PHYSICAL REVIEW B VOLUME 39, NUMBER 4 1 FEBRUARY 1989

Linear dichroism study of the structural phase transition of $BaMnF_4$

Taiju Tsuboi
Physics Department, Kyoto Sangyo University, Kamigamo, Kyoto 603, Japan

(Received 15 September 1988)

Linear dichroism (LD) has been investigated on ferroelectric antiferromagnet $BaMnF_4$ in a temperature range of 15–300 K. The LD is clearly observed to reflect the order parameter of the structural phase transition (transition temperature: $T_I = 252$ K) and antiferromagnetic short-range order (Néel temperature: $T_N = 26$ K) as in the case of linear birefringence. It is confirmed, from a jump of LD at T_I and a value of critical exponent $\beta = 0.23$, that a slight first-order character is involved in the structural phase transition. No additional structural phase transition was observed below T_I.

I. INTRODUCTION

$BaMnF_4$, known as one of the ferroelectric ferromagnets, possesses both ferroelectric and antiferromagnetic properties. An excellent review article on the subject has been given by Scott.[1] It exhibits a structural phase transition at about $T_I = 252$ K.[2] Below T_I the crystal is changed from a layered orthorhombic structure to an incommensurate structure where the incommensurability is along the crystal a axis. On the other hand, two-dimensional (2D) antiferromagnetic short-range order exists below about 80 K, and 3D antiferromagnetic order appears below $T_N = 26$ K.

A considerable amount of investigation has been undertaken on the structural and magnetic phase transitions of this material using various experimental techniques. Various optical and spectroscopic measurements were also performed. Of them, the refractive index (RI) and linear birefringence (LB) measurements have been made by several investigators.[2–5] The LB and RI studies provide useful information about both the order parameter of structural phase transition and the magnetic short-range order.

The linear dichroism (LD) measurement was done by Regis, Candille, and St-Gregoire.[6] They reported the result of LD in a narrow temperature region of 210–290 K around T_I for only the ac plane of crystal, with the light propagating along the b axis. They obtained values of ΔD_{ca} $[=(k_c - k_a)/(k_c + k_a)$, where k_a is the absorption coefficient measured using a linearly polarized light whose electric vector is parallel to the a axis] as LD for the ac plane although the difference of k_c and k_a is usually defined as the LD. To compare LD with LB $(=n_c - n_a$ for the ac plane, where n_c is refractive index along the c axis), the measurement of $k_c - k_a$ $(=\Delta k_{ca})$ is more reasonable than that of ΔD_{ca}. Compared with the LB study, much less is known about the LD of $BaMnF_4$. In this paper we investigate the LD spectra and temperature dependence in a region of 15–300 K. We obtain values of Δk as a LD measurement here.

It would be interesting to know if the LD measurement reveals the presence of both of the structural and magnetic phase transitions. Here we concentrate our attention on what kind of answer the LD study gives to several problems concerning the structural phase transition that are currently interesting to many investigators:[3–7] (1) Does the transition have first-order or second-order character? (2) What value is the critical exponent β of the order parameter associated with the structural phase transition? (3) Is there a second structural phase transition below T_I which suggests a new incommensurate-to-commensurate transition?

II. EXPERIMENTAL PROCEDURE

For optical measurements, we used a single crystal of $BaMnF_4$ which was cleaved along $\{100\}$ planes, oriented by the Laue x-ray backreflection method and then cut in the form of a cuboid of dimensions 3.0, 3.7, and 5.3 mm along the a, b, and c axes, respectively. The crystal faces were then ground and polished. Additionally we also used single crystals with thickness of 0.3–0.6 mm. The orientation of crystal was checked by optical absorption spectroscopy using linearly polarized light. The absorption spectra were measured using a Shimadzu MPS-50L spectrophotometer.

LD was measured using a JASCO J-40A automatic recording circular dichroism (CD) spectropolarimeter in a spectral region of 210–700 nm. The sample was cooled using a cold finger in an Osaka Sanso Cryo-Mini closed-cycle helium cryostat.

III. LINEAR DICHROISM MEASUREMENT

We had a measurement on $BaMnF_4$ previously using the JASCO CD polarimeter and obtained a CD signal quite similar to the LD signal.[8] Thus we suggested that the CD signal is generated from LD and LB by virtue of the optical activity of the crystal. Later Shindo *et al.* published several theoretical papers on the CD signal of anisotropic materials which is obtained from the conventional CD polarimeter.[9–11] Taking into account the analysis of Shindo *et al.* we conclude that the signal obtained by our JASCO CD polarimeter is not a real CD for $BaMnF_4$ but is rather a signal which is approximately proportional to LD, i.e., Δk, because the crystal is an anisotropic one having both LB and LD.

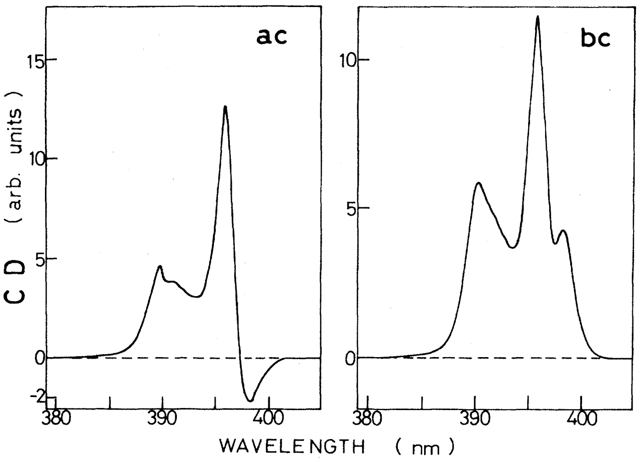

FIG. 1. CD spectra of the C absorption-band region in the ac and bc planes of $BaMnF_4$ at 20 K.

This was confirmed from the comparison of spectra obtained by the CD polarimeter with LD spectra which were obtained from differences among linearly polarized k_a, k_b, and k_c absorption spectra. For example, a difference between the k_c and k_a absorption spectra in the C band,[12] i.e., Δk_{ca} spectrum, is quite similar to the CD spectra obtained for the ac plane (see left panel of Fig. 1) by the CD polarimeter. The same is true for the bc plane (see the right spectrum of Fig. 1). This is true for not only the C band but also other absorption bands. Additionally, it was observed that, when we rotate the ac sample around the b axis by 90°, the signal measured by the polarimeter reverses its sign. Therefore the signal obtained by the CD polarimeter is suggested to reflect the LD signal.

IV. EXPERIMENTAL RESULTS AND DISCUSSION

Figure 2 shows the temperature dependence of the LD measured using 334.4-nm light which corresponds to a wavelength in the E absorption band.[12] Similar results are obtained using light corresponding not only to the other absorption band region but also to the transparent region.

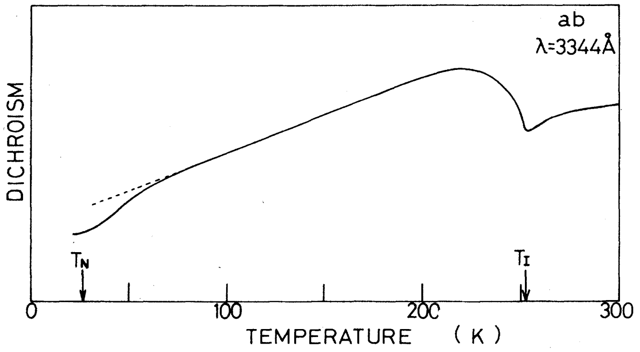

FIG. 2. Temperature dependence of the polarimeter signal, i.e., LD, in the ab plane measured using 334.4-nm light.

The temperature dependence of LD is similar to that of LB signal.[2] When the temperature is decreased from 300 K, the LD varies linearly against temperature, a big dip appears around T_I, and a monotonous decrease of LD appears again in a temperature region between about 200 and 80 K. Below about 80 K, the LD curve bends downward, suggesting it is caused by the magnetic phase transition as the case of LB measurement.[2] On the other hand, the presence of a big dip in the LD curve shows clearly that the structural phase transition affects the LD of crystal.

The magnetic contribution to LD is obtained by the subtraction of the LD due to structural phase transition from the observed LD curve since the LD due to lattice vibrations is believed to have no change against temperature below 80 K from the LB study.[2] If the LD due to structural phase transition is assumed to continue the monotonous decrease below 100 K as observed in the 200–80 K region (see a broken line of Fig. 2), the subtracted LD is quite similar to the temperature dependence of the magnetic short-range order which was estimated from the LB and dielectric constant measurements.[2,13] The short-range order extends over a temperature of about $3T_N$ since $BaMnF_4$ is a 2D antiferromagnet. Thus, the downward bending of LD observed below 80 K is confirmed to reflect the magnetic phase transition.

In Fig. 3 are shown the anomalous behaviors of LD observed around T_I in ab, bc, and ac planes. The LD varies linearly with temperature above about 270 K and it is connected with the lattice vibration of the crystal. The LD value is rising on approaching T_I when temperature is decreased. The rise starts from about 270 K and a sharp rise occurs at T_I in all the three planes. Of the three planes, the ac and ab planes exhibit a continuous rising near T_I but the bc plane exhibits a discontinuous, steplike rising.

To reveal the contribution of the structural phase transition to the LD variation, we subtract the contribution of lattice vibration from the observed LD curve. This is done by assuming that the LD due to lattice vibration varies

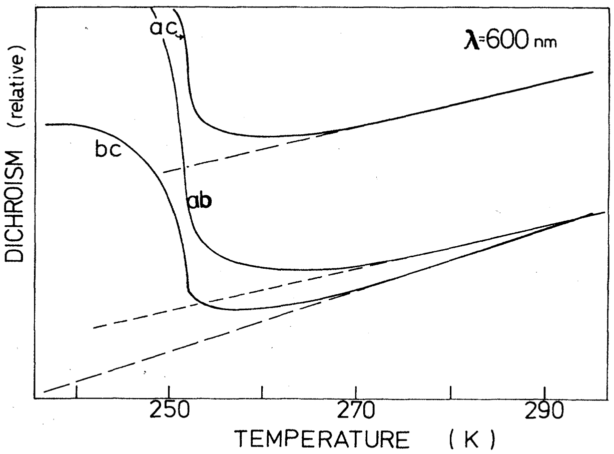

FIG. 3. Temperature dependence of the polarimeter signal, i.e., LD, measured using 600-nm light, around T_I in the ab, bc and ac planes.

linearly against temperature in a region of 320–240 K (see broken lines of Fig. 3), just as the case of LB analysis.[2] Curve *A* of Fig. 4 shows an example of a structural-phase-transition-induced LD curve where the contribution of lattice vibrations is subtracted.

An upward bending is observed to start from about 270 K in curve *A* of Fig. 4. The bending which continues up to a temperature close to T_I is believed to be due to fluctuations of the order parameter since the same behavior has been also observed in LB and neutron diffraction measurements.[2,5,7] Assuming that the similar critical fluctuation is present below T_I,[2] we have constructed a symmetric fluctuation background (curve *B* of Fig. 4). Curve *C* of Fig. 4 shows a LD curve which was obtained by subtracting the symmetric fluctuation contribution from curve *A*. Thus curve *C* reflects the amplitude of static structural order parameter.[2] A value of critical exponent β can be estimated from curve *B* since the exponent of the temperature dependence of LD due to structural phase transition is of the order of 2β as in the case[6] of LB. A best fit to curve *C* in a temperature range of $0 < T_I - T < 20$ K was obtained using a value of $\beta = 0.23$ and $T_I = 252$ K. This β value is not far from previously determined values, i.e., $\beta = 0.28$,[2,3] $\beta = 0.34$,[6] and $\beta = 0.31$,[7] although our value is smaller than these.

Now we can answer the questions concerning the structural phase transition which were pointed out in the Introduction. We can determine whether the transition has first-order or second-order character from the result shown in Fig. 3. The transition has nearly-second-order character since continuous variation is observed around T_I, but its first-order character cannot be neglected since a slightly discontinuous jump is observed in the *bc* plane. The discontinuity at T_I was also observed in the temperature dependence of LB (Refs. 2–4) and RI (Ref. 3) although no discontinuity was observed in neutron diffraction.[7] The observation of slight first-order character is consistent with a theoretical expectation which was obtained by Cowley and Bruce.[14] Furthermore, we obtained $\beta = 0.23$ as the critical exponent (Fig. 4), which is close to $\beta = 0.25$ expected from the Landau theory of the first-order transition.[7] This also supports the presence of first-order character in the structural phase transition.

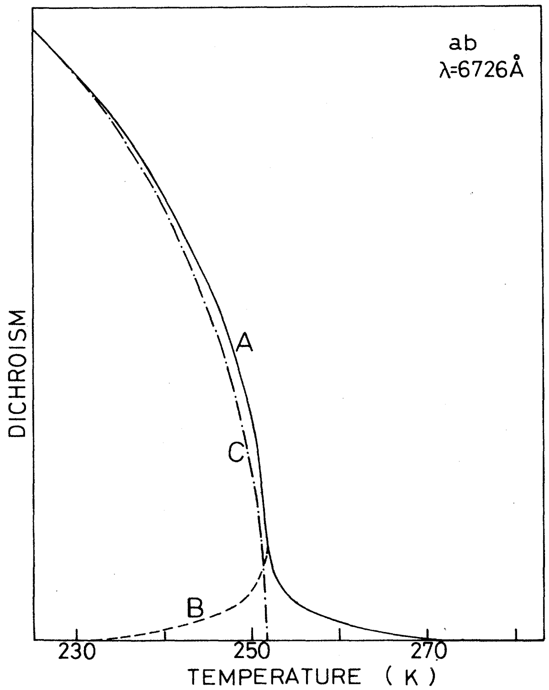

FIG. 4. Temperature dependence of the polarimeter signal, i.e., LD, due to the structural phase transition (see text on curves *A*, *B*, and *C*). The signal was obtained using 672.6-nm light in the *ab* plane.

Our measured LD signal does not support the possibility of a second structural phase transition. The second phase transition has been observed to appear within 8 K below T_I from dielectric measurement by Levstik, Blinc, Kodaba, and Cizikov[15] and the specific-heat measurement by Scott, Habbal, and Hidaka[16] although the separation between temperatures occurring the first and second transitions is not the same between the two measurements. No additional anomaly such as dip or jump, indicating the presence of second phase transition, however, is observed below T_I or even above T_I in our LD measurement, in agreement with the results of LB and RI (Refs. 2, 3, and 5), and x-ray and neutron diffraction measurements.[17] This fact gives support to the suggestion of St-Gregoire *et al.*[5] that such an additional anomaly can be attributed to defects or impurities.

The commensurate-to-incommensurate phase transition occurs at T_I in $BaMnF_4$. The absence of the second structural phase transition indicates that, unlike other incommensurate materials, the incommensurate-to-commensurate phase transition does not occur below T_I with decreasing temperature. By the way, $BaMnF_4$ is a crystal which has both the ferroelectric and antiferromagnetic properties. Therefore, the coexistence of electric polarization and magnetic moment affects not only the dielectric and magnetic properties of this material but also the crystal structure. The unusual feature that the incommensurate-to-commensurate transition does not appear could be caused by such a magnetoelectric effect, but the detailed mechanism is not clear at this moment.

Recently Scott's group measured the rotation of an optical indicatrix and the optical activity of $BaMnF_4$ using a polarimetric technique. They determined that the optical ellipsoid rotates by an angle of about 4′ and the optical activity tensor component is $G_{33} = 5 \times 10^{-5}$ below T_I.[3,18] Therefore, the fact that the CD polarimeter gives a LD signal and that the temperature dependence of the LD signal reflects the phase transition, as observed in the present study, can be explained by the rotation of the optical indicatrix, i.e., the rotation of the main axis of the elliptically polarized light in the crystal, and also by the optical gyration.

V. CONCLUSIONS

We have measured, using CD polarimeter, a LD signal for the anisotropic crystal $BaMnF_4$ with LB and LD, in agreement with the analysis of Shindo *et al.* for the conventional CD polarimeter. From the temperature dependence of the LD obtained, it is confirmed that the LD of $BaMnF_4$ is induced by magnetic and structural phase transitions and lattice vibrations, and that the LD due to a structural phase transition consists of two parts of the structural order parameter and its fluctuations. The present LD study gives the following answers to the problems which are of current interest: (1) the incommensurate structural phase transition has a slight first-order character, and (2) an additional structural phase transition does not occur below T_I (=252 K).

ACKNOWLEDGMENT

We thank Professor W. Kleemann of Universität-GH-Duisburg for kindly supplying $BaMnF_4$ single crystals of good quality to us.

---

[1] J. F. Scott, Rep. Prog. Phys. **12**, 1055 (1979).

[2] F. J. Schaefer, W. Kleemann, and T. Tsuboi, J. Phys. C **16**, 3987 (1983).

[3] R. V. Pisarev, B. B. Krichevtzov, P. A. Markovin, O. Yu. Korshunov, and J. F. Scott, Phys. Rev. B **28**, 2677 (1983).

[4] M. Regis, M. Candille, and P. St-Gregoire, in *Recent Development in Condensed Matter Physics,* edited by J. T. Devreese *et al.* (Plenum, New York) 1981, Vol. 4, p. 107.

[5] St-Gregoire, W. Kleemann, F. Schaefer, and J. Moret, J. Phys. (Paris) **49**, 463 (1988).

[6] M. Regis, M. Candille, and P. St-Gregoire, J. Phys. Lett. (Paris) **41**, L423 (1980).

[7] D. E. Cox, S. M. Shapiro, R. A. Cowley, M. Eibschuetz, and H. J. Guggenheim, Phys. Rev. B **19**, 5754 (1979).

[8] T. Tsuboi and W. Kleemann, Ferroelectrics **63**, 119 (1985).

[9] Y. Shindo, Appl. Spectrosc. **39**, 713 (1985).

[10] Y. Shindo, M. Nakagawa, and Y. Ohmi, Appl. Spectrosc. **39**, 860 (1985).

[11] Y. Shindo and M. Nakagawa, Rev. Sci. Instrum. **56**, 32 (1985).

[12] T. Tsuboi and W. Kleemann, Phys. Rev. B **27**, 3762 (1983).

[13] J. F. Scott, Phys. Rev. B **16**, 2329 (1979).

[14] R. A. Cowley and A. D. Bruce, J. Phys. C **11**, 3577 (1978).

[15] A. Levstik, R. Blinc, P. K. Kodaba, and S. Cizikov, Bull. Am. Phys. Soc. **20**, 558 (1975).

[16] J. F. Scott, F. Habbal, and M. Hidaka, Phys. Rev. B **25**, 1805 (1982).

[17] D. E. Cox, S. M. Shapiro, R. J. Neilmes, T. W. Ryan, H. Bleif, R. A. Cowley, M. Eibschuetz, and H. J. Guggenheim, Phys. Rev. B **28**, 1640 (1983).

[18] V. N. Gridnev, S. A. Kizhaev, O. Yu. Korshunov, B. B. Krichevtzov, P. A. Markovin, R. V. Pisarev, and J. F. Scott, Ferroelectrics **63**, 127 (1985).