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SPONTANEOUS SURFACE MAGNETISATION OF SINGLE CRYSTAL MnF_2 IN THE ANTIFERROMAGNETIC STATE

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Spontaneous magnetisation of (100) and (010) surfaces of a MnF_2 single crystal in the antiferromagnetic state is discovered. A sign of the surface magnetisation is determined by a difference in dielectric constants ϵ of MnF_2 and ambient matter: magnetisation is directed to the substance with a smaller ϵ .

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1. Introduction

Magnetic properties of most of the antiferromagnetic crystals have never been investigated in a very small magnetic field. The only exception is Cr_2O_3 for which a few results were published [1–3]. In these measurements the quadrupole magnetic moment was found below T_N . The existence of such quadrupole moment is possible because rhombohedral Cr_2O_3 belongs to the magnetic class symmetry $D_{3d}(D_3)$ that has operations of inversion (I) and time reversal (R) in combination IR [4]. The same condition is necessary for the magnetoelectric effect to be observed.

In the present work we report the results obtained for a clean MnF_2 single crystal. This is an easy-axis antiferromagnet with $T_N \approx 68$ K. It belongs to the magnetic class $D_{4h}(D_{2h})$ that does not permit weak ferromagnetism (spontaneous volume dipole moment [5]) nor quadrupole magnetic moment to occur. Surprisingly we have observed a signal from both dipole and quadrupole magnetic moments below T_N . These moments resulted from a spontaneous magnetisation of surfaces (100) and (010) of the sample.

Measurements were done with a home-built SQUID magnetometer [2, 3]. Both components of residual magnetic field at the sample position, measured with a superconducting lead sphere, did not exceed 1.5×10^{-2} A/m. The sample was cut by a wire saw from an ingot prepared at the Kapitza Institute for Physical Problems. At the beginning the sample had dimensions of $5.5 \times 4.4 \times 3.7$ mm³.

Before measurements the sample was etched in 1:1 HCl for 1/2 hour (a surface layer of 5–10 μm was removed) and carefully washed in distilled water and pure acetone.

2. Results

In some measurements of magnetisation of MnF_2 sample in a small magnetic field we have observed that for directions [100] and [010] it does not saturate below T_N . Measurements without magnetic field revealed the existence of spontaneous magnetisation in these directions. Its temperature dependence resembles that of a magnetic sublattice. If one subtracts this spontaneous magnetisation from the magnetisation measured in a magnetic field then one gets a constant value as it should be below T_N .

The spontaneous magnetisation was definitively observed for [100] and [010] directions. Along the tetragonal axis [001] the dipole signal was at least an order of magnitude smaller and may result from inclination between the sample and the coil axes. If this dipole signal was sufficiently small then a quadrupolar signal was observed, Fig. 1. Note that this quadrupolar signal may be explained by the spontaneous magnetisation of (100) and (010) faces of the sample with the magnetisation directed outward the sample.

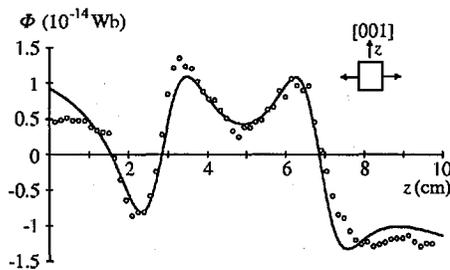


Fig. 1

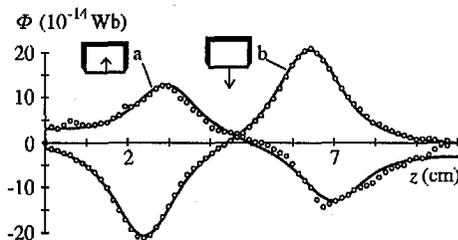


Fig. 2

Fig. 1. Signal $\Phi(z)$ measured along [001] in zero magnetic field at $T = 4.2$ K. Solid line is the least-squares fit with the dipole moment $m_z = -8.4 \times 10^{-11}$ J/T and quadrupole moment -5.36×10^{-12} (J/T) m.

Fig. 2. Signals $\Phi(z)$ measured along [100] in zero magnetic field at $T = 4.2$ K when a large jump in the dielectric constant was only at one (100) face (all other faces were coated with alcohol solution of rosin). Curve "a" — gold surface ($m_z = 2.26 \times 10^{-9}$ J/T), curve "b" — clean surface ($m_z = -4.1 \times 10^{-9}$ J/T).

To alter the conditions at the sample surface we have evaporated the gold film over the whole surface of the sample. We observed that the spontaneous magnetisation has changed its sign. From this experiment it became clear that the sign of the spontaneous surface magnetisation is determined by the electric properties of a substance which contacts with the sample. A room temperature dielectric constant of our sample was equal to $\epsilon \approx 6.5$ which is significantly different from the $\epsilon \approx 1$ of gaseous helium and the very large ϵ of a metal. One of the main problems in interpretation of our experiments resulted from contributions of all sample faces

to the measured signal. We tried to avoid this difficulty by adjusting appropriate conditions at the sample surface so that a large jump in the dielectric constant was only at one face. For this purpose gold was mechanically removed by polishing on a glass plate with a tiny corundum powder from both faces (010), both faces (001), and one face (100). After that, clean surfaces were covered with alcohol solution of resin ($\epsilon \approx 7$, this value is time-dependent due to the evaporation of alcohol). Then the sample was dried and mounted for measuring magnetisation along [100] (gold surface down). The obtained result is shown in Fig. 2 by a curve "a". The spontaneous magnetisation is directed inward the sample. After removing gold, a curve "b" was obtained. The spontaneous magnetisation is directed outward the sample.

In a separate experiment we have investigated the influence of water on spontaneous magnetisation. For this purpose all faces of the sample, except one (100) face, were covered with a thin layer of Stycast 1266 ($\epsilon \approx 7.5$). Then the magnetisation along [100] axis was measured with a clean and dry surface (100). In this case the magnetisation was directed outward the sample. After wetting of the clean surface the magnetisation has changed its sign and become directed inward the sample. When the sample was dried again, the sign and the value of the magnetisation were restored. These results show that the influence of water ($\epsilon \approx 80$) is the same as that of a metal, the spontaneous magnetisation becomes directed inward the sample.

Unfortunately we had no possibility to control the state of the sample surface during the experiment. Nevertheless the main experimental factor — the reproducibility of the results — was employed. Experiments with gold film, alcohol solution of rosin, and water were repeated three times. Each time before changing the condition at the sample surface, it was mechanically polished, etched in diluted HCl, and washed in water and acetone. The obtained results were qualitatively the same as the ones described before, only some changes in amplitude of the dipole signal were observed. In one case when five faces of the sample were covered with alcohol solution of rosin and the last (100) face was clean we obtained $m_z(4.2 \text{ K}) = 6.09 \times 10^{-9} \text{ J/T}$ — the largest value we have ever observed (approximately the same moment has its volume in a field of 8 A/m). This value corresponds to the density of surface magnetisation $2.9 \times 10^{-4} \text{ J/T m}^2$ or $5 \mu_B$ per surface ion Mn^{2+} . This large signal permitted us to make accurate measurements of the temperature dependence of the surface magnetisation presented in Fig. 3. The obtained points are close to the Brillouin function for total spin $S = 5/2$. The signal above T_N was less than 10^{-11} J/T (the noise level). The inset in Fig. 3 shows a log-log plot of the spontaneous magnetisation versus the reduced temperature. The solid line corresponds to the critical exponent $\beta_S = 0.45$. Critical exponents of the spontaneous magnetisation obtained by us in other experiments are in the range of 0.42–0.47, that is significantly different from the critical exponent for the sublattice magnetisation obtained by the magnetic X-ray scattering measurements [6]. This supports our view that spontaneous magnetisation is not a volume effect.

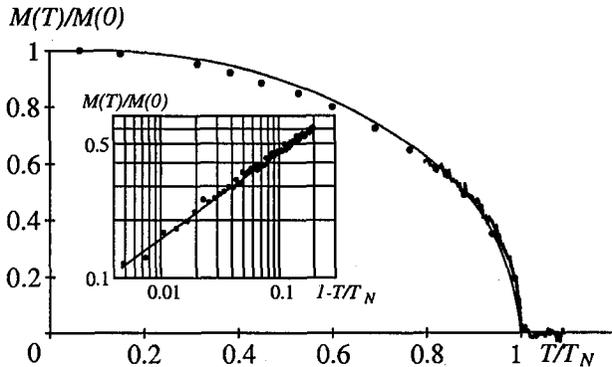


Fig. 3. Temperature dependence of spontaneous surface magnetisation measured along [100] when a large jump in dielectric constant was only at one (100) face (all other faces were coated with alcohol solution of rosin). Points were obtained at fixed temperatures on warm up the sample. Solid line is the record of SQUID output when the sample was slowly cooled down from $T > T_N$. The thin line is the Brillouin functions for total spin $S = 5/2$. The inset: log-log plot of spontaneous magnetisation near T_N versus the reduced temperature $t = 1 - T/T_N$. The straight line corresponds to the critical exponent $\beta_S = 0.45$.

We have also made an experiment on the sample entirely covered with alcohol solution of rosin. No signal was observed in this case.

We attribute spontaneous magnetisation to the surface anisotropy. Physically this anisotropy is analogous to the single-ion anisotropy arising if the crystalline field is distorted from the cubic symmetry [7]. Contrary to the single-ion anisotropy which for ions Mn^{2+} in bulk MnF_2 is *uniaxial*, the surface anisotropy is *unidirectional* and its sign is determined by the difference of the dielectric constants at the sample surface so that the spontaneous magnetisation always points toward the lower ϵ .

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