

LOW-FREQUENCY MAGNETOELECTRIC RESONANCES IN BaMnF<sub>4</sub>

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The frequency dependence of low-frequency magnetoelectric resonances of the transverse magnetoelectric effect is detected and investigated in a BaMnF<sub>4</sub> monocrystal. The resonances are observed as narrow peaks of the magnetoelectric susceptibility, located in the frequency interval 3-18 kHz. The temperature dependence of the resonances is investigated over the temperature range 6.5 to 300°K, in magnetic fields up to 20 kOe and with constant electric fields up to 12 kV/cm. It is shown that the observed resonances are not due to acoustic oscillations of the piezoelectric specimens or to dimensional effects. Application of a magnetic or a constant electric field, for a given orientation of the crystal, affects only the amplitudes of the peaks and does not shift the resonance frequencies. It is concluded that the resonance mechanism is not related to the magnetic domain structure or electric dipolar structure of the crystal. A qualitative explanation of the mechanism of excitation of the resonances is proposed, on the basis of a turnover of the magnetic ordering vector of the magnetic layers of the crystal.

AN earlier communication<sup>[1]</sup> reported the detection and investigation of low-frequency magnetoelectric resonances in a BaCoFe<sub>4</sub> monocrystal possessing a layered structure<sup>[2]</sup>. The strong anisotropy of the magnetic susceptibility and the anomalous form of the magnetization curves of this material over the whole temperature range investigated, from 1.5 to 300°K<sup>[3]</sup>, prevented the drawing of any definite conclusion even about the nature of the magnetic ordering in it. It seemed of interest to investigate the possible existence of low-frequency magnetoelectric resonances in a material crystallographically isomorphic to BaCoF<sub>4</sub>, but with magnetic ordering characteristics known in advance.

The results of an investigation of the static magnetic properties of a monocrystal of BaMnF<sub>4</sub><sup>[4]</sup> showed that this material, crystallographically isomorphic to BaCoF<sub>4</sub><sup>[2,5]</sup>, is a typical compound with two-dimensional magnetic ordering, in which the anisotropy of the magnetic susceptibility is important only below the temperature of the three-dimensional magnetic transition. Above this temperature, the anisotropy does not exceed 6%. In its magnetic properties, BaMnF<sub>4</sub> does not differ qualitatively from BaNiF<sub>4</sub><sup>[6]</sup>.

We have investigated the frequency dependence of the transverse magnetoelectric effect in a BaMnF<sub>4</sub> monocrystal, the preparation of which was described in<sup>[7]</sup>.

The dimensions and orientation of the BaMnF<sub>4</sub> specimen that we had available<sup>[1]</sup> allowed us to make measurements only with the alternating electric field applied along the b axis of the crystal (the notation is the same as in<sup>[5]</sup>). As in<sup>[1]</sup>, we investigated the frequency dependence of the alternating magnetic moment m~ produced in a direction perpendicular to this axis.

The experimental method adopted differed little from that used in the investigation of BaCoF<sub>4</sub><sup>[1]</sup>. A sketch of the experiment is shown in Fig. 1. The speci-

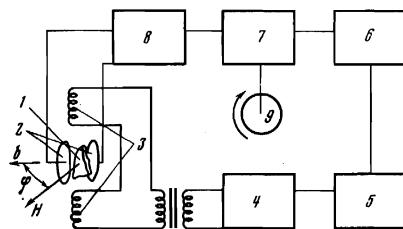


FIG. 1. Sketch of the experimental arrangement. 1—BaMnF<sub>4</sub> specimen; 2—electrodes; 3—coils that record m~; 4—U2-6 amplifier; 5—PDS-021 xy-recorder; 6—ICh-6 frequency meter; 7—G3-34 generator; 8—amplifier for the voltage E~ and the source E; 9—frequency-sweep motor.

men was placed between condenser plates to which was fed an alternating electric field of up to 1.5 kV/cm; the frequency could be varied from 1 to 20 kHz over a period of 5 to 30 minutes. During the sweeping of the frequency, the amplifier was switched to its broad-band mode of operation. During the operation in the wide-band mode, it proved necessary to feed the magnet that produced the field H from storage batteries. This enabled us to increase the signal-to-noise ratio to  $5 \cdot 10^2$ . The absence of any noticeable frequency resonance characteristics of the amplifying network, up to 20 kHz, was carefully verified. In all measurements, the constant magnetic field H was always directed perpendicular to the axis of the coil that recorded m~.

The experimentally obtained frequency dependences of m~ represent a series of sharp resonance peaks, lying in the frequency interval 3 to 18 kHz. No peaks were observed at lower frequencies. It was established that the magnetoelectric resonances in BaMnF<sub>4</sub> have qualitatively similar character to those in BaCoF<sub>4</sub>; their occurrence is therefore not due to the presence of an orbital moment in the Co<sup>+</sup> ion or to the specific anomalies of the magnetic properties of BaCoF<sub>4</sub>. As in the case of BaCoF<sub>4</sub>, the observed picture depended strongly on the crystallographic direction in which the moment m~ was recorded, and also on the orientation of the external magnetic field.

<sup>1)</sup>The authors express their appreciation to S. V. Petrov for providing the BaMnF<sub>4</sub> specimen.

Study of the temperature dependences showed that for given orientation of the crystal with respect to the magnetic field  $H$  (along the  $b$  axis) and for measurement of  $m_\sim$  in a fixed direction, the frequency shift of the peaks did not exceed 10%. But at sufficiently low temperatures, corresponding to a smooth maximum on the susceptibility curve, where the correlations between magnetic layers begin to be pronounced, there appears a new, especially narrow peak at frequency 6.1 kHz; and on lowering of the temperature, there is observed a large increase of its intensity and a frequency shift to 5.8 kHz, which remains constant below  $T_N$ .

Figure 2 shows the frequency dependences of  $m_\sim$  at 6.5, 45, 77, and 290°K, and also the temperature dependence of the intensity of the 5.8–6.1 kHz peak. In this case the direction of the recorded  $m_\sim$  in the crystal plane was chosen for maximum amplitude of the 5.8 kHz peak. After rotation of the crystal 90° about the  $b$  axis, the temperature dependences of  $m_\sim$  have the same character as in Fig. 2, but the intense peak on approach to  $T_N$  occurs at frequency 3.3 kHz. Both these peaks at frequencies 3.3 and 5.8 kHz, on rotation of  $H$  from the  $b$  axis to the perpendicular plane, with preservation of the condition  $H \perp m_\sim$ , decrease in amplitude in proportion to the cosine of the angle  $\varphi$  between the field and the  $b$  axis. Above  $T_N$ , the amplitude of all peaks increased in proportion to the magnetic field intensity up to 20 kOe. Below  $T_N$ , a slight nonlinearity was observed in the  $m_\sim(H)$  dependence, beginning at  $H > 5$  kOe.

We attempted to establish whether the resonances observed in this material might be due to the presence of some superstructure, whose oscillations could be responsible for them. It is very unlikely that such a structure could be the usual magnetic domains, separated by Bloch walls, because the resonances are observed both above and below the magnetic transition temperature, and their frequency changes comparatively slightly. Furthermore, application of a magnetic field of up to 20 kOe does not change the frequency of the resonances, within the limits of experimental error, and it is very difficult to suppose that over such an interval of temperatures and fields the dimensions of the domains would remain constant.

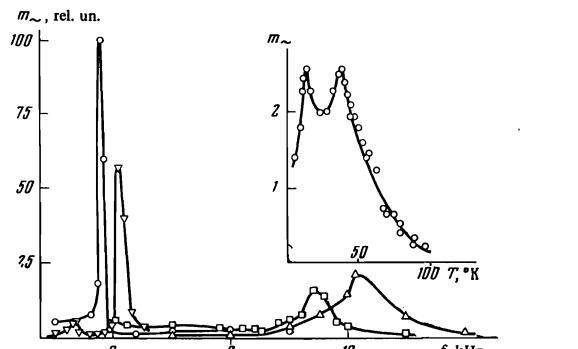


FIG. 2. Frequency dependence of  $m_\sim$  at several temperatures. ○—6°K; ▽—45°K; □—77°K; Δ—290°K. Constant magnetic field  $H = 4$  kOe, parallel to the  $b$  axis; constant electric field equal to zero. At the right is shown the temperature dependence of the amplitude of the resonance peak at frequency 5.8 to 6.1 kHz.

In reference<sup>[5]</sup> it was shown that  $\text{BaMnF}_4$  is pyroelectric, with the electric polarization vector  $P$  directed perpendicular to the  $b$  axis of the crystal. The polarization is produced by distortion and rotation of the octahedra of  $F^-$  ions that surround the  $\text{Mn}^{++}$  ion. It is not possible to reverse the polarization of the material even in fields of up to 100 kV/cm. It was noted that the symmetry of  $\text{BaMnF}_4$  allows the existence of antiferroelectric ordering, with the vector  $Q$  lying along the  $b$  axis.

In principle it is possible that the observed resonances are due to oscillations of an antiferroelectric domain structure. It is scarcely reasonable to consider ferroelectric domains in view of the fact that polarization reversal is extremely difficult. To clarify the relation of the resonances to an antiferroelectric structure, an additional constant electric field  $E$ , of intensity up to 12 kV/cm, was applied to the same electrodes that provided the alternating electric field  $E_\sim$ . It turned out that application of a constant electric field does not shift the resonance frequencies, within the limits of experimental error, but affects only the amplitudes of the peaks. The effect of a polarizing field on the amplitudes of different peaks was found to be quite different. The effect of the field  $E$  on the frequency spectrum was found to be significant only at high temperatures, and this effect was already negligibly small at 77°K. In a field  $E$  up to 5 kV/cm, the resonance frequencies of the peaks that have the greatest intensity lie in the interval 3.5 to 8 kHz.

Figure 3 shows examples of the record of the frequency dependence of  $|m_\sim|$  for certain values of  $E$ , for two different orientations of the magnetic field—along the  $b$  axis and in the plane of the magnetic layers. Investigation of the dependence of  $m_\sim$  on the direction of  $H$  in a plane passing through  $b$  and  $c$ , by a synchronous detection technique, showed that the intensity of some peaks varies as  $\sin \varphi$ , of others as  $\cos \varphi$ . In

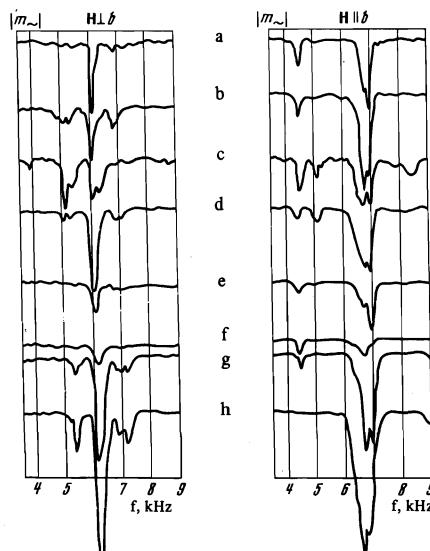


FIG. 3. Dependence of  $|m_\sim|$  on frequency for two orientations of the magnetic field ( $H = 8$  kOe), for various values of the constant electric field  $E$  (in kV/cm): a— $E = -4.2$ ; b— $E = -7.5$ ; c— $E = -12$ ; d, e— $E = -7.5$ ; e— $E = -4.2$ ; f— $E = -1.2$ ; g— $E = 1.2$ ; h— $E = 4.2$ .

fields above 5 kV/cm, the peaks at frequencies 2 to 3.5 kHz begin to increase rapidly. It is characteristic that they have a qualitatively different dependence on E.

Figure 4 shows the dependence of the amplitudes of the peaks that occur at frequencies 3.26 and 6.65 kHz on the intensity of the constant electric field, at temperature 290°K. A change of sign of  $m_{\sim}$  corresponds here to a change by 180° of its phase with respect to the applied alternating field E. It is seen that the dependence is highly nonlinear and reveals large hysteresis; this is evidence of the presence of a dipole domain structure. The direction of traversal for this loop is opposite to the traversal of the usual ferroelectric hysteresis loop. We remark that reconstruction of the domain structure of the specimen proceeds relatively slowly; and in order to obtain peak amplitudes that do not change with time, it is necessary to hold the specimen at each point, after application of a constant field, at least 10 minutes. Such reconstruction is perhaps connected with a change of the antiferroelectricity vector Q, whose direction in a given cell, for a given direction of H, determines the sign of the magnetoelectric effect. Vanishing of  $m_{\sim}$  when it changes sign corresponds to equality of the numbers of domains with different directions of Q.

We must mention two other features that accompany a change of the electric domain structure. First, the value  $E_k$  of the field at which  $dm_{\sim}/dE \approx 0$  is the same for all peaks with frequency above 3.5 kHz. Second, it was established experimentally that the change of sign of  $m_{\sim}$ , for a fixed direction of H, is produced by a constant field E directed perpendicular to the antiferroelectricity vector; and in fields  $E \leq E_k$ , the hysteresis loop obtained is that characteristic of materials with unidirectional anisotropy.

Although the influence of a change of the electric ordering of the BaMnF<sub>4</sub> crystal on the intensity of the resonances is clearly traced, the absence of frequency shifts of the resonance peaks on application of a constant electric field renders very unlikely the examination of their existence on the basis of oscillations of electric domains. Otherwise it would be necessary to suppose that the domain dimensions remain constant throughout such a radical reconstruction.

Still another result indicates that the existence of the resonances described is not connected with crystal dimensions. The BaMnF<sub>4</sub> specimen was split along a cleavage plane perpendicular to its axis; and for one of the

parts of the specimen, having the form of a wedge of angle ~5°, the frequency dependence of  $m_{\sim}$  was again measured. This new spectrum, within the limits of experimental accuracy, coincided with the spectrum of the original specimen as regards both the frequencies and the distribution of peak amplitudes. Hence it also follows that the resonances are not caused by acoustic or any other type of oscillations, with reflection of the waves from the specimen boundaries—just as in the case of BaCoF<sub>4</sub><sup>[1]</sup>.

We arrive at the conclusion that an explanation of the observed resonance peaks must most probably be sought in the layered structure of the material, with weak coupling between layers. It may be supposed that the resonance peaks are due to two-dimensional ordering and are produced by reorientation of the magnetic ordering vector of a given layer with respect to the vector of a neighbor layer. The transition frequency can be very low, since the exchange integral between layers in substances of this type is extremely small<sup>[8]</sup>.

Such a reorientation of a layer, with rotation through 180° of the spins of ions lying in it, must be accompanied by rotation of the magnetization vector of the layer and production of a vector  $m_{\sim}$  in a direction perpendicular to the b axis; it should produce a linear relation between  $m_{\sim}$  and H, as is observed experimentally. It is possible that this same mechanism is responsible for the occurrence of the intense resonance on approach to T<sub>N</sub> and below this temperature. We note also that the results of neutron-diffraction investigation of the crystallographically isomorphic BaNiF<sub>4</sub><sup>[6]</sup> show the presence of two-dimensional ordering also below the temperature of the three-dimensional magnetic transition.

It is natural to suppose that the above-described effect of an electric field on the resonance spectrum of BaMnF<sub>4</sub> is due to a reconstruction of the vector Q, which is formed by a combination of dipole moments  $p_i$  of layers of the crystal that lie along the b axis. Depending on the mutual orientations of the vectors  $p_i$  in neighboring layers, instead of a single frequency there should be three frequencies of transition on reorientation of the magnetic ordering vector of a given layer. To these frequencies correspond three different mutual orientations of the vectors  $p_i$  (the magnetic vector is reoriented in the middle layer, with vector  $p_2$ ): a)  $p_1 \uparrow, p_2 \uparrow, p_3 \uparrow$ ; b)  $p_1 \uparrow, p_2 \uparrow, p_3 \downarrow$ ; c)  $p_1 \uparrow, p_2 \downarrow, p_3 \downarrow$ . In addition, different mutual orientations of the magnetic ordering vectors in the layers between which there is a reorienting layer can correspond to different frequencies of transition and can increase the number of observable resonances.

If we adopt the proposed qualitative picture, then the lack of dependence of the resonance frequencies on the applied constant magnetic and electric fields receives a natural explanation. Change of the amplitudes of the resonance peaks with change of the constant electric field is due to reconstruction of the domain structure of the crystal. At the same time, there is an experimental result that fits poorly into the proposed explanation of the resonance mechanism, namely the presence of resonance even at room temperature: that is, when the correlations in magnetic layers should be very weak. True, it is known that in certain cases<sup>[9]</sup> one can

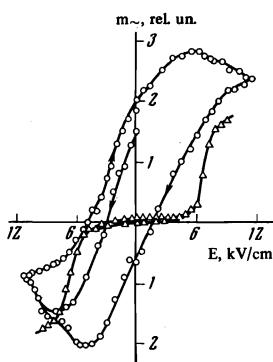


FIG. 4. Dependence of peak amplitudes on constant electric field at frequencies 3.26 ( $\Delta$ ) and 6.65 ( $\circ$ ) kHz, at 290°K, with magnetic field parallel to the b axis.

observe an antiferromagnetic resonance line up to  $T \sim 10T_N$ ; from this follows the existence of short-range antiferromagnetic ordering at distances of the order of tens of atomic dimensions. But we have no proof of the existence of such correlations in the case of  $\text{BaMnF}_4$ .

K. B. Vlasov has remarked that the origin of the resonances may be of a different nature; it may result from oscillations of magnetized walls of antiferroelectric domains in the crystal. It is necessary to consider just walls, and not the volumes of the domains, since it is necessary first of all to take into account the lack of dependence of the resonance frequency on the applied fields  $E$  and  $H$ . This possibility agrees well with the observation of resonances at room temperature, with the slight dependence of the resonance frequencies on temperature, and also with the closeness of the resonance frequencies in  $\text{BaMnF}_4$  and in  $\text{BaCoF}_4$ .

It is considerably more difficult to explain the presence of several oscillation frequencies in the spectrum, the excitation of  $m_\sim$  perpendicular to the field  $E_\sim$  (including the case  $E_\sim \parallel H$ ), and also the dependence of  $m_\sim$  on a constant field  $E$  as shown in Fig. 4.

It is possible that the dipolar electric structure of  $\text{BaMnF}_4$  is considerably more complicated than was supposed in<sup>[5]</sup>. Then the configuration on the antiferroelectric walls and their modes of oscillation can be extremely complicated, and the difficulties enumerated above are perhaps removable. But it is also necessary to explain the existence of a clear correlation between the intensities of the resonance peaks that appear on approach to  $T_N$  and the appearance of two-dimensional ordering of the crystal layers<sup>[4]</sup>, and the nonlinearity in the dependence of  $m_\sim$  on  $H$  below  $T_N$ ; and also to consider that the application of a small pressure<sup>[1]</sup>

greatly changes the parameters of the resonating domain walls. For these reasons, production of the resonances by oscillations of magnetized walls of antiferroelectric domains seems to us unlikely.

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