba in the 8(*c*) positions at 1/4, 1/4, 1/4; Mn in 4(*a*) at 0, 0, 0; Re in 4(*b*) at 1/2, 1/2, 1/2; and 0 in 24(*e*) at *x*, 0, 0. The "ideal" value of the oxygen parameter, *x*, is 0.25 as realized in the simple perovskite structure. A least-squares refinement was carried out with the ordering parameter, *S* (defined as the fraction of Mn ions on B, or 4(*a*) sites), the oxygen parameter, *x*, and the instrumental scale factor. Corrections were made for absorption, with a calculated linear absorption coefficient of 0.1 cm^{-1}. Within error limits of 0.01, *S* was found to be unity, corresponding to complete order, as was found in Ba_2CoReO_6 (*6*). The assumption of a slightly cation-defect composition $Ba_2Mn_{0.997}Re_{0.995}O_6$, based upon the impurity contents determined above, did not produce any appreciable improvement, nor did the incorporation of an overall temperature factor. However, significantly better agreement (at the 95% confidence level) was obtained when the oxygen content was permitted to vary. The final value obtained was 5.89 ± 0.04 atoms per formula unit. Only a small part of this can be accounted for by a cation deficiency of the magnitude mentioned above, and there is thus some indication of an oxygen-defect lattice with some Re ions presumably in a valence state formally less than six. This could account for the discrepancy in lattice parameters mentioned earlier. It must be emphasized, however, that there was a strong correlation between the oxygen content and the instrumental scale factor, and this conclusion must be regarded as rather speculative. The oxygen parameter *x* was found to be 0.2648 ± 0.0005, and the displacement of roughly 0.1 Å towards the more highly charged Re ion is similar to that observed in the compounds, Ba_2CoReO_6 (*6*), Ba_2NiWO_6, and Ba_2CoWO_6 (*2*). The observed and calculated intensities of the nuclear peaks are shown in Table I, and give an *R* factor

$$(\sum |I_{\text{obsd}} - I_{\text{calcd}}| / \sum I_{\text{obsd}})$$

and weighted *R* factor

$$([\sum w(I_{\text{obsd}} - I_{\text{calcd}})^2 / \sum w(I_{\text{obsd}})^2]^{\frac{1}{2}};\ w = 1/\sigma^2)$$

of 0.008 and 0.011, respectively.

Neutron data were collected at 120 and 4.62°K from powdered material contained in an aluminum sample holder. The data are shown in Fig. 3, and also as a difference pattern in Fig. 4. Additional scattering is observed in the same positions as the original nuclear peaks, as would be expected for a simple ferrimagnetic arrangement. The extra intensity in the (111) and (200) positions was found to disappear at about 106°K, and the temperature dependence is very similar to that of the spontaneous moment, confirming that this scattering is magnetic in origin (Fig. 5).

TABLE I

OBSERVED AND CALCULATED NUCLEAR INTENSITIES FROM $Ba_2MnReO_{5.89}$ AT 298°K (SCATTERING AMPLITUDES 0.512, −0.387, 0.92, 0.5803 × 10^{-12} cm FOR Ba, Mn, Re, AND O, RESPECTIVELY (9))

h k l	I_{obsd}	I_{calcd}
(1 1 1)	51.3	51.2
(2 0 0)	5.3	4.9
(2 2 0)	2.5	2.4
(3 1 1)	25.9	25.8
(2 2 2)	81.1	81.9
(4 0 0)	80.3	79.8
(3 3 1)	7.3	7.2
(4 2 0)	4.2	4.0

A much weaker set of peaks is also apparent in Fig. 4. These satisfy the reflection conditions $h + k = 2n$, h (or k) $+ l = 2n' + 1$, where n and n' are integers, and are characteristic of antiferromagnetic ordering of the first kind. The temperature dependence of these peaks was not studied in detail; however, no trace of the (001) reflection could be seen in a scan taken at 88°K, about 20°K below the ferrimagnetic transition. While these peaks could conceivably originate from some crystallographic phase transition, the general decrease in intensity at higher angles is much more suggestive of magnetic scattering. Two other small peaks were also observed at 2θ values of 26.8 and 51.1°. These disappear at about 120°K and were identified as the two principal magnetic reflections of MnO.

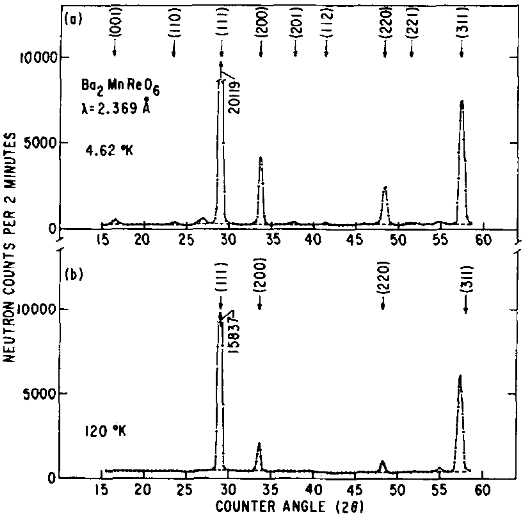

FIG. 3. Neutron data for Ba_2MnReO_6 at 120°K (lower curve) and at 4.62°K (upper curve).

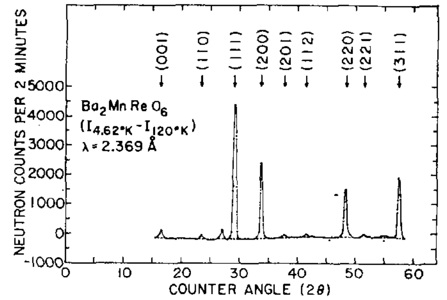

FIG. 4. Neutron difference pattern for Ba_2MnReO_6 showing the contribution from the magnetic scattering at 4.62°K.

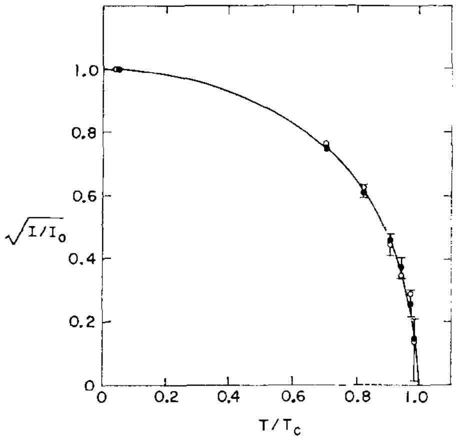

FIG. 5. Variation of reduced magnetic intensity with temperature for the (111) and (200) peaks of Ba_2MnReO_6. The solid line corresponds to the magnetization data in Fig. 2b. Typical error bars for (111) are shown. Those for (200) are comparable but have been omitted for the sake of clarity. ● $(I_M(111))^{1/2}$; ○ $(I_M(200))^{1/2}$.

The data at 4.62°K were therefore analyzed by least squares on the basis of a ferrimagnetic model with canting between adjacent (001) planes. The experimentally determined form factor for Mn^{2+} was used (*10*); that for Re^{6+} was taken from the self-consistent, relativistic free-ion calculation of Cromer and Waber (*11*).

The structure factors for the two sets of peaks are given as follows:

$$F_F = 4(\mu f(\mathrm{Mn}) - \mu f(\mathrm{Re})\cos 2\pi[(h+k+l)/2]) \times \cos\theta\,(h, k, l \text{ all} = 2n \text{ or } 2n+1)$$

$$F_{AF} = 4(\mu f(\mathrm{Mn}) + \mu f(\mathrm{Re})\cos 2\pi[(h+k+l)/2]) \times \sin\theta\,(h+k = 2n,\ h+l = 2n'+1).$$

Good agreement between observed and calculated magnetic intensities was obtained with a moment per Mn ion of 4.8 μ_B and a canting angle 2θ between planes of 25°. Rather surprisingly, however, the moment per Re ion was zero within standard error limits (Table II, Model A). A fairly sensitive check on this is also provided by the ratio of the (111) and (200) magnetic intensities, and from the observed value, the upper limit on the Re moment can certainly be no more than 0.2 μ_B, if one assumes the free-ion form factor.

TABLE II

OBSERVED AND CALCULATED MAGNETIC INTENSITIES FOR $Ba_2MnReO_{5.9}$ AT 4.62°K (FINAL VALUES OF PARAMETERS FOR MODELS A, B, AND C DESCRIBED IN TEXT LISTED AT BOTTOM, WITH STANDARD ERRORS IN PARENTHESES)

		I_{calcd}		
h k l	I_{obsd}	A	B	C
(1 1 1)	22.6	21.5	29.0	22.0
(2 0 0)	11.2	11.5	7.4	11.0
(2 2 0)	8.8	8.9	6.2	8.8
(3 1 1)	10.1	10.7	12	10.7
(2 2 2)	←Overlap with Al (1 1 1)→			
(4 0 0)	←Overlap with Al (2 0 0)→			
(3 3 1)	3.6	3.8	4.2	3.9
(4 2 0)	4.0	3.5	2.9	3.5
(0 0 1)	1.3	1.5	0.8	1.4
(1 1 0)	0.6	0.7	0.8	0.7
(2 0 1)	0.7	0.5	0.3	0.5
(1 1 2)	0.6	0.6	0.6	0.6
(2 2 1), (0 0 3)	0.5	0.3	0.2	0.3
Weighted *R* factor		0.079	0.30	0.078

Model A: $\mu_{Mn} = 4.77$ (6), $\mu_{Re} = -0.03$ (8), $k_{Re} = 1.0$, $2\theta = 25°$ (1)

Model B: $\mu_{Mn} = 4.7$ (2), $\mu_{Re} = 1.0$, $k_{Re} = 1.0$, $2\theta = 24°$ (3)

Model C: $\mu_{Mn} = 4.78$ (6), $\mu_{Re} = 0.2$ (4), $k_{Re} = 2.4$, $2\theta = 24°$ (1)

For comparison, the calculated intensities if μ_{Re} is held fixed at 1 μ_B are also given in Table II (Model B).

This result is in apparent conflict with the magnetization data and indicates that the spin density distribution around the Re ion is considerably more delocalized than that around the free ion, so that the form factor falls off much more steeply for the latter case. This would imply a considerable amount of covalent bonding in the ReO_6 cluster. A similar but less pronounced effect is also evident in K_2ReCl_6 (*12*, *13*).

Thus, Ba_2MnReO_6 bears at least a superficial resemblance to the spinel $CuCr_2Se_4$, which has a spontaneous moment of about 5 μ_B (*14*). Neutron data have shown each Cr moment to be 3 μ_B, consistent with a formal valence state $Cu^{2+}Cr_2^{3+}Se_4$, but no moment could be detected on the Cu ion (*15*). However, in this case the compound also shows metallic-type conductivity (*14*), and the evidence points towards delocalization of the Cu^{2+} orbitals and the formation of a partially filled band (*16*). The compound Ba_2MnReO_6 is a semiconductor (*7*), and hence the Re electron must be associated with the ReO_6 clusters rather than a conduction band. The related compound Sr_2MgReO_6 is also a semiconductor, and has a temperature dependent paramagnetism, but ReO_3, which may be viewed as a defect perovskite in which the A ions are missing and Re^{6+} occupies both B and B′ sites, shows metallic conductivity (*17*). This has been interpreted in terms of a conduction band originating from covalent bonding via mixing of the rhenium t_{2g} and oxygen p_π orbitals.

In view of the above results, we have also made a more detailed analysis of our previously reported neutron data for Ba_2CoReO_6 (*6*), in which a small but significant moment was detected on the Re ion. For the form factor of Co^{2+}, the data obtained in a recent single crystal study of Ba_2CoWO_6 were used (*18*). This falls off somewhat more slowly than the theoretical curve (*19*), such that $f^{Co}_{obsd}(\sin\theta/\lambda)$ can be approximated by $f_{calcd}(0.906\sin\theta/\lambda)$. A least-squares refinement was made with μ_{Co}, μ_{Re} and a scaling parameter k, defined by $f^{Re}_{obsd} = f^{Re}_{calcd}(k\sin\theta/\lambda)$ as variables. The other parameters were held fixed at the values obtained in the nuclear refinement. Excellent agreement is obtained with $\mu_{Co} = 2.6\mu_B$, $\mu_{Re} = 0.4\ \mu_B$ and $k = 2.4$ (Table III, Model A). The latter value corresponds to a curve which falls off quite steeply compared to the free-ion value. However, if k is held fixed at unity, the fit is only slightly and not significantly, inferior, with $\mu_{Co} = 2.5\ \mu_B$ and $\mu_{Re} = 0.3\ \mu_B$.[1]

TABLE III

OBSERVED AND CALCULATED MAGNETIC INTENSITIES OF Ba_2CoReO_6 AT 4.55°K. (FINAL VALUES OF PARAMETERS FOR MODELS A AND B DESCRIBED IN TEXT LISTED AT BOTTOM, WITH STANDARD ERRORS IN PARENTHESES)

		I_{cald}	
hkl	I_{obsd}	A	B
$(000)^{\mp}$	23.8	23.8	24.1
$(002)^-$	3.4	3.9	3.3
$(111)^-$	9.5	9.6	9.8
$(200)^{\mp}, (111)^+$	10.0	9.8	9.4
$(202)^-$	3.1	3.3	2.7
$(002)^+$	1.7	1.1	0.9
$(113)^-$	3.5	3.1	3.2
Weighted *R* factor		0.041	0.049
Model A: $\mu_{Co} = 2.54(5)$; $\mu_{Re} = 0.42(11)$; $k_{Re} = 2.6(7)$			
Model B: $\mu_{Co} = 2.51(3)$ $\mu_{Re} = 0.26(3)$ $k_{Re} = 1.0$			

These results are once again consistent with a picture in which the Re moment is delocalized to a very considerable extent, although not too much quantitative significance can be attached to the value of the moment obtained, since the actual form factor is likely to be quite a complicated function. It is nevertheless possible to conclude from the ratio of the two strongest magnetic peaks $I_{(000)^+}:I_{(111)^-}$, which occur at $\sin\theta/\lambda$ values of 0.034 and 0.092, respectively, that in this compound, a small moment (at least 0.2 μ_B) contributes to the observed magnetic intensities and can be considered as being localized on the Re ion.

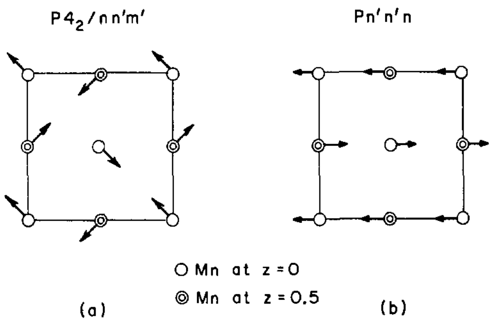

FIG. 6. Two possible magnetic structures for the antiferromagnetic mode of Ba_2MnReO_6 consistent with the observed intensities. The ferromagnetic mode is assumed to be directed perpendicular to the plane of the page. (a) Tetragonal $P4_2/nn'm'$. (b) Orthorhombic $Pn'n'n$, corresponding to the canted model described in text.

A further refinement of the data for Ba_2MnReO_6 was carried out with the Re form factor scaled by a k of 2.4 (Table II, Model C), but the results were virtually the same as for Model A, with k unity.

The existence of a canted structure in Ba_2MnReO_6 is of interest. The canting angle between successive (001) planes is about 25°, considerably less than the turn angle of the spiral in Ba_2CoReO_6, but nevertheless clearly indicative of exchange effects extending beyond negative coupling between adjacent Mn and Re moments. Ordering of the first kind would be favored by negative exchange between near-neighbor Mn–Mn and Re–Re moments. This is, in fact, the arrangement adopted by K_2ReCl_6 and K_2ReBr_6, which can be viewed as ordered perovskites in which the B ions are missing (*12*, *13*). It should, however, be mentioned that collinear ordering of the first kind is only a special case of a much more generalized set of noncollinear structures which are indistinguishable as far as the neutron data are concerned (*20*). One of these is the tetragonal arrangement shown in Fig. 6a, in which the ferrimagnetic mode is assumed to lie along the *c* axis. A reasonable choice of magnetic space group would be $P4_2/nn'm'$, and it is of interest that a number of ordered perovskites containing Re have been reported to be tetragonally distorted (*21*), although the space group does not appear to have been determined. The canted structure assumed, on the other hand, would have orthorhombic magnetic symmetry, and a reasonable

---

[1] The moments reported previously ($\mu_{Co} = 2.1\ \mu_B$, $\mu_{Re} = 0.5\ \mu_B$) are in error due to an incorrect derivation of the magnetic interaction vector term q^2 for some of the peaks in the computer program for the intensity calculations.

choice of space group in this case would be *Pn'n'n* (Fig. 6b).

Further neutron studies of these materials would clearly be of interest from the viewpoint of delocalization effects in 5*d* ions, and attempts are now in progress to prepare single crystals.

Acknowledgments

We wish to gratefully acknowledge helpful discussions with J. J. Hurst, Jr.

References

1. G. Blasse, *Philips Res. Rept.* **20**, 327 (1965). See also G. A. Smolenskii, "Segnetoelektriki i Antisegnetoelektriki." English translation: "Ferroelectrics and Antiferroelectrics," National Technical Information Service, Springfield, Va. (1972); Yu. N. Venevtsev, V. N. Lyubimov, V. V. Ivanova, and G. S. Zhdanov, *J. Phys.* 33, C255 (1972), and references therein.
2. D. E. Cox, G. Shirane, and B. C. Frazer, *J. Appl. Phys.* **38**, 1459 (1967).
3. J. Longo and R. Ward, *J. Amer. Chem. Soc.* **83**, 2816 (1961).
4. A. W. Sleight, J. Longo, and R. Ward, *Inorg. Chem.* **1**, 245 (1962).
5. F. K. Patterson, C. W. Moeller, and R. Ward, *Inorg. Chem.* **2**, 196 (1963).
6. C. P. Khattak, D. E. Cox, and F. F. Y. Wang, *A.I.P. Conference Proceedings* **10**, 674 (1972).
7. A. W. Sleight and J. F. Weiher, *J. Phys. Chem. Solids* 33, 679 (1972).
8. B. N. Figgis and J. Lewis, "Progress in Inorganic Chemistry," (F. A. Cotton, Ed.), Vol. 6, p. 37. Interscience, New York, 1964.
9. C. G. Shull, "Coherent Neutron Scattering Amplitudes," Massachusetts Institute of Technology, Cambridge, Massachusetts, 1972.
10. L. M. Corliss, N. Elliott, and J. M. Hastings, *Phys. Rev.* **104**, 924 (1956).
11. D. T. Cromer and J. T. Waber, "Scattering Factors Computed from Relativistic Dirac–Slater Wave Functions", Los Alamos Scientific Laboratory, Report LA-3056 (1964).
12. V. J. Minkiewicz, G. Shirane, B. C. Frazer, R. G. Wheeler, and P. B. Dorain, *J. Phys. Chem. Solids* **29**, 881 (1968).
13. H. G. Smith and G. E. Bacon, *J. Appl. Phys.* **37**, 979 (1966).
14. F. K. Lotgering, *Proceedings of the International Conference on Magnetism*, p. 533, Nottingham, England (1964).
15. M. Robbins, H. W. Lehmann, and J. G. White, *J. Phys. Chem. Solids* **28**, 897 (1967).
16. J. B. Goodenough, *J. Phys. Chem. Solids* **30**, 261 (1969).
17. A. Ferretti, D. B. Rogers, and J. B. Goodenough, *J. Phys. Chem. Solids* **26**, 2007 (1965).
18. J. Eckert, C. P. Khattak, and D. E. Cox, unpublished work.
19. R. E. Watson and A. J. Freeman, *Acta Cryst.* **14**, 27 (1961).
20. J. S. Kouvel and J. S. Kasper, *J. Phys. Chem. Solids* **24**, 529 (1963); J. M. Hastings, L. M. Corliss, M. Blume, and M. Pasternak, *Phys. Rev. B* **1**, 3209 (1970).
21. F. S. Galasso, "Structure, Properties, and Preparation of Perovskite-Type Compounds," Pergamon Press, New York (1969), and references therein.