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Magnetic Properties and Crystal Distortions of $BiMnO_3$ and $BiCrO_3$*

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Magnetic perovskites $BiMnO_3$ and $BiCrO_3$ were synthesized under very high pressures. There are phase transitions at 500°K and 410°K at atmospheric pressure for $BiMnO_3$ and $BiCrO_3$ respectively, and the crystal distortion of each phase was determined. $BiMnO_3$ is ferromagnetic below 103°K, while $BiCrO_3$ is inferred to be antiferromagnetic below 123°K accompanied with weak ferromagnetic moment. $BiCrO_3$ has an abnormally large effective Bohr magneton number at room temperature phase. The distortion of $BiMnO_3$ decreases slightly below the ferromagnetic Curie point.

§ 1. Introduction

There are several ions which have $(ns)^2$ electronic configuration and which play special roles in crystal chemistry. They are Tl^{+1}, Pb^{2+}, Bi^{3+}, In^{+1}, Sn^{2+}, Sb^{3+}, Ga^{+1}, Ge^{2+} etc. These ions favor special bonding types and special crystal structures.[2] The simplests of these structures are interpreted as the distorted structures of the common ones, and the distortion is such that these ions' sites lose the inversion symmetry (off-center distortion). Theoretical bases of this argument are presented in Appendix A. In perovskite type oxides containing Pb^{2+} also, this may seem to be the case almost without exception, and almost all of these compounds exhibit ferro- or antiferroelectricity. A similar situation might be expected also for Bi^{3+} perovskites. On the other hand, Bi^{3+} is expected to substitute La^{3+} of the ordinary $LaMO_3$ magnetic perovskites (M; trivalent magnetic ion) because of its valence and its ionic radius. There is, however, only one such perovskite reported *i.e.*, $BiFeO_3$, and Bi^{3+} seems to prefer other structures.[3–5] The authors had an idea that very high pressure synthesis may result in perovskites; $BiMO_3$ in which M is not Fe. This is because (1) high pressure may favor perovskite structure which is more tightly packed than other more covalent structures, or (2) high pressure may make the ionic radius ratio of cation to anion more favorable, since the effective ionic radius of oxygen may decrease more than that of cations under the high pressure. And actually the synthesis of new compounds; $BiMnO_3$ and $BiCrO_3$ was achieved using very high pressure firing.[1] In the present research the crystal distortions and magnetic properties of these compounds were examined.

§ 2. Sample Preparation

The raw material powder was packed in a graphite capsule which served as a heater. It was set in a pyrophyllite tetrahedron and was pressed to a definite pressure by a tetrahedral anvil type apparatus. Then it was heated to a definite temperature and was kept for 30 to 60 minutes and then was quenched. The pressure was removed after the quenching. A thermocouple was often omitted because its protection ceramics had an adverse effect of reacting with Bi_2O_3, though the omission was not a small perturbation for a system of such a low heat capacity. The temperature difference between the central and the end part of the sample space was estimated to be about 100°C. Perovskite phases were obtained for the starting materials and firing conditions as listed in Table I. In $BiMnO_3$ in case (A) or (B), the amount of perovskite phase decreased remarkably if Bi_2O_3 was deficient by a few percent. Below 500°C the materials were almost non-reactive.

Though the product was nearly of a single phase, there were weak extra-phase lines which could neither be eliminated nor be assigned. As for $BiMnO_3$, saturation magnetization at 77°K

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* This paper is a continuation and a full report of ref. 1), and is based on a thesis presented to the University of Tokyo (1966) by one of the authors. (F.S.)

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Table I. Starting materials and firing conditions.

	Pressure and temperature	Starting material
$BiCrO_3$	35 ~55 kbar 700~800°C	α $Bi_2O_3+Cr_2O_3$
$BiMnO_3$	35 ~55 kbar 600~700°C	(A) Equimolar mixture of nitric acid solutions of Bi and of Mn was dried and fired in air at 600°C. (B) Mixture of α Bi_2O_3 and β Mn_2O_3. The latter was heat-treated in air at 700°C. (C) The material (A) was prefired in air at 800°C, then α-Bi_2O_3 was added more than compensating the sublimation loss.

gave a quantitative measure of a fraction of perovskite phase. The temperature and atmosphere inhomogeneity seemed to give an adverse effect. Higher temperature of firing, longer firing time, or repeated firing gave no improvement. Actually the raw material (C) was the most successful.

As graphite gives a fairly reducing environment at higher temperatures, reduction took place often. It is a problem how accurately the valence of the magnetic ion in the produced perovskite is trivalent, especially for $BiMnO_3$. There was a small scattering of distortion which seemed to reflect the scattering of the degree of oxidation (about 10% in terms of $|b/a-1|$ for both compounds). As for $BiMnO_3$, the distortion seemed to be larger for lower degree of oxidation and hence for closer approach to the stoichiometry.* In spite of the presence of such a scattering of distortion, there was no detectable change in the ferromagnetic Curie point. As the reproducibility of the crystal distortion and the magnetic Curie point was quite high for various preparation conditions, and especially as the perovskite phase was obtained from the raw material (B), Mn in $BiMnO_3$ is probably very close to trivalent. As the produced perovskite phase is a high pressure stable phase, it decomposes when it is heated in an ordinary pressure. The upper limit of this decomposition temperature was 300°C in vacuum for $BiMnO_3$, and 400°C in air for $BiCrO_3$.

§ 3. Results of X Ray and Magnetic Measurements

The products were examined with X ray diffractometer using Cu K_α radiation and G. M. Counter. At room temperature, both $BiMnO_3$ and $BiCrO_3$ are pseudo-triclinic perovskites with two equal angles and two equal edges, and no superstructure line was ascertained. There is a high temperature phase transion for each compound, and the mode of distortion changes. In each case, the transition is of the first order, and especially in $BiCrO_3$ there is a thermal hysteresis, and the associated two phase region is indicated with the overlap of full lines in Fig. 1. The high temperature phase of $BiMnO_3$ is also pseudo-triclinic, while that of $BiCrO_3$ is pseudo-mono clinic and the latter exhibits many superstructure lines. These super-structure lines were assigned with an unit cell doubled along b direction, and they were analysed assuming that they come from the shifts of Bi^{3+} to different directions. The extinction condition for odd k reflections is $h+l=0$, which is consistent with the ion shift in [101] direction being uniform in each b plane and antiparallel for adjacent b planes (Fig. 2). The analysis is given in Appendix B, and the assignments are given in Table II. The lattice constants of each phase are listed in Table III and their temperature dependences are given in Figs. 1 and 3. The data are those for the samples which seem to be the most close to the stoichiometry. In each phase no appreciable temperature dependence of the distortion was

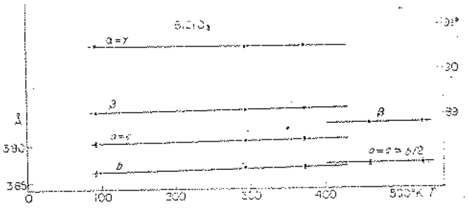

Fig. 1. Lattice parameters of $BiCrO_3$ vs. temperature.

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* On the contrary, as for $BiCrO_3$, the distortion seemed to be smaller for closer approach to the stoichiometry.

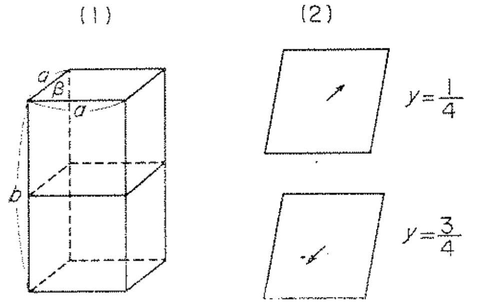

Fig. 2. (1) Doubled unit cell of high temperature phase of $BiCrO_3$.
(2) Shift of Bi^{3+} in each b plane.

observed. The distortion of $BiMnO_3$, however, seems to decrease slightly below the ferromagnetic Curie temperature.

The magnetic moment of $BiCrO_3$ was measured using an automatic magnetic balance. The magnetic fields used were 9.5 kOe, 7.2 kOe, and 5.2 kOe. Above 123°K, the magnetization shows paramagnetic field dependence, but below this temperature, the magnetization was separated into two terms; $\sigma=\sigma_0+xH$. The results are shown in Fig. 4. The magnetic susceptibility shows a thermal hysteresis associated with the high temperature phase transition. The effective

Table II. Superstructure lines in high temperature phase of $BiCrO_3$.

Index	$d_{\mathrm{calc.}}$(Å)	$d_{\mathrm{obs.}}$(Å)	$I_{\mathrm{calc.}}$*	$I_{\mathrm{obs.}}$
110,011	3.469	3.473	$2f^2$	w
111	2.610	2.611	$4f^2$	w
130,031	2.151	2.146	$2f^2$	vw
131	1.891	1.892	$4f^2$	vw
210,012	1.881	1.882	$8f^2$	w
211,112	1.706	1.707	$18f^2$	w
$21\bar{1},\bar{1}12$	1.679	1.679	$2f^2$	vw
230,032	1.551	1.553	$8f^2$	vw

* $\sum_i \frac{|E_i|^2}{16\pi^2 s^2}$

Table III. Lattice parameters.

$BiMnO_3$	300°K	$a=c=3.935$Å $b=3.989$Å $\alpha=\gamma=91°28'$ $\beta=90°58'$
$BiMnO_3$	540°K	$a=c=3.969$Å $b=3.923$Å $\alpha=\gamma=90°42'$ $\beta=89°39'$
$BiCrO_3$	300°K	$a=c=3.906$Å $b=3.870$Å $\alpha=\gamma=90°33'$ $\beta=89°9'$
$BiCrO_3$	460°K	$a=c=3.878$Å $b=7.756$Å $\beta=88°50'$

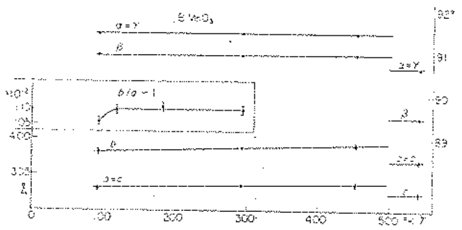

Fig. 3. Lattice parameters of $BiMnO_3$ vs. temperature.

Bohr magneton number obtained from the slope of $1/x-T$ curve is 3.8 for the high temperature phase, while it is 4.7 for the low temperature phase, and the latter value is abnormally larger than the spin only value of Cr^{3+} (3.9). Weak spontaneous moment arises below 123°K and it increases abruptly below 95°K. This weak moment neither depends on firing temperature, nor on the purity, nor on the mixing ratio of the raw materials. A magnetic cooling from room temperature in about 9.5 kOe magnetic field did not introduce any effect on these moments.

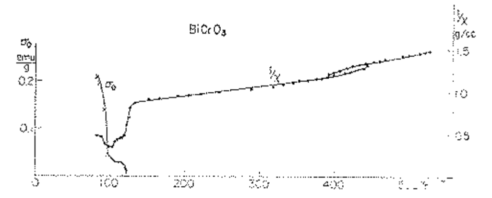

Fig. 4. Reciprocal of magnetic susceptibility and spontaneous magnetic moment of $BiCrO_3$ vs. temperature.

The magnetic data for $BiMnO_3$[1] are shown in Fig. 5. As has been reported, $BiMnO_3$ shows ferromagnetism below about 103°K. The saturation magnetigation value is obtained by the extrapolation of M vs. $1/H$ curve. Although the data were taken for the sample which gave the largest ferromagnetic moment, the value seems slightly smaller than the theoretical value of Mn^{3+}; $4\mu_B$. It is noticed that no appreciable anomaly was observed at the phase transition temperature.

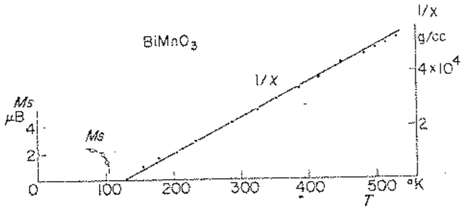

Fig. 5. Reciprocal of magnetic susceptibility and saturation magnetization of $BiMnO_3$ vs. temperature.

§ 4. Discussion

4.1 *Crystal distortion*

From the comparison of unimolecular volumes of various La and Bi perovskites (Table IV), it may be inferred that Bi^{3+} has a comparable ionic radius as that of La^{3+} for 12 coordinated site. (This is in contrast to the fact that La^{3+} has a fairly larger ionic radius than that of Bi^{3+} for 8 coordinated site of the substituted YIG.[6]) Thus we may ascribe the large distortion of Bi^{3+} perovskites rather to the effect of the special electronic configuration of Bi^{3+} than to the misfit of ionic radius. Actually Bi^{3+} ion's off-center distortion was confirmed for the high temperature phase of $BiCrO_3$, and the pseudo-triclinic distortion, which is rather rare among the various perovskite structures, was seen for other phases of the compounds.

Table IV. The comparison of unimolecular volumes of Bi and La perovskites (Å^3)

$LaCrO_3$	58.55	$BiCrO_3$ (300°K) $BiCrO_3$ (460°K)	59.04 58.32
$LaMnO_3$ (O)	60.90	$BiMnO_3$ (300°K) $BiMnO_3$ (540°K)	61.77 61.77
$LaFeO_3$	60.77	$BiFeO_3$	62.10

The distortion of $BiMnO_3$ is more remarkable than that of $BiCrO_3$, and this is inferred to be due to the existence of Jahn-Teller ion Mn^{3+}. Many experiments indicate that $Mn^{3+}O_6^{2-}$ octahedron is elongated along one of the three tetrad axes giving rise to tetragonal distortion.[7] In $BiMnO_3$ (room temperature phase), disregarding the angle distortion, the fact that the axial ratio $b/a>1$ might be the direct consequence of the distortion of $Mn^{3+}O_6^{2-}$ octahedron in contrast to the situation realized in $LaMnO_3$. The degree of distortion (0.014 in terms of $|b/a-1|$), however, is remakably smaller than the ordinary value (which is inferred to exceed 0.1.) As for the quantity $|b/a-1|$*, this is determined by the ratio of the first order term (potential energy of $d\gamma$ electron) and the second order term (interionic restoring potential) of the displacement coordinates of Jahn-Teller mode distortion in the energy expression. In $BiMnO_3$, it is reasonable to consider that the second order term is especially large, because O^{2-}s positions are strongly restricted by their covalent bondings with Bi^{3+}, and strong restoring forces act for Jahn-Teller mode displacement, and this may lead to the fact $|b/a-1|$ is abnormally small.

4.2 *Magnetic properties of $BiCrO_3$*

The spontaneous magnetic moment which appears below 123°K is inferred to be parasitic ferromagnetic moment, though $1/x-T$ anomaly at this temperature is not of a typical form for the parasitic ferromagnetism.[8,9] Anomaly around 95°K might be due to the change of easy direction of magnetization. We believe that 123°K is the antiferromagnetic Neel temperature, and this is considerably lower than that of $LaCrO_3$ (300°K).

As for the parasitic ferromagnetism, if the antiferromagnetic crystal has a symmetry element $R\times t$ (R; time inversion, t; translation) the direction of magnetic moment can not be conserved and parasitic ferromagnetism can not occur. It would be the case for $BiCrO_3$, if the compound has a G type spin structure as $LaCrO_3$ has, and if the crystal has an unimolecular unit cell. Since it is rather probable that $BiCrO_3$ has a G type spin structure, the above argument leads to the conclusion that the unit cell of $BiCrO_3$ should be larger than the unimolecular one. Superstructure lines, however, could not be discerned in our experiments.

The large effective Bohr magneton number observed in the low temperature phase will be explained by a molecular field theory with temperature dependent exchange parameters. Although we do not present the detailed mechanism of this phenomenon, we are sure this fact is not due to the imperfection of the sample such as the existence of a small amount of non reactive Cr_2O_3.

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* The elongated axis is denoted as b in the present case, while it is denoted as c in the ordinary tetragonal distortion.

4.3 *Magnetic properties*
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4.3 Magnetic properties of BiMnO₃

We consider firstly $Mn^{3+}—O^{2-}—Mn^{3+}$ 180° superexchange interaction in $LaMnO_3$. Then there are many cases in relation to the Jahn-Teller distortion.

(1) There is no Jahn-Teller distortion. Two $d\gamma$ orbits remain degenerate (the rhombohedral phase of $LaMnO_3$, some of the solid solutions of $LaMnO_3$).*

(2) There is the Jahn-Teller distortion.

a) Both Mn^{3+}s have their elongated axes of octahedron looking away from the intervening oxygen. (along *c* direction of the orthorhombic phase of $LaMnO_3$).*

b) One Mn^{3+} has its elongated axis of octahedron directed to the intervening oxygen, while the other Mn^{3+} has not (in *c* plane of the orthorhombic phase of $LaMnO_3$).*

Experimentally in cases (1) and (2)b), ferromagnetic interaction is realized.[10-12] Theoretically this fact is reasonably interpreted as in these cases both $p\sigma$-$d\gamma$ transfer integral and $p\sigma$-$d\gamma$ exchange integral may be large and there seems to be a large positive contribution of Anderson's mechanism of super-exchange interaction.[13]

As for $BiMnO_3$, when we assume that $b/a-1$ value reflects the degree of the distortion of MnO_6 octahedron, this distortion is quite small as discussed in 4.1, and the energy splitting of two $d\gamma$ orbits (which is proportional to the degree of the distortion) is so small as to allow the mixing of the upper $d\gamma$ state to the lower one easily, and the situation may be similar to the case of the degeneracy (1). The small decrease of the crystal distortion below the ferromagnetic Curie point, which is considered to be an exchange striction, is consistent with the interpretation that the small crystal distortion is favorable to the ferromagnetic interaction.

Acknowledgements

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Appendix A

(ns)² Electronic Configuration and the Off-Center Distortion

The tendency to lose the inversion symmetry of the ion with $(ns)^2$ electronic configuration is based on the situation that there is a fairly low-lying excited state of odd parity; $(ns)^1(np)^1$ on the even partity ground state; $(ns)^2$, and the former can be mixed to the latter together with an energy reduction in the second order perturbation calculation only when the ion's site loses the inversion symmetry. If this energy reduction associated with the off-center distortion overcomes the ordinary interionic repulsive potential, there occurs ion shifts, and if these ion shifts occur cooperatively, there occurs actually a crystal distortion.

Now the true situation might be rather of a covalent nature than purely ionic as assumed in the present argument, and in extreme cases, the cation and the legand are regarded to form a bonding of special types.

Moreover another aspect related to this type of distortion should be pointed out. The reduction of excitation energy favours the distortion from the above argument, but when the excitation energy is reduced extremely as occurs in semiconductors with narrow band gaps, the mixing of a similar type occurs already through *k* - *p* purturbation, not through crystal distortion, and the effect for the distortion is rather suppressed. This might be the reason why PbO, SnO, SnS, SnSe, GeS, GeSe take distorted structures while PbS, PbSe, PbTe preserve NaCl structure.

Appendix B

Analysis of Superstructure Lines of the High Temperature Phase of BiCrO₃

The ion shift shown in Fig. 2 varies structure amplitude *F* by $\varDelta F$, where

$$F=f\sum_{i=1}^{2}\exp 2\pi i(hu_i+kv_i+lw_i)$$

$$\varDelta F=2\pi i f\sum_{i=1}^{2}(h\varDelta u_i+k\varDelta v_i+l\varDelta w_i)$$
$$\times\exp 2\pi i(h\bar{u}_i+k\bar{v}_i+l\bar{w}_i)\ .$$

Here only Bi^{3+} is considered, and *f* is its ionic scattering factor, $u_i\,v_i\,w_i$ denote its site coordinates, the bar stands for an initial value, $\varDelta$ denotes a variation, and the angle distortion is neglected. Now introducing a displacement parameter *s*,

$$(\bar{u}_1\ \bar{v}_1\ \bar{w}_1)=(0,\ 1/4,\ 0)$$
$$(\bar{u}_2,\ \bar{v}_2,\ \bar{w}_2)=(0,\ 3/4,\ 0)$$
$$(\varDelta u_1,\ \varDelta v_1,\ \varDelta w_1)=(s,\ 0,\ s)$$
$$(\varDelta u_2,\ \varDelta v_2,\ \varDelta w_2)=(-s,\ 0,-s)\ .$$

Then

$$F=2\pi i f s(h+l)\left(\exp\frac{\pi i}{2}k-\exp\frac{3\pi i}{2}k\right)\ .$$

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* As there is no complete structure analysis of $LaMnO_3$, these examples are rather probable inferences than assured facts.

and for superstructure lines ($k=2r+1$), $\bar{F}=0$ and $|F|=|\Delta F|=4\pi fs|h+l|$. This leads to the extinction condition for odd k; $h+l=0$. The correspondence of the observed and the calculated spacings d is shown in Table II. The observed intensities are in reasonable agreement with the calculated sum of the square of the scattering amplitude for each set of diffraction lines.

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Magnetic Properties of Organic Stable Radicals. I. 2,2,6,6-Tetramethyl-4-Hydroxypiperidine-1-Oxyl

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The static magnetic susceptibility and the ESR absorption spectra of 2,2,6,6-tetramethyl-4-hydroxypiperidine-1-oxyl in the temperature range from 1.8°K to 300°K have been measured. This powder sample shows a broad maximum in the susceptibility at the temperature 6.5°K. It has been shown that the temperature dependence of the susceptibility is fitted better by the one-dimensional Heisenberg model than the linear Ising model or a singlet-triplet model. The Curie-Weiss constant and the exchange interaction energy along the chain are estimated to be −6.0°K and −5.0°K, respectively. The linewidth of the ESR absorption spectra increases rapidly as decreasing temperature below 6.5°K.

§1. Introduction

The properties of interacting electron spins as well as isolated ones in organic free radicals, known as magnetic excitons, have been the subject of extensive experimental and theoretical study. So far a broad maximum in the susceptibility has been found in many organic free radicals and radical salts and explained using a singlet-triplet model as follows. This anomalous magnetic behavior arises from some form of strong coupling between the unpaired electrons on adjacent molecules through exchange forces, each pair forming a lower singlet state and an upper triplet state. As temperature is lowered the singlet level becomes increasingly populated as the expense of triplet level so that the susceptibility decreases. On the other hand, Edelstein has employed the linear Ising model to interpret the susceptibility of BDPA and PAC1) and obtained a fairly good agreement. Recently some of the present authors