Anomalous magnetostriction in the layered antiferromagnet $MnCl_2$

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The low-temperature antiferromagnet $MnCl_2$ ($T_N = 1.96$ K), which has a layered crystal structure, is found to have an anomalously strong anisotropy (for iron-group compounds) of the magnetostriction in the antiferromagnetic ($T = 1.8$ K) and paramagnetic ($T = 4.2$ K) regions. The magnetostriction is proportional to the square of the magnetization of the crystal. A formal phenomenological analysis of the results is carried out, and it is shown that the observed magnetostriction is associated with anomalously large magnetoelastic constants (10^8 erg/cm^3) for an *S*-state ion (Mn^{2+}). Possible causes of the effect are discussed.

1. INTRODUCTION

In easy-plane antiferromagnets the magnetoelastic interaction and the associated magnetostriction play an important role in the formation of both the equilibrium configuration of the sublattice magnetizations and the energy gap in the spin-wave spectrum.[1–3] It is of interest to investigate similar effects in crystals having a"soft" phonon spectrum particularly in layered crystals, in which the elastic properties are sharply anisotropic and a number of the elastic constants are small.

As our object of study we have chosen $MnCl_2$ crystals, which have a layered crystal structure in which every layer of Mn^{2+} ions is surrounded by two layers of Cl^- ions, coupled to them by an ionic-covalent bond, and the set of such sandwiches, bound together by van der Waals forces, forms the crystal. The symmetry group of the crystal is D^5_{3d}. Its elastic constants are given in Refs. 4 and 5. In addition, Ref. 5 gives the dispersion curves obtained by neutron scattering for the phonon branches. They exhibit a nonlinearity of the branch of vibrations polarized along the trigonal axis of the crystal and propagating in the plane of the layer, corresponding to the quasiflexural waves examined by Lifshitz for layered crystals.[6,7]

The antiferromagnetic (AFM) ordering in $MnCl_2$ sets in at $T = 1.96$ K with the formation of AFM phase I, and at $T = 1.81$ K there is a transition to AFM phase II.[8,9] A magnetic field imposed in the basal plane narrows the temperature region in which phase II exists, and at $H > 5$–7 kOe only phase I occurs. The magnetic structures of the two phases are similar.[10] In phase I the spins of the Mn^{2+} ions lie in the basal plane of the crystal, forming antiparallel ferromagnetic bands in each of the layers, with the boundaries between bands (in the absence of an external field H) directed along two-fold axes C_2 in the plane of the layer (see Fig. 1). Here each layer is ordered antiferromagnetically. In the absence of H the spins are parallel to the boundaries between bands. The AFM unit cell in the layer can contain 10 magnetic ions (five in each of the opposite orientations). In each of the adjacent sandwich layers the bands of spins located on top of one another are oriented oppositely. Phase II differs from phase I in the width of the ferromagnetic bands in the layers, in the direction of the boundaries between bands, and in the number of ions in the AFM cell (see Ref. 10). One can visualize these structures by assuming that the local magnetization in the layer in both cases is periodically modulated, with a period that is commensurate with the lattice period, while phases I and II differ in the directions and periods of the modulation wave. At $H = 0$ three types of AFM domains coexist for phase I and six types for phase II, differing in the direction of the boundaries between bands in accordance with the three equivalent two-fold axes in the hexagonal plane of the layer. At the present time there is no microscopic justification for this magnetic structure or data on the details of its transformation in a magnetic field of arbitrary direction.

The magnetization of $MnCl_2$ grows linearly with H up to the sublattice collapse field ($H_c \to 32$ kOe at $T \to 0$ K and $H_c \approx 21$ kOe at $T = 1.75$ K). Judging from the isotropicity of the magnetic properties of $MnCl_2$ with respect to magnetization in the plane[11] and from the absence of angular dependence in our antiferromagnetic-resonance (AFMR) measurements for **H** in the plane at an arbitrary angle to C_2, it must be assumed that in a magnetic field stronger than the field at which the magnetic structure is brought into a single domain (1–2 kOe, according to Douglass and Strand-

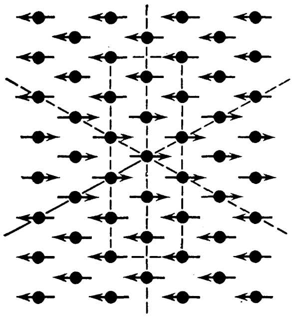

FIG. 1. Schematic illustration of the magnetic structure of the AFM-I antiferromagnetic ordering in $MnCl_2$ according to the description in Refs. 9 and 10, showing the scheme of the magnetic ordering in an individual layer at $H = 0$ for one of the domains. The rectangle encloses the magnetic cell in the layer. The dashed lines correspond to the C_2 axes. The structure of the other domains can be obtained by a 120° rotation about the C_3 axis, which is perpendicular to the plane of the figure.

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borg[12]), the boundaries between the bands of a persistent domain and also the corresponding antiferromagnetism vector in the domain are oriented perpendicular to **H** regardless of the direction of the field with respect to the two-fold axis. It was concluded in Refs. 12 and 13 that despite the complexity of the magnetic structure of $MnCl_2$, all its magnetic properties can be described in an effective two-sublattice model constructed by replacing all the spins which are oriented in the same direction in the AFM unit cell of the layer (and which fall in a single band) by a single effective magnetic moment. The AFMR data[12,13] support such a possibility and, moreover, show that the AFMR branch corresponding to oscillation of the magnetic moment in the basal plane (the low-frequency branch of the AFMR of an easy-plane antiferromagnet) has a gap, and in this case the AFMR is practically isotropic with respect to orientation of **H** in the basal plane. A possible source of this gap is the magnetoelastic interaction (spontaneous magnetostriction[1-3]), which stabilizes the direction of the antiferromagnetism vector in the practically isotropic easy plane of a crystal with two effective magnetic sublattices. There is as yet no data on the magnetoelastic interaction in $MnCl_2$.

In connection with the above, we have measured the magnetostriction in $MnCl_2$ crystals in the AFM phase ($T = 1.8$ K) and in the paramagnetic phase ($T = 4.2$ K) in magnetic fields up to 70 kOe.

There have been few measurements of the magnetostriction in antiferromagnets. According to Belov *et al.*,[14] magnets containing rare earth ions have a strongly anisotropic magnetostriction with relative changes in the linear dimensions $\Delta l/l \sim 10^{-3}$–10^{-2}, while in iron-group compounds the effect is generally 2–3 orders of magnitude weaker. Relatively large values of the coefficients for the anisotropic magnetostriction can be expected for compounds containing ions with a poorly quenched orbital moment (Co^{2+},Fe^{2+}). For Mn^{2+} ions in the S state, the anisotropy of the magnetostriction was expected to be extremely weak. True, in a number of cases Mn^{2+} compounds have exhibited a large exchange magnetostriction (which, in addition to the isotropic part, can contain an anisotropic part which reflects the anisotropy of the crystal). In MnF_2, for example,[15] the magnetostriction (the relative lengthening $\Delta l/l$) at total saturation of the magnetization should amount to $8 \cdot 10^{-4}$ (according to an extrapolation of the data of Ref. 15 to the total-saturation field). Shapira *et al.*[15] attribute this to exchange striction. An analogous value of the exchange magnetostriction has been observed[16] in $RbMnF_3$. For $MnCl_2$, however, the exchange interaction is much weaker than in MnF_2 or in $RbMnF_3$ (T_N is lower by a factor of about 30). Therefore, under otherwise equal conditions one would expect a proportional weakening of the exchange magnetostriction.

The magnetic-field dependence of $\Delta l/l$ in the AFM phase was expected to exhibit three substantially different regions. In the first region, for $H_\perp \langle H_1 \approx 1$–2 kOe ($H_\perp$ is the projection of **H** onto the plane of the crystal), we expected to see a striction due to the transition of the sample to a single-domain state, when the anisotropic contributions which had averaged to zero in the multidomain structure for domains with antiferromagnetism axes at angles of 120° to one another should have given way to anisotropic contribution to the planar components of the magnetostriction for a single-domain AFM state with an antiferromagnetism vector perpendicular to **H**. In the second region ($H_1 < H < H_c$) the striction should have been governed by the turning of the sublattices moments toward the direction of **H** up until the collapse of the sublattices at H_c. Finally, in the third region, an induced paramagnetic striction should have been observed up until total saturation of the magnetization of the sample. At the boundaries of each of these regions the dependence of $\Delta l/l$ on H should have changed noticeably. For $T > T_N = 1.96$ K only the induced paramagnetic striction should have been observed.

The results were unexpected. First, the magnetostriction in both the AFM and paramagnetic regions turned out unprecedentedly large for iron-group compounds, and, second, the magnetostriction in the AFM region did not exhibit the characteristic effects expected at different stages of the magnetization (as we shall see, these effects are present but extremely small).

2. EXPERIMENT

The measurements were made on a capacitive dilatometer similar to that described in Ref. 17. The dilatometer was calibrated using the magnetostriction of nickel at $T = 4.2$ K. The $MnCl_2$ samples were rectangular slabs with typical dimensions of $5 \times 5 \times 1$ mm (the dimensions varied by a factor of 0.5–2.5 for different samples). The plane of the slab coincided with the basal plane of the crystal. The directions of the two-fold axes in the plane of the slab were not controlled. Denoting the length and width of the slab by x and y and the thickness by $z \| C_3$, we can use the following notation for the relative geometry of the direction of measurement of the linear dimension and the magnetic-field direction:

$$\Delta l_y(\mathbf{H}\|y) = \Delta l_y^y, \quad \Delta l_y(\mathbf{H}\|x) = \Delta l_y^x, \quad \Delta l_y(\mathbf{H}\|z) = \Delta l_y^z,$$
$$\Delta l_z(\mathbf{H}\|z) = \Delta l_z^z, \quad \Delta l_z(\mathbf{H}\|x) = \Delta l_z^x.$$

For Δl_y^y and Δl_z^z the measurements were made up to $H = 70$ kOe, while for the remaining orientations the measurements were made up to $H = 13.5$ kOe.

The function $\Delta l(H,T)$ was determined from the magnetic-field or temperature dependence of the frequency of an oscillator circuit which included the capacitance of the dilatometer. Sometimes this function contained discontinuities or varied from one application of the field to the next, especially duriing the first cooling and field on-off cycles (the samples were held in the cryostat for several days; every day they were cooled back down to helium temperatures). This effect was most noticeable in the measurements of Δl_z, where the first applications of the field H in a series of measurements caused a thickening of the sample with the field, while subsequent applications caused a contraction. We attribute the observed multivaluedness to the circumstance that the samples had to be cemented to the supporting surface of the dilatometer and to the moving plate of the measuring capacitor (BF-2 cement). The strong thermal or

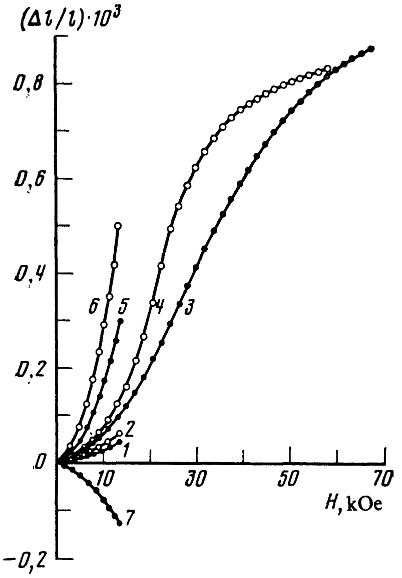

FIG. 2. Magnetostriction of $MnCl_2$ versus the magnetic field for various orientations of **H** with respect to the C_3 axis and various directions of the measured lengthening. The filled dots are for $T = 4.2$ K, the open dots for $T = 1.8$ K. Curves 1,2) $\Delta l \perp \mathbf{H} \| C_3$; 3,4) $\Delta l \| \mathbf{H} \perp C_3$; 5,6) $\Delta l \perp \mathbf{H} \perp C_3$; 7) $\Delta l \| C_3 \perp \mathbf{H}$.

magnetostrictive expansion (contraction) of the sample relative to the metal surfaces cemented to it caused stress in the joints, inhomogeneous stresses in the sample, and nonuniform straining of the sample. For example, in the case of the Δl_z measurements it is easy to imagine a warping of the layers of the sample which are cemented to the surface at the edges of the slab as the slab, hindered by the joints, expands in the plane. In this case one would observe a "thickening" of the sample. The cracking of the joints upon repeated thermal and magnetic-field cycling, manifested in the measurements as jumps in the readings, reduced the stress and thereby improved the reproducibility of the results. A decrease in the area of the joints noticeably reduced the aforementioned multivaluedness. Another condition for reproducibility was that the turning on and off of H had to be slow in order to avoid effects due to the evolution (absorption) of heat in the sample upon magnetization reversal, causing cracking of the sample.[18]

We did not make detailed measurements of the thermal expansion of $MnCl_2$. We can only say that the coefficient of expansion in the plane is negative in the temperature interval 4.2–1.8 K.

Figure 2 shows the results obtained for the **H** dependence of the relative lengthening of the samples at $T = 4.2$ K and $T = 1.8$ K under the conditions for reproducibility indicated above. It is seen that the magnetic-field dependence of the magnetostriction at 4.2 K is qualitatively similar to that in the AFM region. In small fields the striction is quadratic in the field, while saturation occurs in large fields (in which measurements were made only for Δl_y^y). For any direction of **H** the dimensions of the sample in the plane only increase with increasing H. The striction in a field applied in the basal plane, perpendicular to the direction of the length measurement $(\Delta l/l)_y^x$, is substantially (about 3 times) larger than that in a parallel field, $(\Delta l/l)_y^y$, and for $\mathbf{H} \| z$ the striction in the plane, $(\Delta l/l)_y^z$ is noticeably smaller. The striction along the field for $\mathbf{H} \| z$, $(\Delta l/l)_z^z$, is opposite in sign to $(\Delta l/l)_y^y$ and approximately equal in magnitude. The striction $(\Delta l/l)_z^z$ is also negative. In the AFM region one sees practically no change at first in the dimensions of the sample due to the transition to the single-domain structure and to the turning of the antiferromagnetism vector from a random initial direction to the direction perpendicular to **H**. This indicates that the compound has practically no spontaneous magnetostriction of the kind considered in Refs. 1 and 2. More-detailed measurements of $(\Delta l/l)_y^x$ at $T = 1.8$ K have revealed the presence of a very small ($\Delta l/l \lesssim 10^{-5}$) region of negative change in the striction at fields $H < 2$ kOe; this region is apparently a reflection of such a process. Our calculations using the published[4,5] elastic constants of $MnCl_2$ have revealed that such a small spontaneous anisotropic striction cannot explain the observed gap in the low-frequency AFMR.[12,13] We detected no manifestation of the transition between AFM phases II and I in the magnetostriction.

The AFM sublattice collapse field corresponding to $H_c \approx 21$ kOe at $T = 1.8$ K was not evident in the magnetostriction.

Further analysis showed that the magnetostriction in both the paramagnetic and AFM regions, within the experimental accuracy and with the exception of the aforementioned small anisotropic contribution in small fields, depends solely on the total magnetization of the sample, $\mathbf{M}(\mathbf{H},T) = \Sigma \mathbf{M}_i$, where i identifies the sublattice. This circumstance was checked by plotting $\ln(\Delta l/l)$ as a function of $\ln M$. Here the values of $M(H,T)$ were taken from the tables of Ref. 11 after interpolation to a temperature of 1.8 K. It

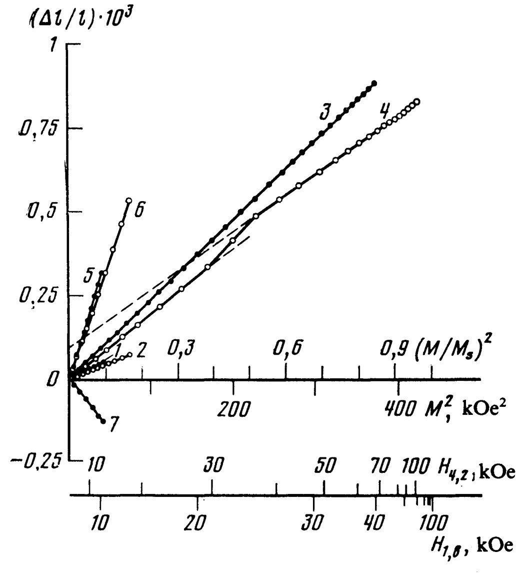

FIG. 3. Magnetostriction of $MnCl_2$ versus the square of the magnetization for various orientations of **H** relative to the C_3 axis and various directions of measurement of the lengthening. The notation is the same as in Fig. 2. In addition to the M^2 scale, for ease of viewing we also give scales for the values of H at which the corresponding values of M^2 are realized in $MnCl_2$.

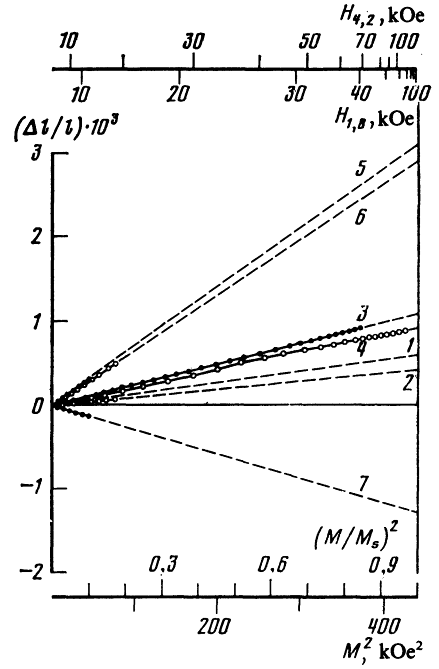

FIG. 4. Extrapolation of the curves of the magnetostriction of $MnCl_2$ versus the square of the magnetization (Fig. 3) to fields corresponding to the saturation magnetization for the given directions. The notation is the same as in Figs. 2 and 3.

turned out that $\Delta l/l \propto M^2(H,T)$ for all experimental temperatures and all field directions. This result is illustrated in Fig. 3, where the experimental data are plotted as a function of $M^2(H,T)$. It is seen that all the curves are linear in these coordinates. The curves corresponding to measurements in the AFM region in this graph exhibit features, unnoticeable on the $\Delta l(H)$ curves, at the value of M that corresponds to the collapse field $H_c \approx 21$ kOe. It is seen that after the collapse field there is a change, though slight, in the slope of $\Delta l/l^{\nu}_{y}(M^2)$. It is characteristic here that both the slope of $\Delta l/l^{\nu}_{y}(M^2)$ and the maximum attainable value of $(\Delta l/l)^{\nu}_{y}$ are lower at $T = 1.8$ K than at 4.2 K. The difference in the slopes is especially pronounced in the region of fields greater than H_c (1.8 K), in spite of the fact that in such fields the sample is in the paramagnetic state in both cases. There is thus a decrease in the induced magnetostriction with decreasing temperature. Using the dependence $\Delta l/l \propto M^2$, we can extrapolate the data of Ref. 3 to fields corresponding to the saturation magnetization of the crystal (Fig. 4) in order to estimate the maximum possible magnetostrictive strains in $MnCl_2$.

3. FORMAL ANALYSIS AND DISCUSSION OF THE RESULTS

A description of the magnetostriction can be obtained by minimizing an expression for the energy density, which includes the magnetic, magnetoelastic, and elastic energies, with respect to the displacements. Here the magnetic energy determines the equilibrium configuration of the magnetic moments of the sublattices in the external field **H**. In view of the complexity of the magnetic structure of $MnCl_2$ and the absence of sufficient information on its transformation in a magnetic field, we describe this structure in an effective model of two sublattices with magnetic moments $\mathbf{M}_1$ and $\mathbf{M}_2$. We assume that the vector $\mathbf{L} = \mathbf{M}_1 - \mathbf{M}_2$ lies in the plane of the crystal and at $H = 0$ is oriented randomly with respect to the direction of measurement of the length of the crystal. Beginning with $H_\perp \approx H_1 \approx 1$–2 kOe, the vector **L** is perpendicular to **H**. In the field interval $H < H_c$ we have

$$|\mathbf{M}_1| = |\mathbf{M}_2| = M_c(T) = {}^1/_2 M(H_c),$$

and the directions of $\mathbf{M}_1$ and $\mathbf{M}_2$ form angles of φ_1 and $\varphi_2 = -\varphi_1$ with **H**; these angles are determined from the condition

$$\cos\varphi_{1,2} = H/H_c = M(H,T)/2M_c(T).$$

For $H > H_c$

$$M_1 = M_2 = {}^1/_2 M(H,T), \quad \mathbf{M} \| \mathbf{H}, \quad \cos\varphi_{1,2} = 1.$$

In this approach the paramagnetic state of the crystal at $T > T_N$ is described in the same way as the paramagnetic state that occurs at $T < T_N$ but in fields $H > H_c$—by formally setting $H_c(T \geqslant T_N) = 0$. For the antiferromagnetic state H_c can in general be different at a given temperature for different field directions (along or perpendicular to the anisotropy axis). For $MnCl_2$ there are no data suggesting such a difference.

In view of what we have said, more-detailed information on the magnetic energy of the crystal and the parameters which determine it will not be needed for solution of the magnetostriction problem if we use the direct experimental data of Refs. 11 and 18 for $M(H,T)$ and $H_c(T)$. For our subsequent discussion it is convenient to introduce the saturation magnetization

$$M_s = M(H \to \infty) = 2M_c(T \to 0) = 2M_0,$$

where M_0 is the satuation magnetization of the sublattice.

The magnetoelastic energy of a two-sublattice antiferromagnet with symmetry group D^5_{3d} can be written as

$$\begin{aligned} F_{\rm me} &= \frac{1}{2M_0^2}[\mathbf{M}_1(\hat{b}\hat{u})\mathbf{M}_1 + \mathbf{M}_2(\hat{b}\hat{u})\mathbf{M}_2 + \mathbf{M}_1(\hat{\beta}\hat{u})\mathbf{M}_2 + \mathbf{M}_2(\hat{\beta}\hat{u})\mathbf{M}_1] \\ &= \frac{1}{2M_0^2}\Big\{\sum_{i=1,2}\Big[\Delta\lambda^{i,i}M_i^2 + A^{i,i}_{ZZ}\Big(M_{iZ}^2 - \frac{1}{3}M_i^2\Big) \\ &\quad + A_\perp^{i,i}(M_{iX}^2 - M_{iY}^2) \\ &\quad + A^{i,i}_{X,Y}M_{iX}M_{iY} + A^{i,i}_{XZ}M_{iX}M_{iZ} + A^{i,i}_{YZ}M_{iY}M_{iZ}\Big] + 2\Delta\lambda^{1,2}\mathbf{M}_1\mathbf{M}_2 \\ &\quad + 2A^{1,2}_{ZZ}(M_{1Z}M_{2Z} - {}^1/_3\mathbf{M}_1\mathbf{M}_2) + 2A^{1,2}_\perp(M_{1X}M_{2X} - M_{1Y}M_{2Y}) \\ &\quad + A^{1,2}_{XY}(M_{1X}M_{2Y} + M_{1Y}M_{2X}) + A^{1,2}_{XZ}(M_{1X}M_{2Z} + M_{1Z}M_{2X}) \\ &\quad + A^{1,2}_{YZ}(M_{1Y}M_{2Z} + M_{1Z}M_{2Y})\Big\}. \end{aligned} \tag{1}$$

Here u_{ij} are components of the strain tensor, X, Y, Z are the axes of a rhombohedral crystal,

$$\Delta\lambda^{i,j} = \Delta\lambda_0^{i,j} + {}^1/_3 A^{i,j}_{ZZ}, \quad i=j, \quad i \neq j,$$

$$\Delta\lambda_0^{i,i} = {}^1/_2[(b_{11} + b_{12})(u_{XX} + u_{YY}) + 2b_{13}u_{ZZ}], \tag{2}$$

$$A_{ZZ}^{i,i}={}^1\!/_2[(2b_{31}-b_{11}-b_{12})(u_{XX}+u_{YY})+2(b_{33}-b_{13})u_{ZZ}], \quad (3)$$

$$A_{\perp}^{i,i}={}^1\!/_2[(b_{11}-b_{12})(u_{XX}-u_{YY})+4b_{14}u_{YZ}], \quad (4)$$

$$A_{YZ}^{i,i}=2[b_{41}(u_{XX}-u_{YY})+2b_{44}u_{YZ}], \quad (5)$$

$$A_{XZ}^{i,i}=4[b_{44}u_{XZ}+2b_{41}u_{XY}], \quad (6)$$

$$A_{XY}^{i,i}=4[b_{14}u_{XZ}+(b_{11}-b_{12})u_{XY}]. \quad (7)$$

The corresponding expressions for the coefficients which determine the intersublattice contributions [the terms in (1) with $i\neq j$] are obtained from (2)–(7) by replacing the components b_{nm} of the intrasublattice magnetoelastic interaction tensor by the components β_{nm} of the intersublattice interaction tensor.

Representation (1) with allowance for (2)–(7) is completely analogous to the representation ordinarily used (see, e.g., Refs. 1, 3, 19) and can easily be transformed into terms of $\mathbf{L}=\mathbf{M}_1-\mathbf{M}_2$ and $\mathbf{M}=\mathbf{M}_1+\mathbf{M}_2$. The form of representation (1), however, admits a transparent interpretation. The terms containing $A_{kl}^{i,j}$ with $k\neq l$ describe the rotation of the principal axes of the magnetic anisotropy tensor of the crystal as a result of the strains. If these terms are small compared to the anisotropy parameters of the magnetic energy (we can always depend on this for magnetostriction), then the terms containing $\Delta\lambda^{j,j}$, $A_{ZZ}^{i,j}$, and $A_{\perp}^{i,j}$ are the magnetoelastic corrections to, respectively, the exchange energy, the principal value of the uniaxial anisotropy tensor, and the intraplane anisotropy. The terms with $i=j$ correspond to the intrasublattice contribution, while those with $i\neq j$ correspond to the intersublattice contribution. In this case representation (1), with allowance for (2)–(4) and for the analogous expressions for $i\neq j$, has the form of an expansion of the corresponding terms of the magnetic energy of the crystal in powers of u_{kl}.

We write the elastic energy in the usual form for rhombohedral symmetry:

$$F_y={}^1\!/_2C_{33}u_{ZZ}^2+{}^1\!/_2C_{11}(u_{XX}^2+u_{YY}^2)+C_{12}u_{XX}u_{YY}+2C_{14}[(u_{XX}-u_{YY})u_{YZ}+2u_{XZ}u_{XY}]+C_{13}(u_{XX}+u_{YY})u_{ZZ}+2C_{44}(u_{XZ}^2+u_{YZ}^2)+(C_{11}-C_{12})u_{XY}^2. \quad (8)$$

Here C_{ij} are the elastic constants. For $\mathrm{MnCl_2}$ at 295 K, Benedek and Frey[4] give $C_{11}=56\pm1$, $C_{12}=8\pm4$, $C_{14}=15\pm5$, $C_{44}=4\pm1$, and $C_{33}=19\pm1$, in units of 10^{10} dyn/cm^2. Escribe *et al.*[5] have calculated the values $C_{13}=12\cdot10^{10}$ and $C_{14}=-6.5\cdot10^{10}$ dyn/cm^2. No data have been published on the temperature dependence of C_{ij}.

Differentiating $F_{me}+F_e$ with respect to u_{ij}, setting the derivatives to zero, and using the above approximation of the spin configuration of $\mathrm{MnCl_2}$ by an effective two-sublattice magnetic structure in an external magnetic field (this is exact for hexagonal symmetry and approximate for rhombohedral symmetry when $\mathbf{H}$ is parallel to the principal axes X, Y, Z), we find the equilibrium strains $\langle u_{ij}(\mathbf{H}\|k)\rangle=\langle u_{ij}\rangle_H^k$. We measured the lengthening only for the directions $l\,\|x,y,z$ in fields $\mathbf{H}\|x,y,z=Z$. Here the directions x and y relative to X and Y were uncontrolled, but there were no noticeable differences between the measurements for samples with different random relative orientations of these axes. Therefore, for our subsequent analysis of the experimental results we can make the identification $x=X$ and $y=Y$ and consider only the strains $(\Delta l/l)_i^k=\langle u_{ii}\rangle_H^k$ with $i,k=X,Y,Z$. These quantities are

$$\langle u_{XX,\,YY}\rangle_H{}^Y=\langle u_{YY,\,XX}\rangle_H{}^X=(2M_i/M_s)^2\{A\pm B+2(C\mp D)\cos^2\varphi_{1,2}\}, \quad (9)$$

$$\langle u_{XX,\,YY}\rangle_H{}^Z(\mathbf{L}\|X)=\langle u_{YY,\,XX}\rangle_H{}^Z(\mathbf{L}\|Y)=(2M_i/M_s)^2\{A+[E-A]\cos^2\varphi_{1,2}\pm B\sin^2\varphi_{1,2}\}, \quad (10)$$

$$\langle u_{ZZ}\rangle_H{}^Y=\langle u_{ZZ}\rangle_H{}^X=\left(\frac{2M_i}{M_s}\right)^2\left\{\frac{1}{C_{33}}(\beta_{13}-b_{13})-2\frac{C_{13}}{C_{33}}A-2\left[\frac{\beta_{13}}{C_{33}}+2\frac{C_{13}}{C_{33}}C\right]\cos^2\varphi_{1,2}\right\}, \quad (11)$$

$$\langle u_{ZZ}\rangle_H{}^Z=\left(\frac{2M_i}{M_s}\right)^2\left\{\frac{1}{C_{33}}(\beta_{13}-b_{13})-2\frac{C_{13}}{C_{33}}A+\left[2\frac{C_{13}}{C_{33}}(A+E)-\frac{1}{C_{33}}(\beta_{13}-b_{13}-\beta_{33}-b_{33})\right]\cos^2\varphi_{1,2}\right\}. \quad (12)$$

Here $|M_i|$ is the magnetization of sublattice i $(i=1,2)$, and

$$A=\frac{1}{C_{\mathrm{I}}^2}[2C_{13}(b_{13}-\beta_{13})-C_{33}(b_{11}+b_{12}-\beta_{11}-\beta_{12})],$$

$$B=\frac{1}{C_{\mathrm{II}}^2}[2C_{14}(b_{14}-\beta_{14})-C_{44}(b_{11}-b_{12}-\beta_{11}+\beta_{12})],$$

$$C=\frac{1}{C_{\mathrm{I}}^2}[2C_{13}\beta_{13}-C_{33}(\beta_{11}+\beta_{12})], \quad (13)$$

$$D=\frac{1}{C_{\mathrm{II}}^2}[2C_{14}b_{14}-C_{44}(b_{11}-b_{12})],$$

$$E=\frac{1}{C_{\mathrm{I}}^2}[2C_{33}(b_{31}+\beta_{31})-2C_{13}(b_{33}+\beta_{33})],$$

$$C_{\mathrm{I}}^2=2[C_{33}(C_{11}+C_{12})-2C_{13}^2],\qquad C_{\mathrm{II}}^2=2[C_{44}(C_{11}-C_{12})-2C_{14}^2].$$

Expression (9)–(12) were obtained for single-domains states corresponding to $\mathbf{L}\perp\mathbf{H}$ over the entire interval of fields up to the sublattice collapse field in the case $\mathbf{H}\perp Z$ and for a definite orientation of $\mathbf{L}$ with respect to X and Y in the case $\mathbf{H}\|Z$. At the same time, for small projections of the field $\mathbf{H}$ onto the plane of the crystal, such that $H_1>H_{x,y}\to0$, this condition should not be satisfied, and either the sample should be multidomain or $\mathbf{L}$ should be oriented randomly with respect to the projection of the plane containing $\mathbf{H}$ and Z onto the basal plane of the sample. Here the contributions containing B in (9) and (10) should either average to zero in the multidomain situation or assume random values from positive to negative. Comparison with experiment immediately shows that the contribution from the B term in (9), which is responsible for the magnetostrictive manifestation of the turning of $\mathbf{L}$ toward the direction $\mathbf{L}\perp\mathbf{H}$ in weak fields, does not exceed 10^{-5}–10^{-6} and is much smaller than the other terms; we shall therefore assume $B\to0$ in the analysis of these other terms.

In the framework of our model expressions (9)–(12) describe the magnetostriction in both the antiferromagnetic region, where

$$M_i=M_c(T),\quad \cos\varphi_{1,2}=|M/2M_c|,$$

and in the paramagnetic region, where we must set

$$M_i = {}^1/_2 M(T, H), \quad \cos\varphi_{1,2} = 1.$$

We see that expression (9)–(12) all reduce to a common form:

$$\left(\frac{\Delta l}{l}\right)_i^k = \langle u_{ii}\rangle_H^k = \left(\frac{2M_c}{M_s}\right)^2 \alpha_1(i,k) + \alpha_2(i,k)\left(\frac{M(H)}{M_s}\right)^2 \quad (14)$$

for $H < H_c, T < T_N$, and

$$\langle u_{ii}\rangle_H^k = [\alpha_1(i,k) + \alpha_2(i,k)]\left(\frac{M(H)}{M_s}\right)^2 \quad (15)$$

for $H > H_c, T < T_N$ and for $0 < H < \infty, T > T_N$, where $\alpha_1(i,k)$ and $\alpha_2(i,k)$ are obtained by comparing (14) and (15) with (9)–(13).

Our treatment in the general case assumes that the elastic and magnetoelastic constant can be functions of temperature. To compare (14) and (15) with experiment we must also bear in mind that after the field corresponding to the transition to the single-domain state, only the magnetic-field contribution to $(\Delta l/l)_i^k$, i.e., $(\Delta l/l)_i^k(H)$, is a measurable quantity, where

$$\left(\frac{\Delta l}{l}\right)_i^k(H) = \left(\frac{\Delta l}{l}\right)_i^k - \left(\frac{\Delta l}{l}\right)_i^k(H=0). \quad (16)$$

Here, as is seen from (14), $(\Delta l/l)_i^k(H=0)$ corresponds to the contribution of the α_1 term for $T < T_N$ and is absent for $T > T_N$.

Comparison with Fig. 3 shows that expressions (14)–(16) correctly describe the experimental dependence of the magnetostriction on the sample magnetization M in the AFM and paramagnetic regions and the transition through the sublattice collapse field for $T < T_N$, although the experimental striction curve $(\Delta l/l)_X^X(H) = (\Delta l/l)_Y^Y(H)$ obtained for $T < T_N$ exhibits a discernable deviation from proportionality to M^2 in a narrow field interval (20–26 kOe) lying somewhat above the sublattice collapse field. However, additional studies are needed to determine the reliability of this deviation, and for the time being we shall therefore consider only the linear (in M^2) parts of the curves in Fig. 3. By comparing (9)–(16) with experiment we can find the parameters A, B, C, D, and E (13) and also, using the known values of C_{ij} from Refs. 4 and 5, the values of some of the b_{ij} and β_{ij} or their linear combinations. In making this comparison we neglected the quantity B (i.e., we assumed $B \to 0$), since the results for $T < T_N$ (discussed above) showed that B is small compared to A, C, D, and E; here we have made the assumption that this relationship is maintained for $T > T_N$ (at 4.2 K). The values thus obtained for A, B, C, D, E, and, thence, b_{ij} and β_{ij} (or their linear combinations are as follows: for $T = 1.8$ K

$$\begin{gathered} B \leqslant 10^{-5}, \quad C = 0{,}96\cdot 10^{-3}, \\ A + 2C = 1{,}71\cdot 10^{-3}, \quad D = -0{,}48\cdot 10^{-3}, \\ A = -(0{,}23 \pm 0{,}03)\cdot 10^{-3}, \quad E = 3\cdot 10^{-4}; \end{gathered} \quad (17)$$

for $T = 4.2$ K

$$\begin{gathered} B \to 0, \quad E = 6.8\cdot 10^{-4}, \\ A + 2C = 2{,}06\cdot 10^{-3}, \quad \beta_{13} + b_{13} = -2.6\cdot 10^8 \text{ erg/cm}^3, \\ D = -0.5\cdot 10^{-3}. \end{gathered} \quad (18)$$

We see that the reason why there is only a slight change in the external-field dependence of the magnetostriction in the region of the sublattice collapse field is that A is small; this, together with the small value of B, can be explained only by an approximate equality of the constants b_{ij} and β_{ij} which appear in these quantities. This result is unexpected for an effective two-sublattice model which reflects the magnetic structure of $MnCl_2$. A key aspect of results (17) and (18) is that to obtain the values found for C, D, and E it is necessary (with allowance for the values of C_{ij}) that the magnetoelastic constants have an anomalously large value for Mn^{2+} ($\sim 10^8$ erg/cm^3). This shows that the giant magnetostriction observed in $MnCl_2$ cannot be explained solely by the fact that the elastic constants of the layered crystal are small. It is noteworthy that the magnetostriction weakens as the temperature is lowered; this apparently cannot be explained by the temperature dependence of C_{ij}.

By comparing expressions (9)–(12) for $\langle u_{ii}\rangle_H^k$ [with allowance for (13)] with expressions (2)–(7) describing the change in the various strain contributions to the magnetic energy, we can conclude that the observed values of A, B, C, D, and E in $MnCl_2$ describe the strain-related change in both the exchange energy and the components $A_\perp$ and A_{ZZ} of the magnetic anisotropy tensor. For example, D involves only the magnetoelastic constants, which are derivatives of $A_\perp^{ii}$ with respect to the strains, whereas C and A are determined by constants which are the corresponding derivatives of the exchange energy. One should thus speak of two anomalies in the magnetoelastic properties of $MnCl_2$. First, there is an anomalously large anisotropy-related magnetostriction for iron-group compounds (terms D and E), which is all the more unexpected for Mn^{2+} ions in the S state. Second, there is a large contribution to the exchange magnetostriction ($A + 2C$), which is unexpected in view of the small exchange constants of $MnCl_2$ in comparison with other compounds in which appreciable exchange magnetostriction has been observed.[15,16]

One can attempt to explain this second feature by considering that $MnCl_2$ has an anomalously low magnetic-ordering temperature in comparison with other iron-group dihalides. For example, the Néel temperature of $NiCl_2$ is $T_N = 49.6$ K, that of $FeCl_2$ is 23.8 K, and that of $CoCl_2$ is 25 K, while $MnCl_2$, despite its larger number of electrons in the $3d$ shell, has $T_N = 1.96$ K. This circumstance may indicate that the low value of T_N in $MnCl_2$ is due to an approximate compensation of the different contributions to the exchange integrals. The dependence of the exchange energy on the interatomic distances, which destroys this compensation, can be just as strong as in compounds with high values of T_N (MnF_2, for example[15]). This hypothesis, however, does not explain the strong anisotropic magnetostriction and the observed temperature dependence of the magnetostriction.

A possible circumstance which should be taken into account in order to understand this section of the results is the presence of features in the phonon spectrum of $MnCl_2$. Glinchuk and co-workers[20] have observed anomalously strong manifestations of the spin-phonon interaction in the temperature dependence of the axial-crystal-field constant and spin-lattice relaxation for the ESR of Mn^{2+} in the layered matrix materials $CdCl_2$ and $CdBr_2$, which are isomorphous to $MnCl_2$. These effects are due to the tendency toward quasi-two-dimensionality of the phonon spectrum in layered crystals. Bar'yakhtar *et al.*[21] considered the features of the magnetoelastic interaction associated with the flexural branch of phonons for a thin ferromagnetic film (filament). It was shown that magnetization suppresses the flexural oscillations and gives rise to a magnetic-field contribution to the change in the negative thermal expansion,[6,7] which is due to quasiflexural oscillations. However, the applicability of the model used in Ref. 21 to such a complex magnetic structure as $MnCl_2$ requires investigation. Furthermore, it is not yet clear whether this model can explain the magnitude and anisotropy of the observed magnetostriction.

In conclusion we note that a very strong anisotropic magnetostriction for iron-group compounds is not just peculiar to $MnCl_2$ if one considers not the derivative of the magnetostriction with respect to the field but rather the value attained for $M \rightarrow M_s$. Extrapolation of the results of Ref. 22 on the magnetostriction in $FeCl_2$ (isomorphous to $MnCl_2$) to the field corresponding to $M \rightarrow M_s$ indicates that the striction corresponding to M_s in the plane of the layer is also anisotropic and reaches a value $\sim 10^{-3}$. In this case, to be sure, the magnetic ion Fe^{2+} is not in the S state, and the exchange interaction in $FeCl_2$ is substantially stronger than in $MnCl_2$.

In summary, a reliable explanation of the anomalously strong magnetostriction observed experimentally in the low-temperature layered antiferromagnet $MnCl_2$ will require further studies with allowance for the features of the magnetic structure and phonon spectrum of the crystal.

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