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Intermediate phase in the anisotropic Heisenberg quasi-two-dimensional antiferromagnet $[C_6H_5(CH_2)NH_3]_2CuBr_4$

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The reorientation of sublattice magnetizations from an antiferromagnetic to a spin-flop phase has been studied in the new Heisenberg quasi-two-dimensional antiferromagnet $[C_6H_5(CH_2)NH_3]_2CuBr_4$. Evidence is offered for the existence of an intermediate phase, brought about by competition between separate easy axes for antiferromagnetic (interlayer) and ferromagnetic (intralayer) ordering. Experimentally determined magnetic phase boundaries are compared with predictions of mean-field theory.

Heisenberg antiferromagnets with tetragonal symmetry are known to display a large number of distinct phases under appropriate conditions of temperature and magnetic field. A much-studied subclass, for example, are the spin-flop systems, in which an increasing easy-axis field induces a first-order transition to a state with perpendicular antiferromagnetic ordering, before reaching the high-field regime where the sublattice magnetizations are equal. Mean-field theory, however, has long suggested the additional possibility of an *intermediate phase*, lying between the low-field antiferromagnetic and the spin-flop phases, separated from them by second-order transitions, and with sublattice magnetizations both unequal and unrelated by symmetry.[1-3] Such a phase would originate through the competition between two different easy axes—selected, respectively, by the intrasublattice (ferromagnetic) and intersublattice (antiferromagnetic) exchange interactions. This is to be distinguished from tetracritical systems in which cubic anisotropy is generated by single-ion terms (quartic in the spin components) in the Hamiltonian.

In this paper we report the (possible) observation of an intermediate phase of this type in a layered metallate compound in which nonmagnetic organic cations can produce a large separation between magnetic layers. We report results of a study on a new quasi-two-dimensional antiferromagnet, $[C_6H_5CH_2NH_3]_2CuBr_4$, in which reorientation of the sublattice magnetizations is observed by measurements made with the magnetic field oriented along different crystal axes.

Consider an antiferromagnet with two sublattices (denoted A and B) in the form of alternating layers of exchange-coupled spins-$\frac{1}{2}$, and with the Hamiltonian

$$\begin{aligned} H=&-2\sum_{i,j\in A}\{J_xS_i^xS_j^x+J_yS_i^yS_j^y+J_zS_i^zS_j^z\}\\ &-2\sum_{i,j\in B}\{J_xS_i^xS_j^x+J_yS_i^yS_j^y+J_zS_i^zS_j^z\}\\ &-2\sum_{i\in A,j\in B}\{J_x'S_i^xS_j^x+J_y'S_i^yS_j^y+J_z'S_i^zS_j^z\}\\ &-2\sum_{i\in A,j\in B}\mu_B\mathbf{H}\cdot\{\mathbf{g}_i\cdot\mathbf{S}_i+\mathbf{g}_j\cdot\mathbf{S}_j\} \end{aligned} \quad (1)$$

The intrasublattice exchange constants J_x,J_y,J_z are taken to be positive (ferromagnetic), and the intersublattice constants J_x',J_y',J_z' are negative (antiferromagnetic). We take the x and z axes to be respectively the easy and intermediate axes for antiferromagnetic ordering, so that $|J_x'|>|J_z'|$, $|J_y'|$, as well as $(ZJ_y-Z'J_y')<(ZJ_x-Z'J_x')$, $(ZJ_z-Z'J_z')$, where Z and Z' are intrasublattice and intersublattice coordination numbers.

The mean-field treatment of Eq. (1) has been discussed in detail by others;[1,3] here we simply give a brief summary for the case in which the field is along the x direction. The two sublattice magnetizations lie in the x-z plane. Letting α and β denote the angles between each of these magnetizations and the x axis, the possible phases are (a) paramagnetic (PM), $\alpha=\beta=0$; (b) antiferromagnetic (AF), $\alpha=0$, $\beta=\pi$; (c) spin flop (SF), $\alpha=-\beta\neq0$; and (d) intermediate (IN), $|\alpha|\neq|\beta|$. If $J_z>J_x$, then the direct transition AF→SF is suppressed. If, in addition, the relation $Z(J_x-J_z)-Z'(J_x'-J_z')>0$ is satisfied, then although the stable low-temperature zero-field phase is still AF, the sequence of phases with increasing H_x is AF→IN→SF→PM, all transitions being second order. The zero-temperature critical fields for the AF-IN, IN-SF, and SF-PM transitions are[1]

$$H_{IA}^x=[Z(J_x-J_z)-Z'(J_x'+J_z')]^{1/2}[Z(J_x-J_z)-Z'(J_x'-J_z')]^{1/2}\,, \quad (2)$$

$$H_{SI}^x=[-Z(J_x-J_z)-Z'(J_x'+J_z')][Z(J_x-J_z)-Z'(J_x'-J_z')]^{1/2}[Z(J_x-J_z)-Z'(J_x'+J_z')]^{-1/2}\,, \quad (3)$$

$$H_{PS}^x=-Z(J_x-J_z)-Z'(J_x'+J_z')\,. \quad (4)$$

For nonzero temperature, the results of Ref. 3 may be used.[4]

We have studied a single crystal of $[C_6H_5CH_2NH_3]_2$-$CuBr_4$ in the form of a dark, shiny, nonhygroscopic plate, with approximate dimensions $4.0\times3.5\times0.45$ mm^3. The demagnetization factors are estimated to be $d_c=0.85$ along the c axis (perpendicular to the plate) and $d_{ab}=0.075$ in the plane of the plate.[5] This salt contains antiferrodistortive layers of planar $CuBr_4{}^{2+}$ anions separated by double layers of $C_6H_5CH_2NH_3{}^+$ cations. The Cu^{2+} ions are arranged in tetragonally elongated octahedra; the structure is similar to that[6] of $(C_2H_5$-

$NH_3)_2CuCl_4$. The lattice constants are a:b:c = 10.558: 10.486:63.473 Å. The large interlayer separation ensures only weak magnetic coupling between layers. The magnetic single-ion anisotropies were explored through electron paramagnetic resonance (EPR) linewidth analysis, given $g_\perp = 2.04$ and $g_\parallel = 2.14$.[7]

The M vs H isotherms for the applied field perpendicular to the plate (along the c axis) are shown in Fig. 1(a). No hysteresis was found. For temperatures below about 6 K, the slopes of the curves increase with increasing field, and then abruptly flatten. Figure 1(b) shows typical magnetization isotherms at 4.5 K with the field lying in the ab plane and the crystal rotated in small increments about the c axis. Two extreme kinds of behavior were seen: For the field along the direction labeled y (making an angle of 30° ± 0.5° with the b axis) M is linear in H out to about 1000 Oe. With H along the perpendicular direction, labeled x, M increases first linearly, up to about 200 Oe, and then sigmoidally, passing through a point of nearly divergent slope. The maximum slope of the S-shape portion of the curve is smaller for intermediate field directions, as shown. The field strength, at the threshold for the onset of deviation from linear behavior, decreases with increasing temperature and disappears altogether at around 12.8 K. The rapid increase in M for H along x must correspond to a magnetization reversal for one sublattice: At zero field the antiferromagnetic order is along the x axis, so that the interlayer exchange anisotropy obeys $|J'_x| > |J'_z|, |J'_y|$.

Figure 1(c) shows the dc susceptibility (M/H) in low (50 Oe) field as a function of T, for field along the x, y, and z directions. The large value of χ at low T when the field is along z also indicates antiferromagnetic ordering along a perpendicular direction, while for H along y the moment is small and the critical field is higher [cf. Fig. 1(d)], suggesting that this is indeed the hard axis. The field strength necessary to produce near-parallel ordering of the sublattice magnetizations is much smaller when the field is along z than when it is along y.

The large moment observed along the z direction in Fig. 1(c) also suggests strong ferromagnetic coupling between z components of the spins within the layers. Further, the field necessary to suppress the SF phase is smallest in the z direction. Thus we expect $J_z > J_x, J_y$, so that a direct transition from an AF to an SF phase is excluded,[1] at least within mean-field theory. This is also supported by our measurements of EPR linewidths[7] at liquid-nitrogen temperature: $\Delta H_c = 80.5 \pm 2.5$ G, $\Delta H_a = \Delta H_b = 72.0$

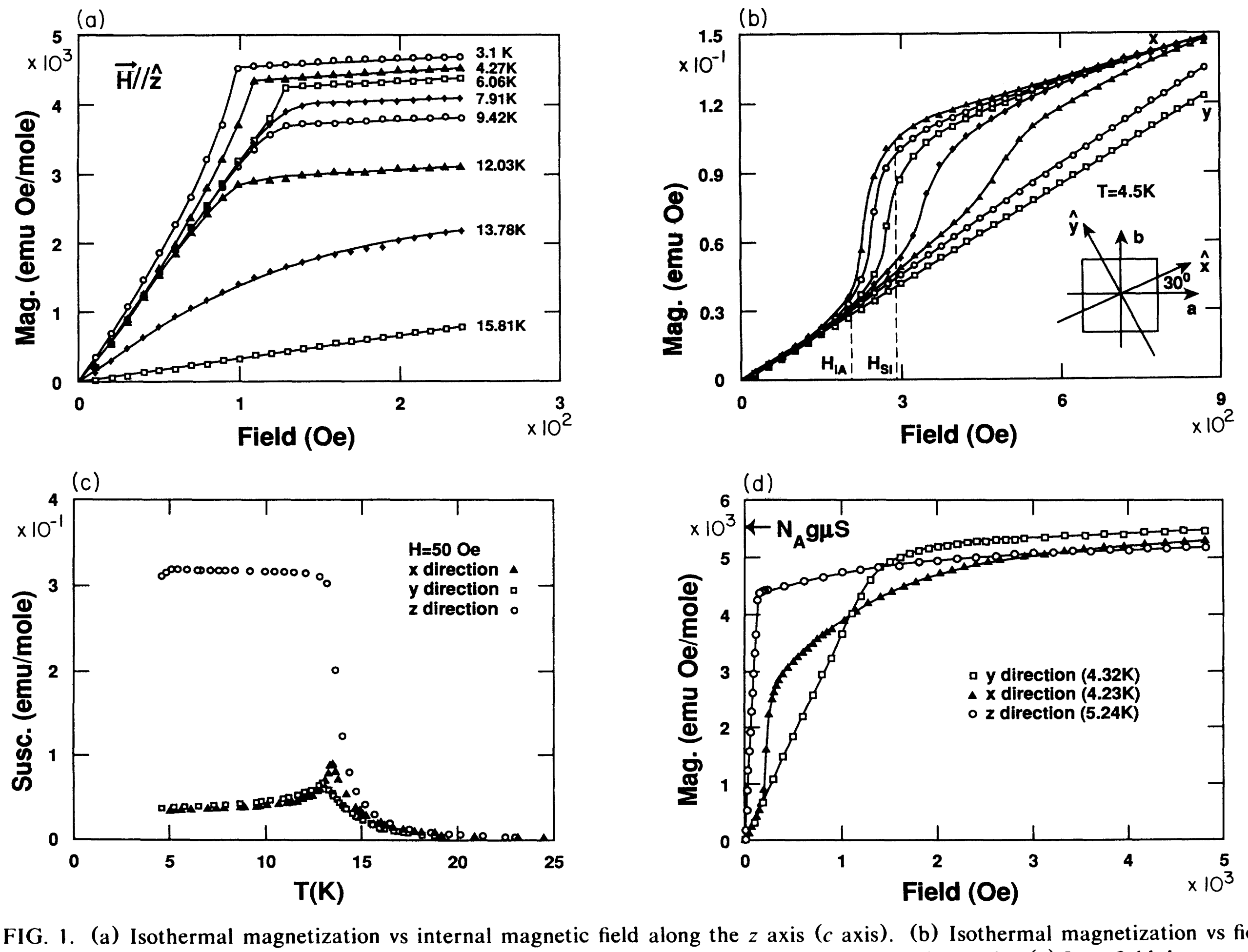

FIG. 1. (a) Isothermal magnetization vs internal magnetic field along the z axis (c axis). (b) Isothermal magnetization vs field parallel to the surface of the plate (ab plane), along directions rotated by 15° increments about the c axis. (c) Low-field dc susceptibility vs temperature along the spin principal axes. (d) Isothermal magnetization vs field along the spin principal axes.

± 2.5 G. We therefore suggest that the sigmoidal portion of the magnetization isotherms, for H along the x axis, indicate the presence of intermediate phase.

To determine T_c more precisely we measured the zero-field differential susceptibility χ_p of a powdered sample with a mutual inductance bridge and a superconducting quantum interference device as flux detector. The transition temperature was located by finding the point of maximum positive slope of the $T\chi_{\parallel}$ vs T curve,[8] and we assume $\chi_{\parallel}$ is the dominant contribution to the slope of the powder susceptibility since the perpendicular components can be taken as constant for $T \leq T_c$. In this manner we estimate $T_c = 12.81 \pm 0.05$ K. In the temperature range 30–200 K we fitted these χ_p data to a high-temperature series expansion for the three-dimensional Heisenberg model on an eclipsed lattice, finding $J = 25.0$ K and $|J'| < 0.1$ K.

In a high field directed along the y axis, the magnetization [Fig. 1(d)] becomes nearly independent of field and close to full saturation (its $T=0$ value), namely $N_A \mu_B g S = 5.718 \times 10^3$ emu Oe/mole with $g = 2.14$ and $S = \frac{1}{2}$. One might expect that the magnetization for H along z should also approach full saturation; however, Fig. 1(d) shows that in this case M is measurably smaller than for H along y. Therefore the moments for large H_z must be canted away from z, and similarly for the case of H along x. Furthermore, the smooth rounding of the isotherm indicates the absence of a sharp SF-PM transition when H is along x. Spin canting of this type could be ascribable either to inequivalent local environments (local magnetic symmetry axes) for spins, or to the presence of an intraplanar antisymmetric (Dzyaloshinskii-Moriya) exchange interaction of the form $\mathbf{D} \cdot (\mathbf{S}_i \times \mathbf{S}_j)$, with $\mathbf{D}$ largely in the y direction. That is, for H directed along z or x, we find a quasiparamagnetic phase,[9] in which the sublattice magnetizations are not quite equal, rather than a true paramagnetic region.

The S-shaped isotherms of Fig. 1(b) are the most singular result of our measurements. It is tempting to interpret this behavior as a simple spin-flop transition in which the usual discontinuity in magnetization appears as a linear regime with rounding of its low- and high-field limits either because of (1) demagnetization effects[10] (domain formation) or (2) a misalignment between H and the easy axis (giving a smeared first-order AF-SF transition). However, we suggest that neither of these explanations is plausible: (1) A correction for the demagnetization effect for the field in the plane of the plate is less than 1%, and the maximum field range for such a transition can be calculated[11] as $\Delta H_{\max} = 4\pi\chi_{\perp} H_{SA}^x < 10$ Oe, which is much less than the broad transition range observed in Fig. 1(b); (2) to smear a first-order AF-SF transition, the misalignment of the field with the easy (x) axis would have to exceed a critical angle, corresponding to the edge of the first-order spin-flop shelf. In this case the discontinuous character of the transition would disappear and the staggered magnetization would rotate continuously toward the intermediate (or hard) axis.[9,12,13] However, using our values for the exchange couplings in this system (see below) we estimate the critical misalignment angle to be about 11°, which provides a substantial margin for error. Furthermore, mean-field calculations show that there would be, in this case, a common inflection point in the isotherms for different field directions.[9,12,13]. Our results show no such feature.

Thus our data do not permit an interpretation in terms of the usual spin-flop transition. An interpretation in terms of an IN phase *is* possible since mean-field theory indeed predicts a linear increase in M_x with field at $T=0$,[1] and this feature would be preserved, together with a rounding of the isotherms at the high- and low-field extremities for $T > 0$. Figure 2(a) shows the temperature-versus-field phase diagram for H along x. The open and solid circles represent, respectively, the lower and upper inflection points of $\partial M/\partial H$ computed along the isotherms, and are denoted as H_{IA} and H_{SI} in Fig. 1(b). The critical fields at zero temperature were obtained by extrapolating the phase lines of Figs. 2(a) and 2(b): $H_{IA}^x \sim 200$ Oe, $H_{SI}^x \sim 280$ Oe, and $H_{PS}^x \sim 110$ Oe. The exchange couplings can then be obtained from Eqs. (2)–(4) and the relation $T_c = ZJ_x - Z'J_x'$. We estimate $J_x = 25.45$ K, $J_x' = -0.17$ K, $J_z = 25.49$ K, and $J_z' = -0.07$ K.

The stability limits of the AF, IN, and SF phases plot-

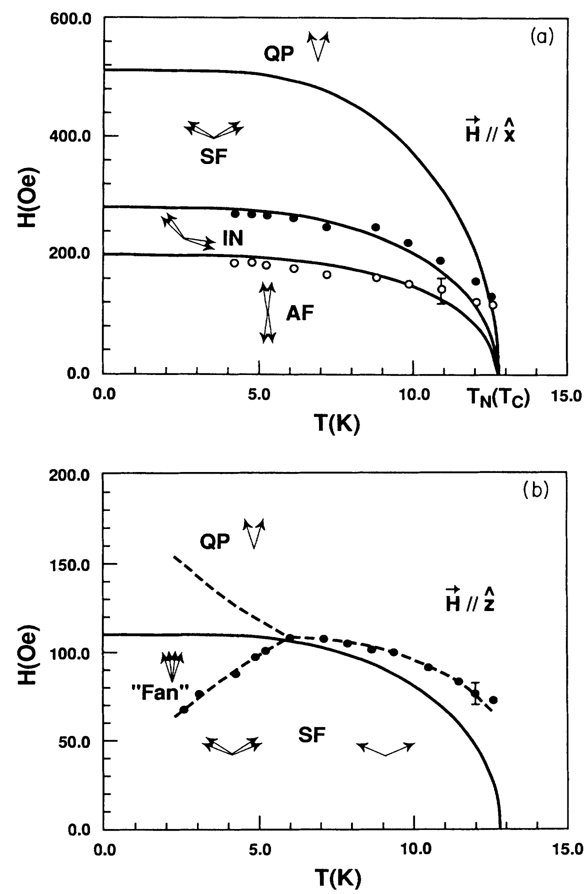

FIG. 2. (a) Phase diagram for magnetic field along the z axis. The solid line is the PM-SF transition line as calculated from mean-field theory, with exchange constants as given in the text. (b) Phase diagram for magnetic field along the x axis. The dots are SF-IN and IN-AF phase boundaries, as estimated from magnetization isotherms. The solid lines are the same transitions as calculated from mean-field theory.

ted as solid lines in Fig. 2(a) were calculated by the mean-field methods of Ref. 1 using the exchange constants given above. The lines meet the T axis at almost the same point owing to the near balance of the quantities $(ZJ_x - Z'J_x')$ and $(ZJ_z - Z'J_z')$. They are in reasonable agreement with the experimental AF-IN and IN-SF phase-transition lines at temperatures below about 10 K. The lack of agreement above this temperature is likely due to the neglect of fluctuations in mean-field theory. For H along x no sharp transition out of the SF phase is seen, probably owing to spin canting as discussed above. The data forming the IN-AF and IN-SF lines appear to be merging into a tetracritical point (at a field near 160 Oe) where the phases induced by competing easy axes could become simultaneously critical.

Our phase diagram for H in the z direction is shown in Fig. 2(b). For T less than about 6 K the critical fields (solid circles) for the transition from the spin flop to the paramagnetic (or quasiparamagnetic) phase are taken to be the points at which the magnetization isotherms of Fig. 1(a) abruptly flatten. The phase boundary of $H_c(T)$ of Fig. 2(b) is an increasing function of temperature in this regime. On thermodynamic grounds this second-order line should eventually approach the H axis with zero slope,[14] but at the lowest temperatures investigated here no hint of such behavior is seen. The stability limit for the SF phase, as calculated from mean-field theory (without antisymmetric interaction) clearly fails to reproduce the sloping phase boundary.

Although the differential isothermal susceptibility is clearly discontinuous on the transition line [cf. Fig. 1(a)] below about 6 K, at higher temperatures the sharp anomaly in the magnetization isotherms disappears and we indicate as the critical field the value where the susceptibility begins its drop to zero. $H_c(T)$ has a maximum at approximately the point at which this change in behavior takes place. We have no definitive information on the source of this feature, but speculate that the transition above 6 K could be to the quasiparamagnetic phase with spins nearly in the z direction but neighboring spins in the same layer held slightly apart in the zx plane by canting due to D_y. In this state the sublattices are identically configured. Below 6 K, on the other hand, the transition may be to a different "fan" phase whose net sublattice magnetizations are still in a spin-flop configuration in the zx plane, but where canting within each sublattice is governed by a D_x weaker than D_y. That is, the transition to the fan phase might involve a sudden twisting of the canting plane between pairs of neighboring spins within each sublattice. Future work will involve constant field scans, to see whether a fan-PM transition line, indicated speculatively in Fig. 2(b), can be observed.

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