Static magnetic properties of the quasi-one-dimensional noncollinear antiferromagnet $RbMnBr_3$

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(Submitted 9 October 1992)
Zh. Eksp. Teor. Fiz. **103**, 691–701 (February 1993)

The process of magnetization of a quasi-one-dimensional easy-plane antiferromagnet $RbMnBr_3$ with noncollinear spin ordering was investigated in detail using a vibrating-sample magnetometer with three pairs of measuring coils. The measurements were performed in magnetic fields up to 60 kOe and in the temperature range 1.7–80 K. It was confirmed that $RbMnBr_3$ undergoes a phase transition corresponding to the collapse of two of the three pairs of magnetic sublattices. The critical field H_c of this phase transition was studied as a function of the direction of the magnetic field and the temperature. The experimental results are in good agreement with the theory developed for a quasi-one-dimensional antiferromagnet with 120-degree spin ordering. The exchange interaction and anisotropy constants were calculated by comparing theory and experiment: $J = 91 \pm 5$ kOe, $J' = 0.057 \pm 0.007$ kOe, and $D = 0.5 \pm 0.06$ kOe. It was found that the application of a magnetic field of 27–32 kOe in the basal plane of the crystal produced additional restructuring of the magnetic structure. The nature of this restructuring and the reasons for it are discussed.

1. INTRODUCTION

In the last few years theoreticians and experimentalists have studied extensively compounds having the general formula ABX_3, where A is an alkali metal, B is a bivalent metal of the $3d$ group, and X is a halogen, and $CsNiCl_3$ crystal structure. This great interest in ABX_3 compounds stems from both their quasi-one-dimensional nature (the exchange interaction between magnetic ions along the hexagonal axis is much stronger than the exchange interaction in the basal plane) and the noncollinear nature of their magnetic structure at temperatures $T < T_N$. In particular, if the exchange interaction is antiferromagnetic, then a planar 120-degree antiferromagnetic structure forms: All spins are coplanar, neighboring spins in the basal plane make an angle of approximately 120° with one another, while along the symmetry axis (C_6) neighboring spins are antiparallel. In the absence of a magnetic field the orientation of the plane containing the spins relative to the crystal axes is determined by the anisotropy (relativistic interactions). The existence of such structures has been confirmed by many experiments on elastic neutron scattering and nuclear and electronic magnetic resonances as well as by static measurements.

The nontrivial relation between the exchange interaction and anisotropy (the "easy plane" anisotropy is stronger than interchain exchange), whose existence has been confirmed in, for example, $CsMnBr_3$,[1,2] results in unusual behavior of this system in a magnetic field: Instead of the usual spin-flop transition, here two pairs of ferromagnetic sublattices (there are six sublattices in all) collapse with the spins remaining in the basal plane. It is very interesting that in contrast to a colllinear antiferromagnet, such a phase transition also occurs when the field makes an angle with the basal plane, if this angle does not exceed a critical value determined by the ratio of the interchain exchange to the anisotropy. The behavior of this phase transition as a function of the temperature, like that of the transition into a three-dimensionally ordered state in the presence of an external magnetic field, has been investigated in $CsMnBr_3$ (Ref. 3) and stimulated a great deal of interest, since a significant difference was observed from the behavior of a standard three-dimensional antiferromagnet.

In Ref. 4 Chubukov investigated theoretically the behavior of 120-degree structure in an external magnetic field $H \perp C_6$ and $H \parallel C_6$ within a six-sublattice model based on the Hamiltonian

$$\mathcal{H} = 2J\sum_{i,j}{}' S_i S_j + 2J'\sum_{i,j}{}'' S_i S_j + D\sum_i (S_i^z)^2 - H\sum_i S_i, \qquad (1)$$

where S_i and S_j are the spins of the Mn ions, J is the exchange integral along the C_6 axis of the crystal, J' is the exchange integral in the basal plane, $J' \ll J$ holds (the exchange interaction is antiferromagnetic, i.e., J and $J' > 0$), and D is the anisotropy constant, whose sign ($D > 0$) determines the orientation of the spin plane relative to the crystal axes and $D \ll J$. The first sum describes the exchange energy along the chain, the second sum describes the exchange energy in the basal plane, and the third and fourth sums describe the anisotropy energy and the Zeeman energy of the spins in a magnetic field H. The z axis is oriented along the hexagonal axis of the crystal.

Chubukov studied the case of large anisotropy $D/3J' > 1$. He found that if the field H is directed along the C_6 axis, then the hexagonality and the one-dimensionality do not contribute any anomalies: As the field increases, all spins turn continuously in the direction of the magnetic field, so that the angle between the C_6 axis and the equilibrium position of each spin is

$$\cos\beta = \frac{H}{8JS + 18J'S + 2D}, \qquad (2)$$

and the transverse spin components form, as previously, a 120-degree structure. In the field $H = H_{sat}^{\parallel} = 8\,JS + 18\,J'S + 2D$ a spin-flip transition occurs and the spins become aligned with the field. In a magnetic field much weaker than

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the spin-flip field $H \ll H_{sat}$ in the limit $D, J' \ll J$ the magnetization is proportional to the field:

$$M^{H \| C_6} = g\mu_B N_A S \frac{H}{H_e}, \tag{3}$$

where $H_e = 8JS$ is the exchange field along the C_6 axis, N_A is Avogadro's number, and μ_B is the Bohr magneton.

If, however, the field satisfies $H \perp C_6$, then anisotropy competes with the interchain exchange: the anisotropy strives to keep the spin in the basal plane while the exchange strives to orient the spins perpendicular to the magnetic field. Since the anisotropy dominates ($D/3J' > 1$), the spins do not leave the plane in the process of reorientation. In weak fields, one pair of sublattices becomes oriented almost perpendicular to the field ($\alpha \approx \pi/2$) and the two other pairs become oriented at angles of $\beta \approx \pi/6$ and $\gamma \approx 5\pi/6$. As the field increases, the angles α and $\beta + \gamma$ change very little and the angle $\beta - \gamma$ decreases according to the law

$$\cos\frac{\beta-\gamma}{2} = \frac{1}{2}\left(1 + \frac{z}{2-z}\right),$$
$$z = H^2/H_c^2, \quad H_c^2 = 48JJ'S^2, \tag{4}$$

and vanishes at the critical field $H = H_c$, which corresponds to collapse of two pairs of sublattices. The magnetization with $H < H_c$ is

$$M^{H \perp C_6} = g\mu_B N_A S \frac{H}{3H_e}\left(1 + \frac{2}{(2-(H/H_c)^2)^2}\right). \tag{5}$$

In fields above H_c the angles α and β decrease, vanishing at $H = H_{sat}^{\perp}$, and the magnetization for $H_c < H \ll H_{sat}^{\perp}$ becomes virtually the same as in the case $H \| C_6$.

The behavior of the spin system in an oblique magnetic field is interesting: when the angle between the field and the basal plane is not very large, the phase transition corresponding to collapse of two sublattices still occurs.[2] As the magnetic field tilts out of the basal plane, the critical field increases according to the law

$$H_c^2(\varphi) = H_c^2 \frac{d-1}{d\cos^2\varphi - 1}, \tag{6}$$

where $d = D/3J'$ and φ is the angle between the field and the plane. As φ approaches the critical value φ_c, determined from the relation $\cos^2\varphi_c = 1/d$, $H_c^2(\varphi)$ approaches the exchange field H_e.

We felt that it would be very interesting to investigate in detail another antiferromagnet with $CsMnBr_3$ magnetic ordering in order to be able to study experimentally the properties of this unusual magnetic structure in fields above the phase-transition field H_c [in $CsMnBr_3$ it is quite high—64 kOe at $T = 1.8$ K (Ref. 2)]. This paper is concerned with the magnetization of $RbMnBr_3$ single crystals.

Data from neutron diffraction analysis of powders and susceptibility measurements[5] indicate that $RbMnBr_3$ becomes magnetically ordered at temperatures $T < T_N = 8.8$ K, the magnetic order being close to that in $CsMnBr_3$ with all spins lying in the basal plane of the crystal and forming a noncollinear structure, but the angle between the neighboring spins is $128.5° \pm 1.4°$. Neighboring spins along the C_6 axis are oriented antiparallel. The conclusion that a long-period magnetic structure, incommensurate with the crystal structure, exists in $RbMnBr_3$ is made on the basis of the observed splitting of the (1/3, 1/3, 1), (2/3, 2/3, 1), and (4/3, 1/4, 1) diffraction peaks, and the small asymmetric displacement of the peaks with respect to the position of the single peaks for the usual 120-degree structure. We emphasize that the total intensity of these peaks, ignoring the splitting, is close to that computed in the 120-degree model.

2. EXPERIMENTAL PROCEDURE AND SAMPLES

A vibrating-sample magnetometer, similar to the one described in Ref. 6, was used to measure the magnetization in $RbMnBr_3$. A magnetic field of up to 60 kOe was generated by a system of two superconducting coils. The presence of three pairs of measuring coils made it possible to measure simultaneously three mutually perpendicular components of the magnetization of the sample, one of which (M_x) is parallel to the magnetic field and the other (M_z) is oriented in the direction of vibration of the sample.

The absolute accuracy of the magnetization measurements was $\approx 5\%$. The crystal was oriented with an accuracy of 1–2°.

The investigations were performed in the temperature range 1.7–80 K, but the main measurements were performed at temperatures from 1.7 to 12 K. A gold + iron/chromel thermocouple measured, to within 3%, temperatures of the sample above 4.2 K. Below 4.2 K the temperature was measured to within 0.2 K from the helium saturated vapor pressure. The (H, T, φ) phase diagrams were constructed by measuring the magnetization in the direction of the field as a function of the temperature in different magnetic fields; the method is described in Ref. 3, which is devoted to the investigation of $CsMnBr_3$.

The magnetization measurements were performed on $\approx 1.5 \times 1.5 \times 1.5$ mm^3 and approximately 30 mg single crystals. $RbMnBr_3$ was prepared by melting together $MnBr_3$ and RbBr. The vacuum-sealed ampul containing $RbMnBr_3$ was lowered through the furnace, which was maintained at a constant temperature of 500 °C. Next, the single crystal was annealed for 10 days at $\approx$300–350 °C ($RbMnBr_3$ melts at 452 °C). The crystals obtained were very hygroscopic, and in air they quickly transformed into a white substance, probably $RbMnBr_3 \cdot 2H_2O$. For this reason, in each experiment the sample was cut from the center of a bulk single crystal and immediately coated with polystyrene glue. The dried glue formed a thin film which protected the sample from hydration. This procedure enabled us to eliminate the appreciable paramagnetic contribution to the measured magnetization; this was checked by making sure that the "saturation effect" characteristic of a paramagnet in strong magnetic fields was absent.

3. EXPERIMENTAL RESULTS

The magnetization M_x parallel to the field as a function of the field H for $H \| C_6$ and $H \perp C_6$ at $T = 1.7$ K is displayed in Fig. 1a. According to the figure, the theoretical curves for the 120-degree model (solid lines) describe the experimental data quite well. The difference is that in fields above the

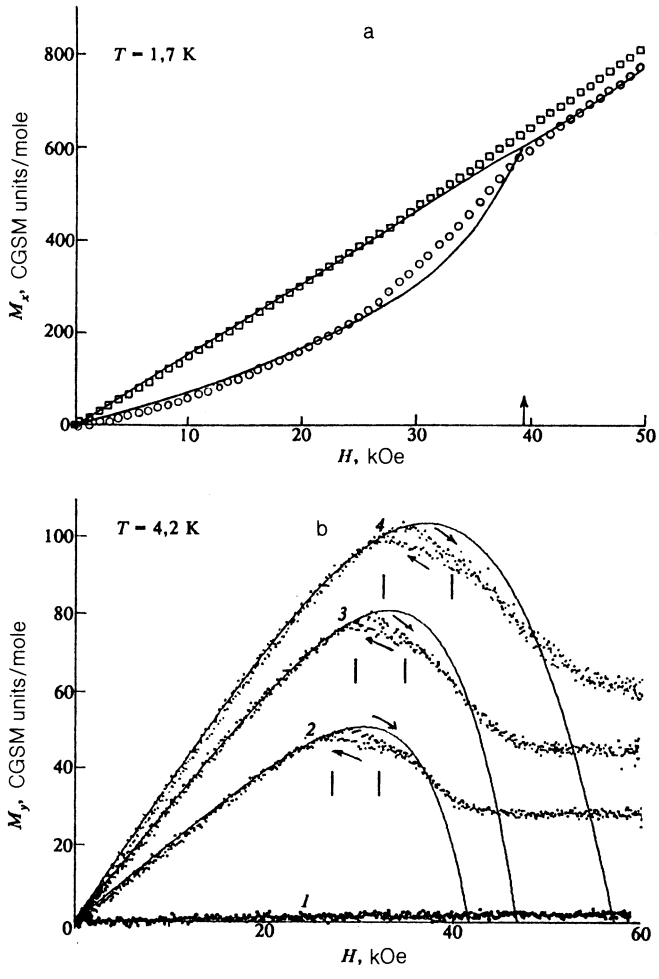

FIG. 1. Magnetizations M_x (a) and M_y (b), parallel and perpendicular, respectively, to the magnetic field versus the field H. The solid lines were calculated using the formulas (3) and (5) for M_x (□—$H \| C_6$; ○—$H \perp C_6$) and the formulas of Ref. 2 for M_y. The data obtained with the field H making angles of 0.5° (1), 16° (2), 26° (3), and 36° (4) with the basal plane are presented in Fig. 1b.

critical field ($H_c \approx 39$ kOe) the magnetizations $M_x^{H \| C_6}$ and $M_x^{H \perp C_6}$ are not the same, as theory predicts, but rather they differ by $\approx 10\%$. The fact that $M_x^{H \| C_6}$ and $M_x^{H \perp C_6}$ are different in fields above the critical field was also observed in $CsMnBr_3$ crystals.[2,7] We note that $M_x^{H \| C_6}$ and $M_x^{H \perp C_6}$ remain different even at temperatures above T_N, right up to 80 K, i.e., in the entire temperature range where the magnetic properties are quasi-one-dimensional.

The magnetization component M_y, perpendicular to the magnetic field, as a function of H with the field making small angles with the basal plane is displayed in Fig. 1b ($T = 4.2$ K). Due to the anisotropy of the magnetization at $H > H_c$, a nonzero transverse-magnetization signal occurs at $\varphi \neq 0$. The absence of a magnetization component perpendicular to the field with the field lying strictly in the basal plane is direct proof of the fact that the easy-plane anisotropy indeed is greater than the interchain exchange—in the reorientation process under discussion the spins do not leave the basal plane.

Since the theory developed for the modern 120-degree model describes quite well the static magnetic properties of $RbMnBr_3$, the constants in the spin Hamiltonian can be calculated using Eqs. (3)–(5). The absolute value of the magnetization along the field is determined by the value of the exchange integral J in the spin chain, and knowing the critical field H_c it is also possible to determine the interchain exchange J'. According to our measurements $J = 91 \pm 5$ kOe and $J' = 0.057 \pm 0.007$ kOe. In calculating these constants we assumed that the spin is classical, $S = 5/2$, though according to the neutron elastic scattering data[5] the effective magnetic moment of Mn extrapolated to zero temperature is $3.6 \pm 0.15\,\mu_B$, which is evidence for the existence of strong zero-point oscillations.

As the sample is heated, the convexity in the curve $M_x^{H \perp C_6}(H)$ is smoothed out, the critical field H_c decreases, and the break in the curve of the parallel magnetization component versus the field at the field H_c becomes less pronounced. It is impossible to determine H_c from such measurements. Therefore a somewhat different measurement procedure was employed to determine $H_c(T)$ at temperatures $T > 4.2$ K: The temperature dependence of the magnetization was measured in different magnetic fields at $\varphi = 0°$, 10°, 20°, 30°, 40°, and 50°. The curves $M_x^{H \perp C_6}(T)$, obtained with $\varphi = 0$ (field in the basal plane), are displayed in Fig. 2. The breaks in these curves correspond to two phase transitions, due to collapse of two sublattice pairs and disruption of the three-dimensional magnetic order. The (H, T) phase diagram reconstructed from these measurements is presented in Fig. 3a.

Figure 3b demonstrates the change occurring in the position of the magnetization breaks when the field cants out of the basal plane. The maximum angle between the field and the plane for which breaks could be observed was 50°. When the field cants away from the basal plane, the position of the

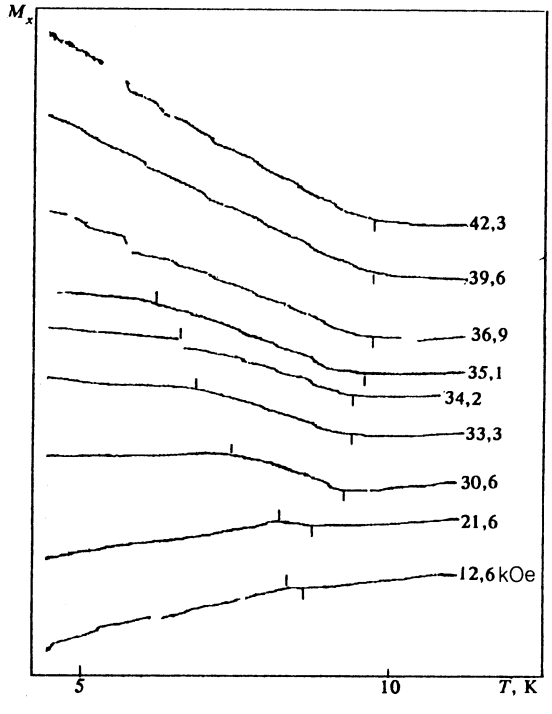

FIG. 2. Magnetization component M_x parallel to the field versus the temperature in different magnetic fields $H \| C_6$.

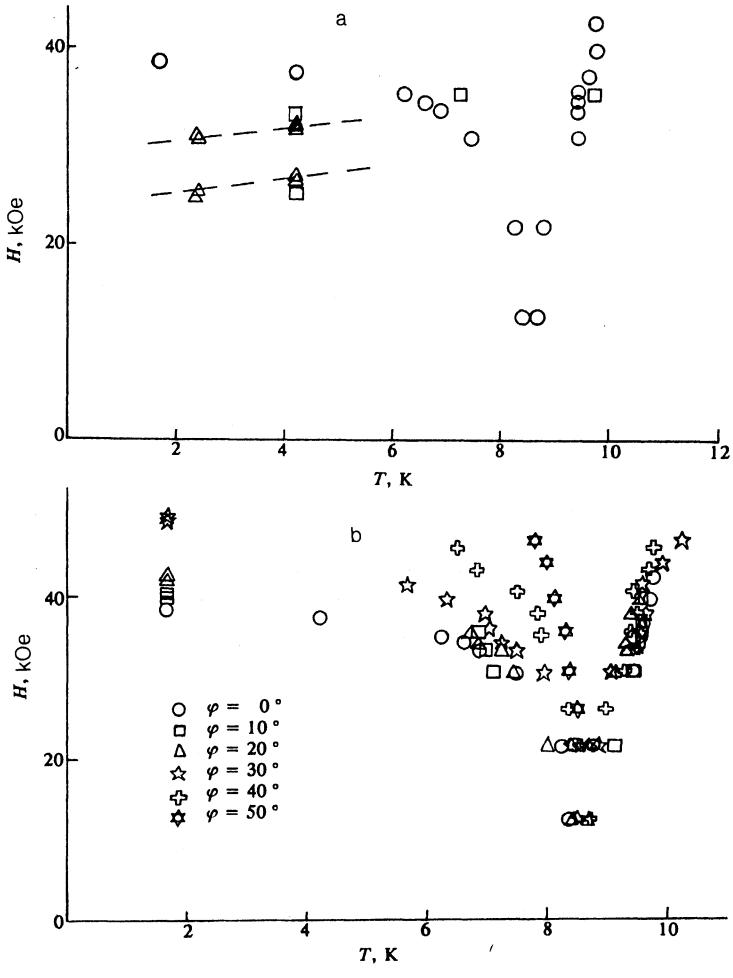

FIG. 3. H versus T phase diagram of $RbMnBr_3$ with $H \perp C_6$ (a) and with different angles between H and the basal plane (b). In Fig. 3a the circles mark the magnetization breaks, the squares are the data of [9], and the dashed lines correspond to the position of the observed hysteresis of magnetization.

line of the phase transition into a three-dimensionally ordered state remains virtually unchanged and the line of the critical fields versus the temperature is shifted appreciably in accordance with the formula (6).

The break in the curves of the magnetization component M_y perpendicular to the field versus the field with $H = H_c(\varphi)$ is much more pronounced than in the curves $M_x(H)$ (see Fig. 1b). This enabled us to determine the critical field for different angles φ up to $T = 1.7$ K. The values of $H_c(\varphi, T = 0)$, which are virtually identical to $H_c(\varphi, T = 1.7\ \text{K})$, can be determined by extrapolating the functions $H_c(\varphi, T)$ to zero temperature. In Fig. 4 the best curve (6) with the parameters $H_c = 39.3$ kOe and $d = D/3J' = 2.9$ is drawn through the experimental points $H_c(\varphi, T = 1.7\ \text{K})$. Using the value found for J', we obtain the anisotropy constant $D = 0.5 \pm 0.06$ kOe.

An anomaly, observed best with decreasing temperature, was noted in the experimental curves of the parallel magnetization component versus the field in the region 26–32 kOe. The anomaly was less than 0.5% of the magnetization itself and it was comparable to the noise level, while its position as a function of the field could only be determined to within 2–3 kOe. This effect is most pronounced in the field dependence of the perpendicular magnetization $M_y(H)$ (Fig. 1b), where the anomalous change in the magnetization is now about 10% and obviously exceeds the noise level. As one can see from Fig. 1b, the field dependence $M_y(H)$ exhibits hysteresis. It is obvious that this hysteresis is associated with some restructuring of the spin system and it occurs, according to the experiment, when the projection of the field on the basal plane reaches the value 31.9 ± 1.0 kOe in increasing fields and 26.7 ± 0.7 kOe in decreasing fields, irrespective of the magnitude of the field component along the C_6 axis.

The effect becomes weaker with increasing tempera-

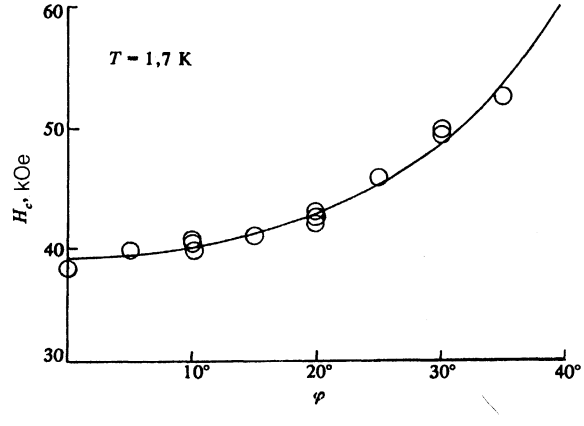

FIG. 4. Critical field H_c versus the angle between the basal plane and the direction of the magnetic field H.

ture. This method of observation does not permit the existence of the effect to be established at temperatures $T > 6$ K, but it can be stated with confidence that in the temperature range 1.7–5.4 K the field at which the effect occurs is virtually independent of the temperature. The dashed lines in Fig. 3a mark the range of existence of this effect in the phase diagram.

4. DISCUSSION

Our experimental investigation of magnetization in $RbMnBr_3$ shows that the magnetic properties of this crystal are close to those of easy-plane quasi-one-dimensional antiferromagnets with 120-degree spin structure (similar to $CsMnBr_3$). However, there is certainly a deviation from this type of magnetic ordering. This deviation is manifested in the presence of additional reorientation of the magnetization of the system, occurring when a magnetic field of 27–32 kOe is applied in the basal plane, together with hysteresis as a function of the field. We note that it is in this region of magnetic fields that the unusual hysteresis phenomena are observed in resonant microwave absorption.[8]

The nature of this change in the magnetization is unclear and can be interpreted in several ways: 1) as a change in the period of the long-period magnetic structure, incommensurate with the crystal structure; 2) as a process of monodomainization of the crystal; or, 3) as some additional phase transition in a distorted triangular structure. There is a definite justification for each interpretation.

1. The first interpretation is supported by the direct experiment on determination of the magnetic structure—measurement of neutron diffraction in an external field, performed recently by Kawano *et al.*,[9] who confirmed the existence of a phase transition corresponding to the collapse of two pairs of sublattices (in Fig. 3a the small squares are the data of Ref. 9) as well as the previously observed[5] splitting of the (1/3, 1/3, 1) and (2/3, 2/3, 1) neutron peaks and investigated the behavior of these peaks in a field $H \perp C_6$. It was found that the intensity of the peak (1/3, 1/3, 1) drops sharply when the field reaches a magnitude of 2–3 T, whereas the splitting of the peak increases significantly. This phenomenon is interpreted as a change in the cant angle θ of the 120-degree spin structure from 8.4° to 15.6°, i.e., as a change in the period of the magnetic structure. It is conjectured that the crystal symmetry group of the crystal is D^4_{6h} and the splitting of the neutron scattering peaks is associated precisely with the incommensurateness of the magnetic structure. The electron spin resonance results can also be explained by the sharp change in the period of the magnetic structure.[8]

2. Bearing in mind the small distortion of the crystal structure, recorded with the help of x-ray analysis[10] and recently confirmed by birefringence experiments,[11] this interpretation of the splitting of the neutron scattering peaks could be incorrect. In this case there is no long-period magnetic structure in $RbMnBr_3$, and the splitting of the neutron scattering peaks is caused by the distortion of the 120-degree structure because in the distorted crystallographic structure the exchange integrals between neighboring spins in the basal plane are not equal. The angle $\theta = 8.4°$ probably reflects to some extent the distortion of the 120-degree structure. In such a distorted structure the elementary symmetry analysis predicts the appearance of six types of orientational domains,[8] and the monodomainization field may turn out to be quite high.

3. The question of the properties of the antiferromagnetic system on a triangular lattice with nonequivalent exchange between neighboring spins in a magnetic field remains open and requires detailed theoretical analysis. It has therefore not been excluded that in fields of 27–32 kOe an unknown phase transition could be responsible for the additional change in the magnetization direction.

In conclusion we happily thank B. Ya. Kotyuzhanskii for allowing us to use his experimental apparatus to perform some of the measurements.

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[1]I. A. Zaliznyak, L. A. Prozorova, and S. V. Petrov, Zh. Eksp. Teor. Fiz. **97**, 359 (1990) [Sov. Phys. JETP **70**(1), 203 (1990)].
[2]S. I. Abarzhi, A. N. Bazhan, L. A. Prozorova *et al.*, J. Phys.: Cond. Matter **4**, 3307 (1992).
[3]T. Goto, T. Inami, and Y. Ajiro, J. Phys. Soc. Jpn. **59**, 2328 (1990).
[4]A. V. Chubukov, J. Phys. C **21**, 441 (1988).
[5]C. J. Glinka, V. J. Minkiewicz, D. E. Cox *et al.* in *18th Annual Conference on Magnetism and Magnetic Materials*, 1973, p. 659.
[6]A. N. Bazhan, A. S. Borovik-Romanov, and N. M. Kreines, Prib. Tekh. Eksp. **1**, 412 (1973).
[7]B. Ya. Kotyuzhanskii and D. V. Nikiforov, J. Phys.: Cond. Matter **3**, 385 (1991).
[8]I. M. Vitebskii, O. A. Petrenko, S. V. Petrov *et al.*, Zh. Eksp. Teor. Fiz. **103**, 326 (1993) [JETP **76**, 178 (1993)].
[9]S. Kawano, Y. Ajiro, and T. Inami, J. Magn. Magn. Mater. **104–107**, 791 (1992).
[10]H. von Fink and H.-J. Seifert, Acta Cryst. B **38**, 912 (1982).
[11]T. Kato, K. Iio, T. Hoshino *et al.*, J. Phys. Soc. Jpn. **61**, 275 (1992).

Translated by M. E. Alferieff