Mechanisms of dielectric anomalies in $BaMnF_4$†

J. F. Scott*
Clarendon Laboratory, Oxford University, Oxford OX1 3PU, United Kingdom
(Received 14 March 1977)

The b-axis dielectric anomaly at the commensurate-incommensurate phase-transition temperature in $BaMnF_4$ has been calculated. Its shape and magnitude agree with the data of Samara and Richards. The a-axis anomaly below T_N is also explained; its shape and magnitude are due to the canting of Mn spins. It is a first-order effect and $\sim 10^5$ larger than in Rado's second-order theory for Cr_2O_3.

$BaMnF_4$ undergoes a continuous structural distortion at about 250 K,[1] in which the primitive unit cell doubles in the bc plane.[2–4] The wavelength of the distortion along the twofold a axis is incommensurate with the lattice constant of the high-temperature phase.[5] The transition is characterized by the presence of a "soft" optical phonon, which is polar in the incommensurate phase, with dipole along the a axis.[2] Measurement of the temperature dependence of this optical mode allowed predictions[2] of a λ-shaped a-axis dielectric anomaly for temperatures near $T_C = 250$ K; these predictions were confirmed in detail by the recent measurements of Samara and Richards.[6] Their work also showed the presence of a b-axis dielectric anomaly, unpredicted in previous work, with shape opposite that of the a-axis anomaly; i.e., $\epsilon_b(T)$ rises rapidly from its value 21.5 at T_C to 23.0 for $T \leq 180$ K. The purpose of the present note is to suggest an explanation for that anomaly.

In the original Raman study[2] of $BaMnF_4$, two low-frequency optical modes were found. One was strongly temperature dependent, with low-temperature frequency 40 cm^{-1}, and was inferred to have polarization along $\hat{a}$. The second was weakly temperature dependent, with frequency 28 cm^{-1} at 77 K, and was inferred to have polarization along $\hat{b}$. The intensities of these two modes vanished above T_C.

The presence of the mode at ~ 28 cm^{-1} in the incommensurate phase of $BaMnF_4$ should increase the b-axis dielectric constant. The value ϵ_b below T_C can be related to $\tilde{\epsilon}_b$ at $T \gtrsim T_C$ by the equation

$$\epsilon_b(\omega = 0) = n_b^2 \prod_j \left(\frac{\omega_{LO}^j}{\omega_{TO}^j} \right)^2 , \qquad (1)$$

where n_b is the b-axis index of refraction; ω_{TO}^j, ω_{LO}^j are the j transverse and longitudinal optical-mode frequencies of long wavelength; and the product is over the modes of B_2 symmetry. This can be approximated as

$$\epsilon_b(0) = \tilde{\epsilon}_b(0) (\omega_{LO}/\omega_{TO})^2 , \qquad (2)$$

where ω_{LO} and ω_{TO} are for the mode at about 28 cm^{-1}. For all other B_2 modes present below T_C but not above T_C, the ratio ω_{LO}/ω_{TO} is assumed nearly unity.

Far infrared measurements at 2.4 K give[7] $\omega_{LO} \sim 34.9$ cm^{-1} and $\omega_{TO} \sim 33.7$ cm^{-1} for $BaMnF_4$, from which Eq. (2) predicts

$$\epsilon_b = \tilde{\epsilon}_b \times 1.07, \quad \epsilon_b = 21.5 \times 1.07 = 23.0 . \qquad (3)$$

This value $23.0 = \epsilon_b$ is in exact agreement with the data of Samara and Richards[6] for $T << T_C$ but T greater than the temperature (~ 70 K) at which magnetic ordering begins.

The shape of the curve $\epsilon_b(T)$ vs T below T_C can be explained in the following way. The mode at about 28 cm^{-1} has zero oscillator strength above T_C (since it is not at zero wave vector). Because the structural transition is continuous, the oscillator strength of this mode increases with decreasing temperature below T_C, approximately as the magnitude of the displacement parameter.

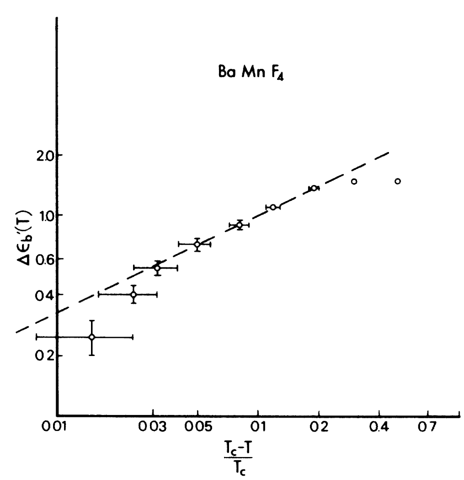

FIG. 1. Dielectric anomaly $\Delta\epsilon_b'(T)$ vs T for $BaMnF_4$, from Ref. 6. $\Delta\epsilon_b$ is taken as zero ($\epsilon_b = 21.5$) at $T_C = 248 \pm 2$ K. The dashed line is the mean-field expectation.

In Fig. 1 the $\epsilon_b'(T)$ are plotted on a log-log plot, and compared with the mean-field prediction

$$\Delta\epsilon_b'(T) = d[(T_C - T)/T_C]^{1/2} , \tag{4}$$

where d is a dimensionless constant. Good agreement is found between $180 \leq T \leq 235$ K. Between 220 K and $T_C = 247$ K, Shapiro *et al.*[5] found that the order parameter varied as

$$\varphi(T) = \varphi_0[(T_C - T)/T_C]^{0.225} . \tag{5}$$

The data of Ref. 6 do not seem sufficient to deduce an exponent in this region, but the apparent deviation of the data in Fig. 1 from the $\frac{1}{2}$ mean-field exponent near T_C is not incompatible with the results of Shapiro *et al.*[6]

The theory presented here does not explain the abrupt saturation of $\epsilon_b'(T)$ at about 180 K. Below 70 K another b-axis anomaly occurs. It is thought to be due[9] to the onset of in-plane spin ordering[10] and to the paramagnetoelectric effect.[11]

Below T_C $BaMnF_4$ lowers its symmetry from C_{2v} to C_2. The distortion along the a axis is not commensurate with the high-temperature lattice; but this characteristic does not alter the C_2 point-group symmetry. The magnetoelectric properties are therefore assumed characteristic of magnetic point group symmetry 2′. For this symmetry, the magnetoelectric tensor α_{ij} defined as

$$H' = \alpha_{ij} E_i H_j \tag{6}$$

has the form

$$\alpha_{ij} = \begin{vmatrix} 0 & 0 & \alpha_{13} \\ 0 & 0 & \alpha_{23} \\ \alpha_{31} & \alpha_{32} & 0 \end{vmatrix} , \tag{7}$$

where $\hat{a}$ is axis 3; $\hat{b}$ is 1; and $\hat{c}$ is 2.

In $BaMnF_4$ the spins are canted[13] along $\hat{c}$ (a fact unknown in Refs. 4 and 5). The α_{ij} in Eq. (7) produce a nonzero term $\alpha_{ac} E_a H_c$ when averaged over all spins. This term will renormalize the a-axis dielectric constant below T_N, where $\langle H_c \rangle$ becomes nonzero. The presence of such a $\Delta\epsilon(T)$ renormalization was first pointed out by Rado,[14] who derived explicit expressions for Cr_2O_3. His theory cannot readily be applied to $BaMnF_4$, which has an off-diagonal magnetoelectric tensor and canted spins. Rado's theory for $\Delta\epsilon(T)$ yields a number of order 10^{-6} at $T=0$ for Cr_2O_3, an unmeasurably small quantity, and an $M^2(T)$ temperature dependence (M is the sublattice magnetization). In contrast, the measured[6,9] $\Delta\epsilon_a(T)$ in $BaMnF_4$ is 0.1 at $T \approx 0$ and varies as $M(T)$, as shown[15] in Fig. 2.

The disagreement between the experimental $\Delta\epsilon_a(T)$ and Rado's theory arises primarily from the canted spins. For a ferroelectric like $BaMnF_4$ the free energy

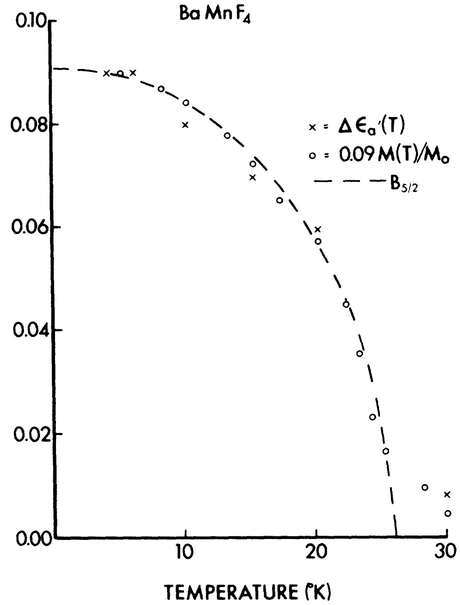

FIG. 2. Dielectric anomaly $\Delta\epsilon_a'(T)$ vs T for $BaMnF_4$, from Refs. 6 and 9, compared with $M(T)$ from Ref. 15. $M(T)$ varies approximately as a Brillouin function for spin-$\frac{5}{2}$.

involves the square of the total electric field, where

$$E_{\text{total}} = E_0 + \mathcal{E}_{\text{app}} , \tag{8}$$

where E_0 is the electric field due to the spontaneous polarization ($E_0 = 4\pi P_a$) and $\mathcal{E}_{\text{app}}$ is the external applied field. Thus, the free energy is of form

$$F = \epsilon E_0^2 + 2\epsilon E_0 \mathcal{E}_{\text{app}} + \epsilon \mathcal{E}_{\text{app}}^2 \tag{9}$$

and is linear in applied fields for small E_{app}. We would like to use perturbation theory to calculate a correction to F linear in $\mathcal{E}_{\text{app}}$.

In Rado's theory the renormalization $\Delta\epsilon(T)$ below T_N due to magnetoelectric effects is zero to first order and proportional to $\alpha^2(T)$ in second order. Since α is of order 10^{-4}–10^{-6}, this gives an unmeasurably small effect and one proportional to $M^2(T)$.

For canted spins, several mechanisms[16–19] give *first*-order contributions to $\Delta\epsilon(T)$. Either Rado's single-ion anisotropy, or Dzyaloshinskii anisotropic exchange involves terms of form

$$V = N\mu_B g a_\perp \langle m | S_z S_x | m \rangle \mathcal{E}_{\text{app}} \neq 0 \tag{10}$$

(here S_z is the spin component along the b axis; S_x is an orthogonal component) since $\langle S_x \rangle \propto M \sin\phi$, where ϕ is the canting angle (3 mrad in $BaMnF_4$). This gives[20]

$$\Delta\epsilon_a(T) \sim \alpha(T) \sim M(T) , \tag{11}$$

as observed, and a magnitude[21] of order 10^{-1} (dimensionless), instead of Rado's 10^{-6}, and in agreement with[6,9] the measured 10^{-1}.

In summary, the shape and magnitude of $\Delta\epsilon_b(T)$ for $T \leqslant T_C$ and $\Delta\epsilon_a(T)$ for $T \leqslant T_N$ are calculated to be in agreement with experiment. The $\Delta\epsilon_b$ anomaly at the in-plane spin-ordering temperature has not been calculated, but could be due to paramagnetoelectric interaction of form

$$\mathcal{H}' = \sum \gamma_{ijk} E_i H_j H_k \tag{12}$$

or to a linear interaction taken to second order

$$\mathcal{H}'' = \sum_n E_n^2 H_n \ , \tag{13}$$

where E_n, H_n are local fields at the nth ion. Two things favor the later interpretation. First, since H_n is $\approx H_1 \hat{b}$, the specific form[12] of the tensor γ_{ijk} in Eq. (12) predicts a large ϵ_a anomaly but no large ϵ_b anomaly. Second, from Eq. (13) the temperature dependence of $\epsilon_b(T)$ should be given by $\langle \sum \vec{S}_j \cdot \vec{S}_1 \rangle$, i.e., proportional to the magnetic energy, which is predicted to be[22] a sigmoidal curve from $T=0$ to $T \sim 2T_N$, with inflection point at T_N. The b-axis dielectric data agree with this description, as shown in Fig. 3.

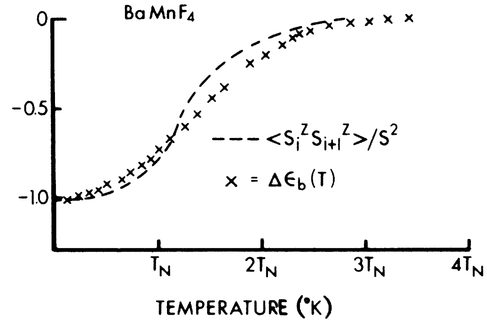

FIG. 3. Dielectric anomaly $\Delta\epsilon_b'(T)$ vs T for $BaMnF_4$, from Ref. 6, compared with the nearest-neighbor magnetic energy (Ref. 22) normalized to unity at $T=0$.

ACKNOWLEDGMENTS

We thank L. Holden for private communication concerning LO and TO splittings in the far-infrared data of $BaMnF_4$. Discussions with D. L. Fox, N. J. England, and G. A. Gehring were very helpful.

---

†Work supported in part by NSF Grant No. DMR-76-0456 and by a grant from the Science Research Council.

*Permanent address: Dept. of Physics and Astrophysics, University of Colorado, Boulder, Colo. 80309.

[1] E. G. Spencer, H. J. Guggenheim, and G. J. Kominiak, Appl. Phys. Lett. 17, 300 (1970).

[2] J. F. Ryan and J. F. Scott, Solid State Commun. 14, 5 (1974).

[3] I. J. Fritz, Phys. Lett. A 51, 219 (1975); Phys. Rev. Lett. 35, 1511 (1975).

[4] V. Dvorak, Phys. Status Solidi B 71, 269 (1975).

[5] S. M. Shapiro, R. A. Cowley, D. E. Cox, M. Eibschütz, and H. J. Guggenheim, *Proceedings of the Conference on Neutron Scattering, Gatlinburg, Tennessee, June, 1976*, edited by R. M. Moon, Natl. Tech. Info. Ser. (U.S. Dept. of Commerce, Springfield, Va., 1976), p. 399.

[6] G. A. Samara and P. M. Richards, Phys. Rev. B 14, 5073 (1976).

[7] L. Holden and M. C. K. Wiltshire (unpublished).

[8] M. Di Domenico, M. Eibschütz, H. J. Guggenheim, and I. Camlibel, Solid State Commun. 7, 1119 (1969).

[9] G. A. Samara and J. F. Scott, Solid State Commun. 21, 167 (1977).

[10] L. M. Holmes, M. Eibschütz, and H. J. Guggenheim, Solid State Commun. 7, 973 (1969).

[11] S. L. Hou and N. Bloembergen, Phys. Rev. 138, A1218 (1965).

[12] R. R. Birss, Rep. Prog. Phys. 26, 307 (1963).

[13] E. L. Venturini and F. R. Morgenthaler, AIP Conf. Proc. 24, 168 (1975).

[14] George T. Rado, Phys. Rev. Lett. 6, 609 (1961); Phys. Rev. 128, 2546 (1962).

[15] S. V. Petrov, M. A. Popov, and L. A. Prozorova, Zh. Eksp. Teor. Fiz. 62, 1884 (1972) [Sov. Phys.-JETP 35, 981 (1972)].

[16] M. Date, J. Kanamori, and M. Tachiki, J. Phys. Soc. Jpn. 16, 2589 (1961).

[17] R. Hornreich and S. Shtrikman, Phys. Rev. 161, 506 (1967).

[18] M. Mercier, E. F. Bertaut, G. Quezel, and P. Bauer, Solid State Commun. 7, 149 (1969).

[19] R. Englman and H. Yatom, *Magnetoelectric Phenomena in Crystals*, edited by A. J. Freeman and H. Schmid (Gordon and Breach, London, 1975), p. 17.

[20] This follows from $\langle S_x S_z \rangle = \langle S_z^2 \tan\phi \rangle \approx \langle S_z^2 \rangle \langle \phi \rangle$, where for $T \leqslant T_N$, $\langle S_z^2 \rangle \approx$ const (due to in-plane spin order); and $\langle \phi \rangle \sim \alpha(T) E_0 \sim M(T)$, i.e., the canting is assumed due to the spontaneous electric polarization and magnetoelectric coupling. David L. Fox and J. F. Scott, J. Phys. C 10, L329 (1977).

[21] Equating energy densities below T_N:

$$\Delta\epsilon(\mathcal{E}+E_0)^2 = V = N\mu_B g a_0 \langle S_z S_x \rangle (\mathcal{E}+E_0)$$

yields

$$\Delta\epsilon \sim N\mu_B g a_0 S^2 \phi / E_0 \equiv 10^{-5} a_0 \ .$$

a_0 is unknown, but is thought to be large in ferroelectrics [G.T. Rado, Phys. Rev. Lett. 13, 335 (1964)] compared with $a_0 \sim 1$ in Cr_2O_3.

[22] L. J. de Jongh and A. R. Miedema, Adv. Phys. 23, 1 (1974).