Landau theory of the magnetic phase diagram of $CsMnBr_3$

M. L. Plumer and A. Caillé
Centre de Recherche en Physique du Solide et Département de Physique, Université de Sherbrooke, Sherbrooke, Québec, Canada J1K 2R1
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The magnetic-field–temperature phase diagram of $CsMnBr_3$ determined by recent neutron-scattering results is explained here by an investigation of a previously developed nonlocal Landau-type free energy. The degeneracy of helically and linearly polarized spin configurations at the Néel temperature is broken by a magnetic field and is shown to be responsible for the novel type of multicritical point observed at $T=T_N$, $H=0$. The theory also accounts for the spin structures of the observed ordered phases as well as the temperature dependences of the phase boundaries.

Recent neutron diffraction results[1–3] suggest that the low-temperature antiferromagnetic order in $CsMnBr_3$ ($T_N \cong 8.3$ K) is an example of the new $V=Z_2\times S_1$ universality class exposed by Kawamura.[4] The spin ordering of this hexagonal ($P6_3/mmc$) insulator is referred to as the 120° structure where the moments lie perpendicular to the c axis with a period-3 basal-plane modulation. In addition, there is a simple antiferromagnetic (period-2) configuration along the c axis. The basal-plane modulation can be viewed as a helically polarized spin density where both the polarization vector $\mathbf{S}$ and wave vector $\mathbf{Q}$ lie perpendicular to the c axis. Kawamura has demonstrated that the two chirality states (left- and right-handed helicity, i.e., $\pm\mathbf{Q}$) associated with helically polarized systems give rise to an Ising-like (Z_2) character in addition to the usual xy (S_1) symmetry of a single-helicity system. The critical exponents, for example, associated with this new universality class differ considerably from those previously calculated for helical spin systems.

A magnetic field applied in the basal plane of $CsMnBr_3$ has very recently been shown by the neutron-scattering results of Gaulin *et al.*[5] to reveal an unusual type of multicritical point at $H=0$, $T=T_N$ in the magnetic phase diagram (see Fig. 1). A similar feature in the magnetic phase diagram of Ho is suggested by the thermal expansion data of Steinitz, Kahrizi, and Tindall,[6] where a transition to an incommensurate helical spin state (with $\mathbf{Q}\perp\mathbf{S}$) occurs at $T_N \cong 132$ K in zero field. The existence of a multicritical point of this type was anticipated for 120° spin structures by Lee *et al.*[7] and in the case of incommensurate helical spin ordering by Schaub and Mukamel.[8] It is of interest to note that Lee *et al.* also recognized the importance of chirality in helical spin systems and suggested that the multicritical point may be associated with a new universality class. This point was pursued further by symmetry and Monte Carlo analyses of a two-dimensional triangular lattice.[9] Although the results of that work are not directly applicable to three-dimensional systems, they appear to contain some features related to the ideas of Kawamura and this suggests that the multicritical point observed in the magnetic phase diagram of $CsMnBr_3$ may indeed be related to the new $Z_2\times S_1$ universality class.

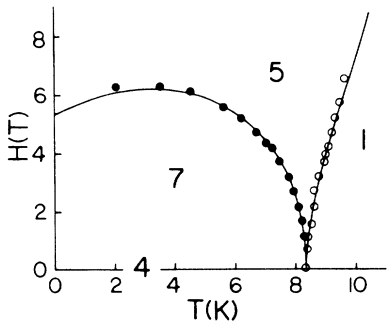

FIG. 1. Magnetic phase diagram of $CsMnBr_3$ where $\mathbf{H}\perp\hat{\mathbf{c}}$ and phases 1, 4, 5, and 7 refer to paramagnetic, helical, linear, and elliptical, respectively. The lines are the results of fitting expressions (8) and (9) to the data of Ref. 5 (circles).

In this work, we demonstrate that the experimentally determined magnetic phase diagram of $CsMnBr_3$ is explained by the analysis of a Landau-type free energy. The principal effects of a magnetic field on the spin structure in materials with hexagonal symmetry like $CsMnBr_3$ and Ho have been examined in a previous work by us[10] on the magnetic phase diagrams of axial and planar antiferromagnetics. That study, however, was primarily devoted to the case of weak planar anisotropy. In $CsMnBr_3$, this anisotropy is known to be relatively strong (see, e.g., Ref. 11) and an appropriate free energy is investigated here. We make clear later the regime of applicability of the results in Ref. 10 to the present case. The structure of the free energy shows that the degeneracy of linearly polarized (phase 5 in Fig. 1) and helically polarized (phase 4) configurations at the Néel temperature is broken by the application of a magnetic field in the basal plane and that this is responsible for the unusual type of multicritical point at $H=0$, $T=T_N$. The linearly polarized and elliptically polarized (phase 7) magnetic states predicted by the analysis to be stabilized by the magnetic field are consistent with observed results. We also obtain a good fit of analytic expressions for the temperature dependences of the phase boundaries to the data (see Fig. 1). Effects due to critical fluctuations are not accounted for in the present mean-field treatment. This work does, however, provide a

framework for a renormalization-group study of, for example, crossover phenomena, which is of particular interest in relation to the $Z_2 \times S_1$ universality class.[12] The present study also serves to complement and extend earlier work on the molecular-field theory of helical spin structures.[13]

A general nonlocal Landau-type free energy functional of the spin density was formulated in Ref. 14 and used there to investigate the magnetic ordering in $CsNiF_3$. This formalism has also been shown to successfully describe the novel multicritical point in the magnetic phase diagram of $CsNiCl_3$ (Ref. 15) and is the basis for the theory of Ref. 10 as well as the present work. The spin density is expressed in the general form

$$\mathbf{s}(\mathbf{r}) = (V/N) \sum_{\mathbf{R}} \rho(\mathbf{r}) \delta(\mathbf{r} - \mathbf{R}) , \tag{1}$$

$$\rho(\mathbf{r}) = \mathbf{m} + \mathbf{S} e^{i\mathbf{Q}\cdot\mathbf{r}} + \mathbf{S}^* e^{-i\mathbf{Q}\cdot\mathbf{r}} , \tag{2}$$

where $\mathbf{R}$ is summed over Mn^{2+} sites (which form a simple hexagonal lattice), $\mathbf{m}$ is the uniform magnetization induced by an applied field $\mathbf{H}$, and $\mathbf{S}$ and $\mathbf{Q}$ characterize the long-range magnetic order. For systems with hexagonal crystal symmetry, there are axial anisotropy terms in the Landau free energy expansion[14,15] of the form $-A_z s_z^2$, etc., where $\hat{\mathbf{z}}$ is parallel to the hexagonal c axis. A configuration of the spin density with $\mathbf{s} \perp \hat{\mathbf{z}}$ is thus preferred if $A_z < 0$. It is assumed here that $|A_z|$ is sufficiently large in $CsMnBr_3$ to maintain this basal-plane alignment, even though there are competing exchange terms in the free energy if a magnetic field is present.[10] From the results of Refs. 10 and 15 it is then clear that the free energy, expanded to fourth order in $\mathbf{s}$ (with $\mathbf{s} \perp \hat{\mathbf{z}}$), relevant to the present study is given by (following the notation[16] of Ref. 10)

$$F = A_Q S^2 + \tfrac{1}{2} A_0' m^2 + B_1 S^4 + \tfrac{1}{2} B_2 |\mathbf{S}\cdot\mathbf{S}|^2 + \tfrac{1}{4} B_3 m^4 + 2B_4 |\mathbf{m}\cdot\mathbf{S}|^2 + B_5 m^2 S^2 - \mathbf{m}\cdot\mathbf{H} , \tag{3}$$

where $S^2 = \mathbf{S}\cdot\mathbf{S}^*$ and all terms are due to isotropic exchange effects. Temperature dependence enters through the second-order coefficients in the usual way as

$$A_Q = a(T - T_Q), \quad A_0' = a(T - T_0') , \tag{4}$$

where $T_Q > 0$, $T_0' < 0$, and all fourth-order coefficients are assumed to be independent of temperature. As emphasized in Ref. 14, in a *nonlocal* formulation of the free energy (also a feature of earlier theories[13]) all of the coefficients B_i are *a priori* independent of each other. This form of Landau free energy thus stabilizes a long-range magnetically ordered phase ($S \neq 0$) at $T = T_Q \equiv T_N$ in zero applied field. Note that the free energy is minimized by a configuration of the uniform magnetization $\mathbf{m} \| \mathbf{H}$.

The origin of the multicritical point of the phase diagram shown in Fig. 1 is immediately clear from a qualitative analysis of the free energy.[10] The structure of the ordered phase at $T = T_N$ is determined by terms that are second order in $\mathbf{S}$. In zero field, linear and helical polarizations of the spin density are thus degenerate in energy at the Néel temperature since both configurations make the same contribution $A_Q S^2$ (also noted by Kaplan[17]). This degeneracy at $T = T_N$ is broken by a magnetic field $\mathbf{H} \perp \hat{\mathbf{z}}$ through the term $B_4 |\mathbf{m}\cdot\mathbf{S}|^2$ which favors a linear polarization with $\mathbf{S} \perp \mathbf{m}$ if $B_4 > 0$. (The degeneracy can also be broken by axial anisotropy in zero field.[15,17]) The helical polarization (where $\mathbf{S}\cdot\mathbf{S} = 0$) characterizing the 120° spin structure of $CsMnBr_3$ at $H = 0$ is stabilized at temperatures $T < T_N$ by the *fourth-order* term $B_2 |\mathbf{S}\cdot\mathbf{S}|^2$ if $B_2 > 0$ (see Refs. 10 and 18). At temperatures $T < T_N$ and fields $H > 0$, there is a competition between these two terms and the elliptically polarized state may be stabilized so that the phase diagram of Fig. 1 is realized. Note that the structure of the phase diagram has features in common with tetracritical behavior usually associated with magnetic anisotropy.[19]

A detailed analysis of the free energy confirms the above qualitative arguments. The spin polarization vector is taken to be of the form

$$\mathbf{S} = (\mathbf{S}_1 + i\mathbf{S}_2) e^{i\phi} , \tag{5}$$

where ϕ represents the phase factor,[18,20] and $\mathbf{S}_1$ and $\mathbf{S}_2$ are real vectors given by[10]

$$\mathbf{S}_1 = S \cos\beta \hat{\boldsymbol{\rho}}_1, \quad \mathbf{S}_2 = S \sin B \hat{\boldsymbol{\rho}}_2 , \tag{6}$$

where $\hat{\boldsymbol{\rho}}_1 \perp \hat{\boldsymbol{\rho}}_2 \perp \hat{\mathbf{z}}$. Using these expressions in (3), with $\mathbf{H} \| \hat{\boldsymbol{\rho}}_1$, gives a free energy

$$F(S,\beta,m) = A_Q S^2 + \tfrac{1}{2} A_0' m^2 + \tfrac{1}{2} B S^4 + \tfrac{1}{4} B_3 m^4 + B_5 m^2 S^2 - mH + 2(B_4 m^2 - B_2 S^2) S^2 \cos^2\beta + 2B_2 S^4 \cos^4\beta , \tag{7}$$

where $B = 2B_1 + B_2$. Note that there is no ϕ dependence in this expression, which is a consequence of truncating the free energy expansion at s^4. The dominant sixth-order term that determines the equilibrium value of the phase angle is discussed below. In addition to the paramagnetic state $S = 0$ (phase 1), there are three ordered states ($S \neq 0$) which minimize the free energy (7), characterized by the value of β: $\beta = \pi/4$ (at $H = 0$), which describes the helically polarized state (phase 4), $\beta = \pi/2$, which describes the linearly polarized state with $\mathbf{S} \perp \mathbf{H}$ (phase 5), and $\cos^2\beta = \frac{1}{2} - B_4 m^2 / 2B_2 S^2$, which characterizes the elliptically polarized state (phase 7). Transitions between the phases are all second order. The boundaries between phases 1 and 5 and between phases 5 and 7 in the magnetic phase diagram are determined by[10]

$$H_{15} = (-A_Q/B_5)^{1/2} [\Delta' + (1 - B_3/B_5) A_Q] , \tag{8}$$

$$H_{57} = (-A_Q/B_{12})^{1/2} [\Delta' + (1 - B_{13}/B_{12}) A_Q] , \tag{9}$$

where $\Delta' = A_0' - A_Q = a(T_Q - T_0')$, $B_{12} = BB_4/B_2 + B_5$, and $B_{13} = B_3 + 2B_4 B_5 / B_2$.

The case of stronger anisotropy (large $|A_z|$) was considered in Ref. 10 and the resulting phase diagram appears in Fig. 5(a) of that work where an additional elliptical phase 3 is stabilized at high fields and low temperatures. With respect to $CsMnBr_3$, this other phase occurs at a theoretically negative value of the temperature parameter T and only the right-hand side of that phase dia-

gram is applicable.

A magnetic field applied parallel to the c axis ($H_{\parallel}$) does not distort the helical phase 4 and there is a second-order transition to the paramagnetic phase where $S \rightarrow 0$.[10] The full $(H_{\parallel}, H_{\perp}, T)$ phase diagram is shown schematically in Fig. 2 and demonstrates that the 1-4 phase boundary actually represents a line of multicritical points where phases 1, 4, 5, and 7 intersect.

A numerical fit of expressions (8) and (9) to the data of Ref. 5 was performed as follows, where results are expressed in cgs units (with the magnetization given in electromagnetic units per gram). The susceptibility in the paramagnetic phase associated with a field $\mathbf{H} \perp \hat{\mathbf{c}}$ is given by $(\chi_0')^{-1} = a(T - T_0')$ and may be compared with corresponding data[20] to obtain the estimates $a \cong 82$ and $T_0' \cong -250$ K so that $\Delta' \cong 2.1 \times 10^4$ (using $T_Q = 8.3$ K). This leaves two parameters for each phase boundary curve to be fit to the data: B_3 and B_5 for H_{15}, and B_{12} and B_{13} for H_{57}. Using the data at 6, 7, 8.6, and 8.9 K yields the estimates $B_3 \cong 1350$, $B_5 \cong -22$, $B_{12} \cong 21$, and $B_{13} \cong -345$. These results are consistent with having B_1, B_2, and $B_4 > 0$ and are the same order of magnitude as found in the case of $CsNiCl_3$.[15] Note that since $B_5 < 0$, the critical temperature of the 1-5 phase boundary is enhanced by the magnetic field.[15] The lines drawn in Fig. 1 are the result of the above fitting procedure and demonstrate that the theory presented here is, in the very least, consistent with the experimental data. Expressions (8) and (9) are strictly valid only in a regime where S and m are small (F is expanded only to fourth order in $\mathbf{s}$, i.e., it is assumed that $CS^6 \ll BS^4$) so that discrepancy between theory and experiment may be expected at low temperatures or high field values.

Further analysis of the free energy reveals additional information on the structure of the spin density in the ordered phases. The wave vector $\mathbf{Q}$, which minimizes F for hexagonal systems like $CsMnBr_3$, was shown in Ref. 14 to be $\mathbf{Q} = \pm (4\pi/3a)\hat{\mathbf{a}} + (\pi/c)\hat{\mathbf{c}}$ as a result of antiferromagnetic interchain and intrachain exchange-type interactions. This result may also be expressed as $\mathbf{Q} = \frac{1}{3}\mathbf{G}_{\perp} + \frac{1}{2}\mathbf{G}_{\parallel}$, where $\mathbf{G}$ is a reciprocal lattice vector and $\parallel$ and $\perp$ refer to parallel and perpendicular to the c axis. This shows explicitly the period-3 basal-plane and period-2 c-axis modulations. Note that these results refer to the simple hexagonal lattice of Mn ions where the c axis is one-half the length of the corresponding c axis of the crystallographic unit cell, which contains two chemical formula units.

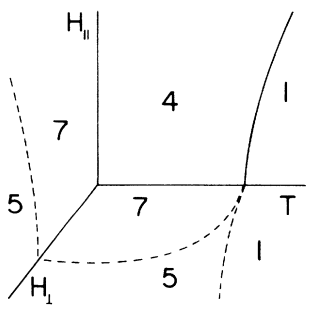

FIG. 2. Schematic magnetic phase diagram where $\mathbf{H}_{\parallel} \| \hat{\mathbf{c}}$ and $\mathbf{H}_{\perp} \perp \hat{\mathbf{c}}$. Phases 1, 5, and 7 exist in the three-dimensional space $(H_{\parallel}, H_{\perp}, T)$, whereas phase 4 is stabilized only in the $H_{\perp} = 0$ plane. The 1-4 phase boundary represents a line of multicritical points.

Expressions for the three sublattice magnetizations $\mathbf{s}_a$, $\mathbf{s}_b$, and $\mathbf{s}_c$ in the basal plane at sites $\mathbf{R}_{\perp} = 0$, $\mathbf{a}$, and $2\mathbf{a}$, respectively, can then be obtained from the spin density (1) written as

$$\mathbf{s} = \mathbf{m} + 2S[\cos\beta\cos(\phi + \mathbf{Q}\cdot\mathbf{R})\hat{\rho}_1 - \sin\beta\sin(\phi + \mathbf{Q}\cdot\mathbf{R})\hat{\rho}_2], \quad (10)$$

where (2), (5), and (6) have been used. The dominant term in the free energy which determines the phase angle ϕ is sixth order in $\mathbf{s}$ and is due to exchange effects:[18]

$$F_{c1} = C_1[(\mathbf{S}\cdot\mathbf{S})^3 + (\mathbf{S}^*\cdot\mathbf{S}^*)^3]. \quad (11)$$

Using expressions (5) and (6) for $\mathbf{S}$ then gives the result

$$F_{c1} = 2C_1 S^6 \cos^3 2\beta \cos 6\phi. \quad (12)$$

For the helical state at $H = 0$ where $\beta = \pi/4$, $F_{c1} = 0$, and the phase angle is determined by small sixth-order planar anisotropy effects.[18] For the elliptical phase where $\pi/4 < \beta < \pi/2$ and for the linear phase where $\beta = \pi/2$, ϕ is determined by the sign of C_1 where $C_1 > 0$ gives $\phi = m\pi/3$ and $C_1 < 0$ gives $\phi = (2m+1)\pi/6$. Consider, for example, the contribution to the spin structure of the linear phase 5 due to long-range order (proportional to S) as determined by (10). For the case $\phi = \pi/6$, the three sublattice magnetizations are given by $\mathbf{s}_a = -S\hat{\rho}_2$, $\mathbf{s}_b = 2S\hat{\rho}_2$, and $\mathbf{s}_c = -S\hat{\rho}_2$, which are consistent with a preliminary interpretation of the neutron-diffraction data by Gaulin *et al.* The other possibility, $\phi = 0$, yields $s_a = 0$, $\mathbf{s}_b = 3^{1/2}S\hat{\rho}_2$, and $\mathbf{s}_c = -3^{1/2}S\hat{\rho}_2$ so that one-third of the Mn^{2+} chains do not participate in the long-range order. It is of interest to note that a harmonic of the fundamental modulation with a wave vector $\mathbf{Q}_2 = \frac{1}{2}\mathbf{G}_{\parallel}$ is also predicted by Landau theory[18,20] where, for $\beta = \pi/2$, $\mathbf{S}_2 \sim S^3 \sin 3\phi\hat{\rho}_2$. (Additional harmonics are induced by anisotropy effects.[13,17]) Experimental detection of this component of the spin density in phase 5 would provide convincing evidence that the phase angle is given by $\phi = \pi/6$. The effect of adding this Fourier component to (2) is under investigation.

The symmetry analysis presented here and in Ref. 15 has provided the basis for a recent scaling theory and renormalization-group study[12] of the novel multicritical behavior of $CsMnBr_3$ and $CsNiCl_3$. That work demonstrates the important role of chiral degeneracy[4] and shows that the multicritical points observed in these two systems have critical behavior associated with $n = 2$ and $n = 3$ (respectively) chiral fixed points, in contrast with usual bicritical and tetracritical points.[19,21]

In conclusion, this work has demonstrated that the magnetic phase diagram of $CsMnBr_3$ recently determined by the neutron diffraction results of Gaulin *et al.*[5] can be explained by the analysis of a nonlocal Landau-type free energy[10] and has provided the framework for a more de-

tailed analysis[12] to account for effects due to critical fluctuations. The novel multicritical point at $H=0$, $T=T_N$ was shown to be a consequence of an applied magnetic field breaking the degeneracy of helically and linearly polarized states at the Néel temperature. The results of this work are relevant for all materials with hexagonal crystal symmetry that exhibit helical magnetic order (such as[4] Ho, Dy, Tb, and VX_2, $CsVX_3$ where $X=$Cl, Br, I). It is of interest to determine the magnetic phase diagrams close to the Néel temperature of these related systems.

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