Phase transitions in the easy-axis ferromagnet $CuRb_2Br_4 \cdot 2H_2O$ in weak magnetic fields

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The effect of a magnetic field on the magnetic properties of the Heisenberg ferromagnet $CuRb_2Br_4 \cdot 2H_2O$ is investigated experimentally and theoretically. The temperature dependence of the magnetic susceptibility in a magnetic field H comparable with the anisotropy and demagnetization fields is found to have singularities when the phase-transition temperature $T_C(H)$ in the magnetic field is lower than the critical temperature T_C. It is also found that $T_h > T_C$, where T_h corresponds to the temperature of the susceptibility maximum that is not connected with the phase transition in the magnetic field. These singularities are shifted with increasing fields towards lower and higher temperatures, respectively. The H–T diagram is plotted. The observed behavior of the magnetic susceptibility in a magnetic field agrees qualitatively with the results of analysis based on the Landau theory of second-order phase transitions.

A second-order phase transition takes place in anisotropic ferromagnets even in the presence of a magnetic field, provided the latter is weak enough (weaker than the anisotropy and demagnetization fields). This gives rise to characteristic field and temperature dependences of the spontaneous magnetization, of the magnetic susceptibility, and of the heat capacity, from which additional information can be extracted on the magnetic properties of the system being studied (see the review by Kamilov and Aliev[1]). Although phase transitions in a magnetic field in an easy-axis ferromagnet have been investigated theoretically in detail,[2,3] only a few experimental investigations of such systems have been reported.[4–7]

We study here the effect of a magnetic field applied across the easy axis on magnetic phase transitions in the ferromagnetic crystal $CuRb_2Br_4 \cdot 2H_2O$ in order to determine the singularities of the magnetic ordering in a magnetic field and to plot the H–T diagram. The uniaxial ferromagnet $CuRb_2Br_4 \cdot 2H_2O$ is very convenient for the investigation of the critical behavior in a magnetic field, while the presence of weak anisotropy makes the critical temperature field-dependent and permits a study of the influence of the magnetic field on the phase transition.

The compound in question is one of a group of model Heisenberg ferrodielectrics with general formula $CuM_2X_4 \cdot 2H_2O$ (where M = Rb, K, NH_4; X = Cl or Br), whose weak anisotropy is determined by that of the exchange interaction. The crystal structure of the compound is described by the space group D_{4h}^{14}. At atmospheric pressure it becomes ferromagnetically ordered at atmospheric pressure at, temperatures below $T = 1.85$ K, with a magnetic moment directed along the tetragonal axis of the crystal.

The singularities of the critical behavior of a magnet in a magnetic field manifest themselves distinctly in the form of maxima on the magnetic-susceptibility field dependence. We therefore studied the character of the magnetic ordering of the magnetodielectric $CuRb_2Br_4 \cdot 2H_2O$ by measuring the temperature dependence of the susceptibility in magnetic fields (up to 300 Oe) in a wide temperature range (0.4 K $< T <$ 3.0 K). High pressure was used to vary the magnetic anisotropy that determines the character of the H–T phase diagram. The Curie temperature and the $CuRb_2Br_4 \cdot 2H_2O$ crystal anisotropy increase with increasing pressure.[8]

EXPERIMENT

The magnetic susceptibility was measured with a low-frequency differential magnetometer. The 30-Hz modulating magnetic field was produced by a superconducting coil and was $\lesssim 0.3$ Oe. The measuring coil placed inside the high-pressure chamber consists of three pairs of coaxial differential sections with $N_1 = 2000$ and $N_2 = 600$ turns per section). This permits simultaneous measurements in two crystallographic directions and yields the pressure in the high-pressure chamber. The measurement section was 50 mm long and 1.1 mm in diameter.

The mutual-induction emf of the sections, including the contribution of the high-pressure vessel, was cancelled out to within 1%, ensuring 10^{-5}–10^{-6} susceptibility sensitivity of the measurements.

The magnetizing field was produced by a superconducting solenoid. The dc magnetic field was uniform to within less than 0.5% over a 3-cm length along the solenoid axis. The directions of the dc and ac magnetic fields coincided with the axis of the cylindrical sample.

The magnetic measurements were performed in a ^{3}He cryostat, in which temperatures higher than 1.6 K were obtained and stabilized by electron heating of a liquid-helium bath, while the lower temperatures were obtained by pumping off ^{3}He vapor with NGG-2 or NVZ-20 pumps and with a BN-3 booster pump.

The temperature in the ^{3}He bath was measured with a semiconductor resistance thermometer calibrated against the ^{3}He vapor pressure. The thermometer was mounted on the outer wall of the high-pressure chamber at the same level as the sample. The absolute temperature error is estimated at several mK.

We investigated cylindrical single crystals (diameter 1 mm, approximate length 1 mm, and mass ≈ 0.01 g).

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The high-pressure chamber (HPC) was made of BrB_2 beryllium bronze. Its working-channel diameter was 6 mm and its housing diameter 26 mm. High quasi-hydrostatic pressures were produced by the usual method using a 1:1 mixture of transformer oil and kerosene as the transmitting medium. The pressure was determined from the superconducting-transition temperature of tin with an error less than $\pm$ 0.3 kbar.

The longitudinal magnetic susceptibility $\chi_{\parallel}$ was measured along the C_4 fourfold symmetry axis, and the transverse susceptibility in a plane perpendicular to the C_4 axis. The crystallographic C_4 axis was determined by x-ray diffraction and independently by crystal-optics methods.

The temperature dependence of the magnetic susceptibility was plotted either point-by-point or with a PDP-004 automatic x–y plotter.

RESULTS

The variation of the magnetic susceptibility of $CuRb_2Br_4 \cdot 2H_2O$ in a magnetic field reflects most clearly the effect of the field on the critical behavior of the magnet. In contrast to the usual susceptibility curve ($H = 0$), application of a dc magnetic field reveals anomalies, at $T_h > T_C$ in the paramagnetic field and at $T_C(H) < T_C$ in the ordered phase (T_C is the phase-transition temperature in the absence of a magnetic field). The singularities connected with the magnetization effects in a magnetic field are observed in both the easy ($\mathbf{H} \| C_4$) and difficult ($\mathbf{H} \perp C_4$) magnetization directions. In strong fields the susceptibility curve has no distinct singularities in the critical region and it is difficult to determine the temperatures $T_C(H)$ and T_h.

Transverse magnetic susceptibility

Figure 1 shows the temperature dependence of the susceptibility in a direction perpendicular to the tetragonal axis at a hydrostatic pressure 9.5 kbar and at different values of the dc magnetic field $\mathbf{H} \perp C_4$.

The $\chi_{\perp}(T)$ curves for lower pressures are similar but shifted towards lower temperatures, since $dT_C/dP > 0$. At

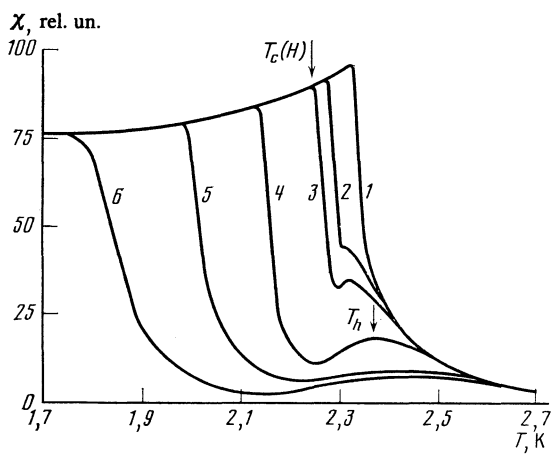

FIG. 1. Temperature dependences of the magnetic susceptibility of $CuRb_2Br_4 \cdot 2H_2O$ in the difficult magnetization direction at a pressure 9.5 kbar in dc magnetic fields: 1—$H = 0$; 2—$H = 50$ Oe 3—$H = 70$ Oe; 4—$H = 110$ Oe; 5—$H = 200$ Oe; 6—$H = 250$ Oe.

$T = T_C(H)$ an abrupt jump of the susceptibility is observed, corresponding to transition of the system into the ferromagnetic phase.[1)] In this phase $\chi_{\perp}$ depends very little on T and H. With increasing field, the critical temperature drops and the transition is smeared out. In addition, the plot of $\chi_{\perp}$ against temperature has in a magnetic field $H > H_{cr} \approx 50$ Oe and at $T = T_h^{\perp} > T_C$ a maximum that shifts with increasing field towards higher temperatures, becomes smeared out, and decreases in amplitude. The observed dependences of $\chi_{\perp}$ on T and H can be explained on the basis of the Landau theory of second-order phase transitions.

The free energy of an easy-axis ferromagnet in a transverse magnetic field near the critical temperature can be represented by an expansion in powers of the magnetization m:

$$F = {}^1/_2 a\mathbf{m}^2 - {}^1/_2 K m_z^2 + {}^1/_4 b\mathbf{m}^4 - m_x H. \quad (1)$$

The z and x axes are directed here along the easy-magnetization axis and along the vector $\mathbf{H}$, respectively; a and b are the thermodynamic coefficients; $K > 0$ is the anisotropy constant.

The conditions that the free energy (1) be a minimum with respect to m_x and m_z lead to the equations

$$H = m_x[a + b(m_x^2 + m_z^2)], \quad (2)$$

$$0 = m_z[a - K + b(m_x^2 + m_z^2)]. \quad (3)$$

It follows from (2) and (3) that two phases exist in the magnet, paramagnetic ($m_z = 0$) and ferromagnetic ($mz \neq 0$); m_x differs from zero in both cases. It is easily seen (see, e.g., Ref. 2) that the transition from the paramagnetic to the ferromagnetic phase occurs at the temperature

$$T_C(H) = T_C - (b/\alpha K^2) H^2, \quad (4)$$

where $\alpha > 0$ is determined from the expansion of $a - K = \alpha(T - T_C)$.

In the low-temperature phase $T < T_C(H)$ the transverse susceptibility is independent of T or H and is equal to $\chi_{\perp} = \chi_{xx} = 1/K$ (it was assumed for simplicity in the derivation of (4) that the parameters α, K, and b are independent of temperature).

In the paramagnetic phase $[T > T_C(H)]$ the transverse susceptibility is given by

$$\chi_{\perp} = (a + 3bm_x^2)^{-1}. \quad (5)$$

It can be easily shown that at $H \leqslant H_{cr} = 4K(K/3b)^{1/2}/3$ the susceptibility depends monotonically on the temperature. At $H > H_{cr}$ it follows from (2) and (5) that $\chi_{\perp}(T)$ has a minimum at $a = 3bm_x^2$. This maximum is achieved at

$$T_h^{\perp} = T_C - \frac{K}{\alpha} + \frac{3}{2\alpha}\left(\frac{b}{2}\right)^{1/2} H^{2/3}. \quad (6)$$

The value of $\chi_{\perp}$ at the maximum is

$$\chi_{\perp}(T_h^{\perp}) = 1[3(b/2)^{1/3} H^{2/3}]^{-1}, \quad (7)$$

and the half-width at the maximum is proportional to $H^{2/3}$.

The mean-field theory thus accounts well enough for the experimental situation, including the shift of T_C towards lower temperatures in a magnetic field, the weak dependences of the transverse susceptibility on T and H at $T < T_C(H)$, as well as the appearance of a maximum of the $\chi_{\perp}(T)$ plot, and its subsequent decrease, broadening, and

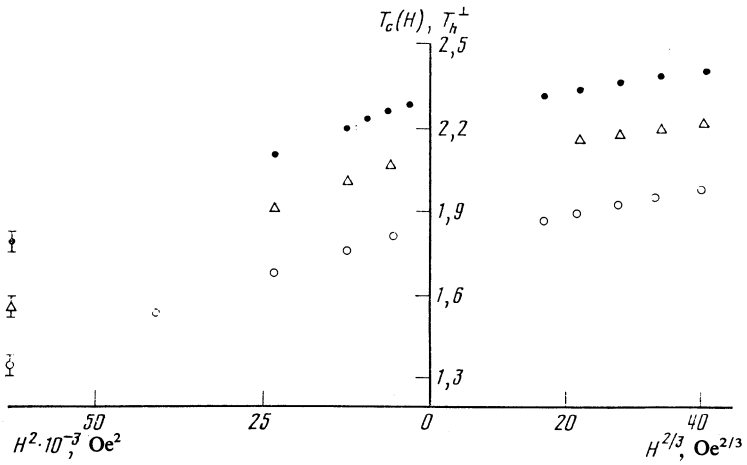

FIG. 2. Changes of the temperatures $T_C^\perp(H)$ and $T_h^\perp$ in a magnetic field at fixed pressures P [kbar]: ○—$P=0$; △—$P=5.2$; ●—$P=9.5$.

shift towards high temperatures as the field H increases. Moreover, theory and experiment agree not only qualitatively but also quantitatively. It can thus be seen from Fig. 2 that the experimental field dependences of $T_C(H)$ and $T_h^\perp$ for different hydrostatic pressures are satisfactorily described by relations (4) and (6). Figure 3 shows a plot of $\chi_\perp^{-1}$ vs $H^{2/3}$ at $T=T_h^\perp$ and at the same pressures. Here, too, all the experimental points lie, within the limits of measurement error, on a straight line in accordance with Eq. (7). Moreover, $\chi_\perp(T_h)$ is practically independent of pressure, meaning according to (7) that the parameter b is independent of pressure. The same holds for the free-energy parameters α and K, which determine the slopes of the curves in Fig. 3.

The experimental field dependence of the critical temperature $T_C^\perp(H)$ in weak fields is described not by the quadratic function (4) but by the power law

$$T_C(H)-T_C(0)\propto H^\omega,$$

where the value $\omega=2.5\pm0.1$ is in close agreement with the field exponent in the molecular-field approximation. The difference observed is obviously due to the need for taking into account in the mean-field theory the fluctuations of the magnetization component along the easy axis near T_C.

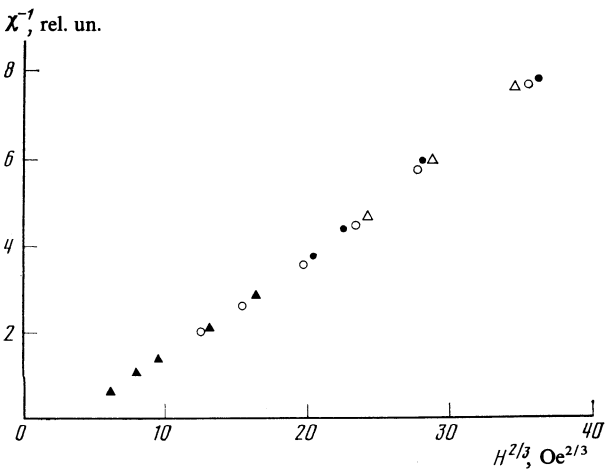

FIG. 3. Change of $\chi^{-1}(T_h)$ in a magnetic field at fixed pressures [kbar]: $\chi_\parallel$: ▲—$P=0$; $\chi_\perp$: ○—$P=0$; △—$P=5.2$; ●—$P=9.5$.

Longitudinal magnetic susceptibility

In the measurements of the longitudinal magnetic susceptibility the modulated and dc magnetic fields were directed along the C_4 axis. Investigation of the behavior of the susceptibility $\chi_\parallel(T)$ in a magnetic field show that the $\chi_\parallel(T)$ curves are qualitatively similar to the $\chi_\perp(T)$ plots, but the mechanism that produces the singularities in a field parallel to the easy axis is somewhat different. In a zero magnetic field $\chi_\parallel$ increases rapidly as the Curie temperature is approached from the paramagnetic phase, to a value close to $1/4\pi N$ (N is the sample demagnetizing factor), and then stays practically constant with further decrease of temperature. This points to formation of a domain structure at $T=T_C$ and attests to ferromagnetic ordering.

If a longitudinal magnetic field is applied, the temperature $T_C(H)$ at which the susceptibility discontinuity occurs decreases and the $\chi_\parallel(T)$ plot acquires a maximum at $T_h^\parallel > T_C$ that behaves like the corresponding maximum of the $\chi_\parallel(T)$ plot, but appears in substantially weaker fields. Obviously, superposition of an external magnetic field along the easy-magnetization axis lowers the temperature at which the domain structure is produced. This temperature can be estimated from the relation $4\pi NM \propto H$, i.e., the demagnetizing field determines the $T_C^\parallel(H)$ dependence. In the molecular-field approximation we have $T_C(0)-T_C(H)\propto H^2$, A rigorous calculation carried out for thick plates in the case of a weak-field applied along the easy axis[9] leads to a similar $T_C^\parallel(H)$ dependence. It is clear that $T_C^\parallel(H)$ should be the same for $\chi_\parallel$ and $\chi_\perp$ in a zero magnetic field, as is indeed observed in experiment. On the other hand, the maximum of $\chi_\parallel(T,H)$ at $T>T_C$ is due to the usual singularity of the magnetic susceptibility at the critical point. The value of $\chi_\parallel$ at the maximum, just as in the case of $\chi_\perp$, is determined by Eq. (7), so that $\chi_\parallel(T_h^\parallel)$ and $\chi_\perp(T_h^\perp)$ at equal values of H differ by the constant K/α. Just as in the case of $T_h^\perp$, the exponent 2/3 in the function $T_h^\parallel$ should be replaced in the weak-field region by the scaling exponent. Since, however, the sample under investigation has a low T_C, the temperature interval in which the scaling relations hold is very narrow and an experimental determination of the exponents ω and ρ (as well as of all other exponents) is a difficult task.

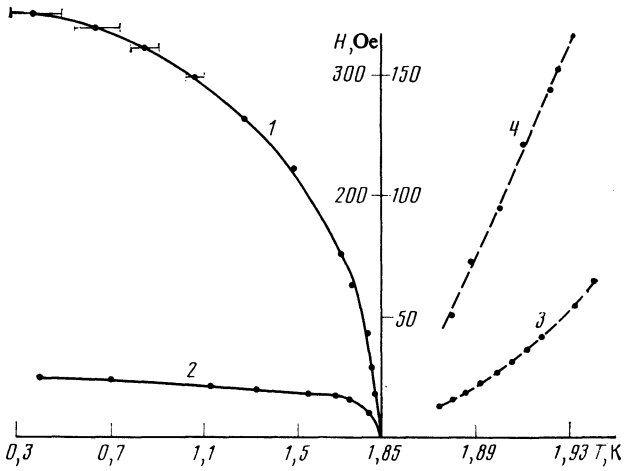

FIG. 4. H–T diagram.

The H–T diagram

According to the results, the critical temperature T_C that characterizes the phase transition at $H = 0$ takes on in an external magnetic different values, $T_C(H)$ and T_h, whose field dependences are reflected on the H–T diagram (Fig. 4). The temperature $T_C^{\perp}(H)$ determines an orientational phase transition in the magnetically ordered phase. The plot (curve 1) obtained in a field $H \perp C_4$ separates the canted and collinear phases having a magnetic moment oriented along the field. We note that the $T_C^{\perp}(H)$ relation can be deduced also in a transverse field from the magnetization isotherms, according to which a transition to a uniformly magnetized phase takes place at a temperature T_C when the external field reaches the value of the anisotropy field H_a. The relations $T_C^{\perp}(H)$ and $T_C(H_a)$ determined by two independent methods (from susceptibility measurments and from the magnetization isotherms in the difficult magnetization direction) are thus in satisfactory agreement. This confirms that the behavior of curve 1 is determined by the change of the magnetic anisotropy as a function of temperature. The pressure-induced increased field anisotropy in the crystal in question shifts the phase boundary towards stronger fields and expands the canted phase.

In an easy-axis ferromagnet, in a field parallel to the easy axis, the temperature $T_C^{\parallel}(H)$ is due to an intense paraprocess and characterizes a transition from a multidomain state to a uniformly magnetized one, curve 2 being their phase boundary. This transition proceeds in the investigated crystal without hysteresis and is of second order. The domain state remains in equilibrium in fields $H < H_d$ (H_d is the demagnetizing field) in the temperature range $0\ \mathrm{K} < T < T_C$.

Curves 3 and 4 represent the field dependences of the maximum temperatures of the longitudinal and transverse susceptibilities in the paramagnetic region. The maximum of $\chi(T_h)$ corresponds, on the plot of the magnetization vs temperature, to a singular point at which the magnetization growth rate changes. The differences between the $T_h^{\perp}(H)$ and $T_h^{\parallel}(H)$ dependences is due to magnetic anisotropy, i.e., in a field $\mathbf{H} \perp C_4$ we have $T_h^{\perp} - T_C \propto (H - H_a)^{\rho}$, where $\rho = 0.67$, while $H_a = 25$ Oe is the anisotropy field at the critical temperature T_C and is due to short-range-order spin-spin correlation.[10]

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[1)]This value is rather tentative, since the system, naturally, has a nonzero magnetic moment at $T > T_C(H)$ induced by the magnetic field and directed along this field. Since there is no spontaneous magnetization (no magnetic-moment component directed along the easy axis) in this case, we call this phase paramagnetic.

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