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SPONTANEOUS MAGNETOELECTRIC EFFECT

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Two ferroelectric substances, $PbFe_{1/2}Nb_{1/2}O_3$ and $PbMn_{1/2}Nb_{1/2}O_3$, were investigated. It was found experimentally that each substance exhibited three states in which the magnetic susceptibility obeyed the Curie-Weiss law, as well as antiferromagnetic ordering at liquid helium temperatures. It was found that, in the antiferromagnetic state, a spontaneous magnetic moment appeared in both substances at a phase transition in magnetic and electric fields and the value of this moment depended appreciably on the applied fields. It was concluded that this spontaneous moment was of magnetoelectric origin.

IT is well known that a linear relationship may be observed between electric and magnetic fields in some magnetically ordered crystals. The possibility of such a relationship was demonstrated theoretically by Dzyaloshinskiĭ[1] on the basis of a thermodynamic theory, which he had developed for magnetic phase transitions. Also, the relationship has been observed experimentally in a number of substances.[2-5]

These and similar experiments have shown that when an external electric or magnetic field is applied, the magnetization of a sample or the electric polarization is observed. This relationship appears in its "purest" form in substances which do not have a spontaneous el electric or magnetic moment.

The theory also applies when the magnetocrystalline symmetry class permits the existence of a linear relationship between the polarization **P** and the magnetization **M** and also if a substance has an ordered internal spontaneous field of ferroelectric origin.

The presence of a simple inversion, not combined with the time reversal operation R, in the magnetic symmetry of a crystal forbids a linear magnetoelectric effect. Therefore, the absence of a center of inversion in a ferroelectric crystal gives rise to a linear relationship between **P** and **M** at a magnetic transition, if such a transition takes place without the doubling of the cell. The possibility of the existence of a relationship between **P** and **M** in substances exhibiting ferroelectric and magnetic properties has already been discussed by Smolenskiĭ, Bokov, and Mitsek[6] and by Lyubimov,[7] who have pointed out that electric and magnetic ordering should influence each other.

The present paper reports an experimental study of the existence of a relationship between **P** and **M**, which may be manifested as a spontaneous magnetization in crystals exhibiting ferroelectric and magnetic properties. It is very difficult to estimate the expected magnetization. We can only assume that, in the case of an exchange-type magnetoelectric interaction, which gives rise to a maximum value of the magnetoelectric effect constant α of the order of 10^{-4}, the value of the spontaneous moment may reach 100 G. We must remember that a magnetic moment of this order is observed in weak ferromagnetism and therefore experiments should be carried out so as to distinguish between the magnetoelectric effect and weak ferromagnetism. This can be done by altering the electric and magnetic domain structure of a substance. It is evident that the direction of the expected spontaneous magnetoelectric magnetization is related to the direction of the electric polarization and such magnetization cannot be observed in the case of polydomain ferroelectric ordering.

Secondly, as demonstrated in[8], the constant α changes its sign from one magnetic domain to another and the spontaneous magnetoelectric magnetization can be observed only when a sample consists of a single magnetic domain. It is, therefore, obvious that by altering the nature of the splitting of a sample into magnetic and ferroelectric domains, we can determine whether the observed magnetic moment is due to the magnetoelectric interaction or the relativistic weak ferromagnetism. Such "control" of the domain structure may be achieved by the application to a crystal of external electric and magnetic fields at the moment of transition to an ordered phase.

We investigated single crystals of $PbMn_{1/2}Nb_{1/2}O_3$ and $PbFe_{1/2}Nb_{1/2}O_3$, which exhibit ferroelectric and magnetic properties and in which Mn^{3+} and Fe^{3+} ions are located in oxygen octahedra of a perovskite cell. Single crystals of $PbMn_{1/2}Nb_{1/2}O_3$ and $PbFe_{1/2}Nb_{1/2}O_3$ were grown in platinum crucibles of 100 and 50 ml capacity from solutions of $PbMn_{1/2}Nb_{1/2}O_3$ and $PbFe_{1/2}Nb_{1/2}O_3$ in $PbO-PbF_2$ and $PbO-PbCl_2$ melts, respectively. The compositions of the solvents were: one part of PbO to four parts of $PbCl_2$ and one part of PbO to one part of PbF_2. The $PbFe_{1/2}Nb_{1/2}O_3$ was synthesized at 850°C in a stream of oxygen and the $PbMn_{1/2}Nb_{1/2}O_3$ was synthesized at 920°C in a nitrogen atmosphere. Each compound was carefully ground and mixed with the solvent before being placed in a crucible. Crystals of both compounds were grown in a Silit shaft furnace, in which the maximum temperature was 1100°C for the iron compound and 1200°C for the manganese compound. The rate of cooling of the $PbFe_{1/2}Nb_{1/2}O_3$ was 15 deg/h and that of the $PnMn_{1/2}Nb_{1/2}O_3$ was 8–10 deg/h. The crystals obtained were black and of cubic shape. The largest $PbFe_{1/2}Nb_{1/2}O_3$ crystals were up to 0.8 mm along the cube edge while the $PbMn_{1/2}Nb_{1/2}O_3$ crystals grew up to 1.25 mm.

X-ray diffraction analysis of the synthesized compounds and of single crystals grown from them showed that the composition of both was of the single-phase type. The parameters of the unit cells of the synthesized compounds and of the crystals prepared from them were equal (within the limits of ± 0.005 Å) and they agreed with the published values.[9] The room-temperature permittivity of $PbFe_{1/2}Nb_{1/2}O_3$ was 1800 and that of $PbMn_{1/2}Nb_{1/2}O_3$ was 800. The magnetic structure of the compounds was not determined.

Since we were interested in the properties of these compounds in the antiferromagnetic state, our investigation was carried out at low temperatures, down to 1.5°K. The measurements of the magnetic properties were carried out using a torsional balance in a cryostat, similar to the balance described earlier in[10]. The balance was improved by attaching its arm to a quartz filament and a photoelectric method was used for determining the null position. The sensitivity of the balance was 10^{-8} of magnetic susceptibility units per gram.

An electric field was applied to a sample by means of a special cell, in which the sample was bonded to two plane-parallel electrodes, and one of these electrodes was in the form of a deep can made of brass foil. When this can electrode was connected to the balance cover and to the copper can of the cryostat, the influence of electrostatic forces on the readings of the balance was practically eliminated even when a voltage of 400 V was applied to the inner electrode. The assembled cell was suspended in the cryostat by a quartz filament to which two thin copper electric leads were bonded.

Figure 1 shows the temperature dependences of the reciprocal of the susceptibility of both substances. In addition to changes in the susceptibility at T = 9°K for $PbFe_{1/2}Nb_{1/2}O_3$ and at T = 11°K for $PbMn_{1/2}Nb_{1/2}O_3$, which were typical of antiferromagnetic transitions, it was interesting to note the presence of three states which satisfied the Curie-Weiss law. One of the possible qualitative explanations of such behavior was put forward by Smolenskiĭ et al.,[6] who investigated the magnetic properties of $PbFe_{2/3}W_{1/3}O_3$ and found two temperature regions with different Curie-Weiss laws. A neutron-diffraction investigation of this substance[11] indicated magnetic ordering below the ferroelectric transition point. The change in the susceptibility was explained by assuming that only some of the magnetic ions present in a unit cell of this compound were ordered. The disordered spins of the remaining ions gave rise to a paramagnetic susceptibility component. Practically the same conclusions were reached by Drabkin, Mal'tsev, and Plakhtiĭ,[12] who investigated the scattering of neutrons by $PbFe_{1/2}Nb_{1/2}O_3$ at room temperature and at 78°K. The long-range ordering of all magnetic ions represented a low-temperature antiferromagnetic transition. It is worth mentioning that, in contrast to the results obtained by Bokov, Myl'nikova, and G. A. Smolenskiĭ,[13] the dependence of the magnetization of these samples on the magnetic field was not completely linear.

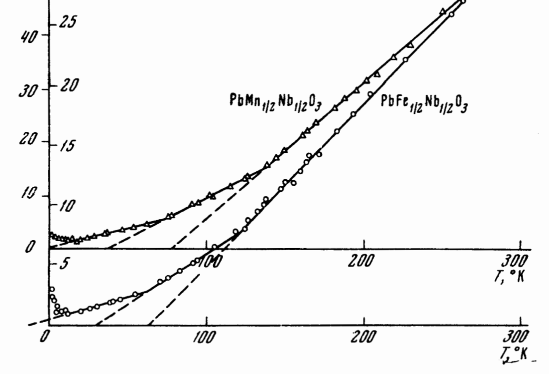
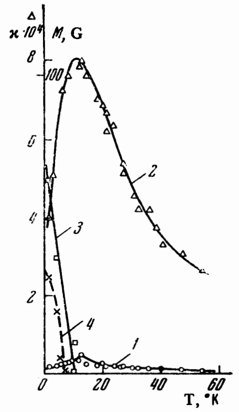


FIG. 1.

The most interesting was the behavior of the magnetic properties of both investigated compounds in the state of "total" antiferromagnetic ordering. In this state, the compound $PbMn_{1/2}Nb_{1/2}O_3$ exhibited a weak magnetic moment with a complex temperature dependence when the sample was not subjected to electric and magnetic fields and at the transition temperature. This magnetic moment did not disappear above the transition temperature T = 11°K but it decreased smoothly to zero on approach to the average "paramagnetic" phase (curve 1 in Fig. 2). In this range of temperatures, the hysteresis loop was not observed and the value of the magnetic moment was only slightly larger than the experimental error. Figure 2 shows also the temperature dependence of the susceptibility of $PbMn_{1/2}Nb_{1/2}O_3$ at low temperatures (curve 2).

FIG. 2.



The spontaneous magnetic moment of $PbFe_{1/2}Nb_{1/2}O_3$ was equal to zero in all phases (within the limits of the experimental error) if no fields were applied at the transition point.

The situation was completely different when constant electric and magnetic fields were applied during the process of ordering of the crystals. In the case of $PbMn_{1/2}Nb_{1/2}O_3$ it was sufficient to apply both fields during the transition through T = 11°K, while in the case of $PbFe_{1/2}Nb_{1/2}O_3$ it was necessary to apply the fields during transition between the two "paramagnetic" phases observed at low temperatures. The application of electric and magnetic fields at the temperature of the antiferromagnetic transition T = 9°K of the iron compound had no effect.

When $PbMn_{1/2}Nb_{1/2}O_3$ passed through the transition point T = 11°K while electric and magnetic fields were applied, the magnetic susceptibility changed slightly but the temperature dependence of the spontaneous magnetic moment altered basically and became similar to the usual ferromagnetic magnetization curve showing a rapid rise of the value of the moment (curve 3). The temperature dependence of the magnetic moment, which appeared in $PbFe_{1/2}Nb_{1/2}O_3$ due to the application of electric and magnetic fields, was of exactly similar nature (curve 4). In both cases, the direction of the spontaneous magnetization coincided with the direction of the magnetic field applied at the transition temperature.

The value of the spontaneous moment depended on the magnetic field intensity applied during the transition The curve showing this dependence for the moment of $PbFe_{1/2}Nb_{1/2}O_3$ at 4.2°K is given in Fig. 3 (curve 1). It was established that fields of ~7 kOe produced practically "total saturation" of the induced moment.

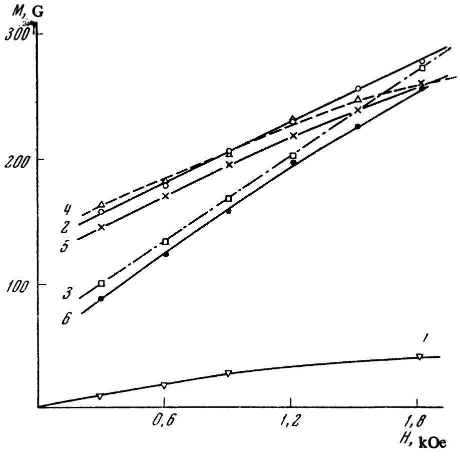


FIG. 3.

The influence of an electric field applied at the transition point was much weaker. The spontaneous magnetic moment of $PbFe_{1/2}Nb_{1/2}O_3$ was practically unaffected by the absence of an electric field if a magnetic field was applied during a phase transition at 63°K. However, the application of an alternating electric field of 1000 cps frequency and about 1000 V/cm intensity at the transition point reduced the spontaneous magnetic moment by about 40%. The spontaneous moment did not disappear completely because ferroelectric ordering was observed also at higher temperatures. The dependence M(H) of $PbMn_{1/2}Nb_{1/2}O_3$ at 1.5 and 4.2°K, obtained using only a magnetic but no electric field, is represented by straight lines 2 and 3 in Fig. 3. Similar straight lines were obtained also for $PbFe_{1/2}Nb_{1/2}O_3$.

The application of an electric field to a sample of $PbMn_{1/2}Nb_{1/2}O_3$ at helium temperatures altered appreciably its magnetic moment. An electric field of 4 kV/cm, applied at 1.5°K at right-angles to the magnetic field and to the spontaneous magnetic moment (induced at the phase transition), increased the magnetic moment of this sample by 4% in weak magnetic fields H. The magnetization curve 4 in an electric field was found to be nonlinear. A similar curve 6 was obtained at 4.2°K. However, in this case the application of an electric field reduced the spontaneous magnetic moment in weak magnetic fields H. When the electric field was removed, the magnetization curve 5 shifted but remained nonlinear. Thus, the application of both fields produced an irreversible change in the magnetization of the sample. The nonlinearity of the magnetization curve after the removal of the electric field could be due to a slow dispersal of a space charge. No such influence of an electric field on $PbFe_{1/2}Nb_{1/2}O_3$ was observed.

The characteristic features of the influence of external electric fields on the magnetic properties of crystals require further study but the existence of a relationship between P and M in the two investigated substances, exhibiting ferroelectric and magnetic properties, can be regarded as proved experimentally. The existence of a spontaneous magnetic moment at helium temperatures is evidently due to the magnetoelectric interactions in the investigated substances.

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234