Theory of Adiabatic Nuclear Magnetic Ordering in Cu

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The phase diagram for the nuclear magnetic ordering of Cu in a magnetic field is theoretically found to exhibit three distinct phases in accordance with recent measurements. It is a consequence of the frustrated ground-state properties of an antiferromagnetic fcc structure with nearest-neighbor Heisenberg and dipolar interactions, a model also of relevance for the resonating-valence-bond problem. The adiabatic process is discussed, and nonadiabaticity caused by off-diagonal spin-spin interactions in the ordered, canted phase is found to be in accordance with the experimental value.

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Magnetic ordering of the nuclear spins for Cu has been observed below 60 nK, with the use of susceptibility measurements.[1] Recent neutron-scattering measurements[2] have confirmed this and revealed that the structure is a simple type-I antiferromagnet. There are, however, three distinct phases as a function of an external field, with very different static susceptibilities and neutron-scattering intensities. This has not previously been understood and it is the purpose here to clarify this and also discuss what happens during the adiabatic demagnetization process. The problem is that of a frustrated antiferromagnetic ground state and is therefore closely related to the resonating-valence-bond problem,[3] which is currently much discussed in connection with the high-T_c superconductors. The nuclear Cu system is an ideal model system and may be of considerable relevance for a closer understanding of such ground-state problems.

Copper has a fcc lattice structure and the nuclei of Cu have spin $I=\frac{3}{2}$. These interact via the dipolar interaction and the Ruderman-Kittel[4] interaction, which is dominant, as calculated from first principles.[5] Furthermore, the nearest-neighbor (nn) interaction is dominant by an order of magnitude.[5] The interactions give rise to, in the mean-field theory, a simple type-I antiferromagnetic (AFM) structure. Since all nn bonds form triangles the system is very frustrated and the AFM structure is in simple theories infinitely degenerate with respect to linear combinations of ordering vectors $\mathbf{k}_a=(\pi/a)\hat{\boldsymbol{\alpha}}$, where $\hat{\boldsymbol{\alpha}}$ is a unit vector along the cubic directions x, y, and z; a is the lattice constant. The dipolar interaction requires only that the spins are perpendicular to the $\mathbf{k}_a$ vector. In a field the general structure is then described by any of the degenerate 1-**k**, 2-**k**, or 3-**k** linear combinations (denoted by I, II, or III). By unpolarized neutron scattering, or any other linear method, it is not possible to distinguish between the multi-**k** structures or a multidomain single-**k** structure. I shall now demonstrate that nonlinear effects indeed lift the degeneracies and stabilize different phases as observed experimentally. The phases are distinct because of different quantum-mechanical ground-state correlations. Indeed, correlation effects play a significant role in Cu. Thus the ordering temperature T_N is reduced to $0.25T_N$ (mean field) when correlation effects are included.[5]

Consider a nearest-neighbor fcc antiferromagnet with nn Heisenberg interactions J and dipolar interactions D per bond in an external field H:

$$\mathcal{H}=\tfrac{1}{2}\sum_{a,b}\{J\mathbf{I}_a\cdot\mathbf{I}_b+D[\mathbf{I}_a\cdot\mathbf{I}_b-3(\mathbf{I}_a\cdot\hat{\mathbf{r}})(\mathbf{I}_b\cdot\hat{\mathbf{r}})]\}-H\sum_a I_a^z, \tag{1}$$

where a and b represent sums over the four sublattices in the fcc structure, see Fig. 1, and $\hat{\mathbf{r}}$ is the interconnecting unit vector. If we assume the same moments M for the four spins at $a=1$, 2, 3, and 4, the mean-field Hamiltonians are

$$\mathcal{H}_{\mathrm{MF}}^{\mathrm{para}}=-6J'M^2-\sum_a(H-3J'M)I_a^z,$$
$$\mathcal{H}_{\mathrm{MF}}^{\mathrm{AFM}}=2J'M^2-(2J')^{-1}H^2-J'M\sum_a I_a^{z'}, \tag{2}$$

where z' denotes the local quantization axis along the local canted moments, $J'=4J+D$. For structures I and II, $H=4J'M\sin\theta$, and for structure III, $H=2J'M(1+\sin\theta)$.

Let us define the population factor $p=\exp(-\beta J'M)$;

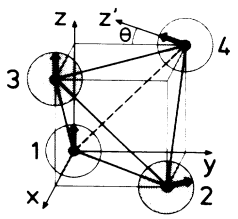

FIG. 1. Three-dimensional representation of a 3-**k** structure III for the fcc lattice indicating the four sublattices. Various structures can be distinguished by their different projections onto the x-y plane; see Fig. 3.

for $H > 4J'M$, $p = \exp[-\beta(H - 3J'M)]$, the average magnetic moment $M = (3 + p - p^2 - 3p^3)/2Z$, and the reduced partition function $Z = 1 + p + p^2 + p^3$, $\beta = 1/kT$ and k the Boltzmann constant. The free energy per spin is

$$F^{\text{para}} = -\tfrac{3}{2}J'M(M+1) - kT\ln Z - \tfrac{3}{2}H',$$
$$F^{\text{AFM}} = -\tfrac{3}{2}J'M(M+1) - kT\ln Z - MH' - (8J')^{-1}H'^2, \quad (3)$$

where $H' = H - 4J'M$. The entropy assumes the form $S/k = \beta J'M(\frac{3}{2} - M) + \ln Z$. At the critical field $H_c = 4J'M$ there is a second-order phase boundary. The resulting phase diagram is shown in Fig. 2. The structures I, II, and III are degenerate for all fields $H < 4J'M$, within the mean-field theory. This was the result previously found.[1] However, for $kT > kT_0 = 0.95$ one finds that with unequal sublattice moments structure III is favorable. This stabilizes III against I and II for $T > T_0$ even within the mean-field theory. Furthermore the phase transition to the paramagnetic phase is now of first order.

By an ideal adiabatic cooling process, the system is made to start out in an equilibrium state at a given temperature in a high magnetic field H.[6] If H is decreased rapidly compared with the spin-lattice relaxation time, no heat dQ is exchanged with the lattice, which implies that the entropy must be constant, since $dQ = T\,dS = 0$.

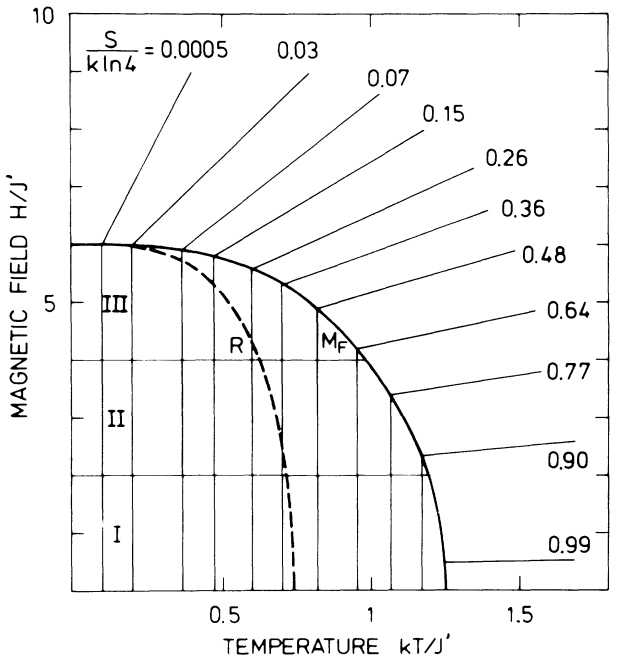

FIG. 2. The calculated mean-field phase diagram (MF) including isentrops (thin lines). The thin horizontal lines indicate approximately the phase separation between the structures I, II, and III according to Fig. 3. The phase line R represents the fluctuation-reduced phase line. It has been made to coincide with one experimental (H,S) transition (Ref. 1). All other observations (Ref. 1) are then in good agreement with the predicted phase diagram R. Full lines indicate second-order transitions and dashed lines, expected first-order transitions.

The energy levels of $\mathcal{H}_{\text{MF}}^{\text{para}}$, Eq. (2), are equidistant with a separation $H - 3J'M$. If kT decreases as $H - 3J'M$, it follows that the population factor p is constant as well as the entropy S/k. The isentrop in a (T,H) plot is thus simply a straight line through $H = 3J'M$. The slope is determined by the initial polarization M, which is also constant. At the phase boundary to the AFM structure, the field is replaced by the constant internal field $J'M$. The isentrops are therefore independent of field in the ordered phase, within mean-field theory. The isentrops are indicated by thin lines in Fig. 2, and the entropy is normalized by the maximum entropy $S_{\max} = k\ln(2I+1) = k\ln 4$. Experimentally one finds, however, two distinct crossings of phase lines in the ordered phase, when following a constant-entropy curve. This is incompatible with the above results of the mean-field theory.

Let us now consider the effect of off-diagonal terms in the Hamiltonian (1). In the paramagnetic phase the dipole part includes terms of the kind $I_a^z I_b^+$ and $I_a^z I_b^-$, which create or destroy spin flips on site b. The effect of this can be evaluated by perturbation theory. The effect of the dipolar single-flip terms is to make the isentrops deviate from the straight lines in Fig. 2 by a bending to lower fields when approaching the phase boundary. The effect is relatively small and is not important qualitatively. Dipolar terms of the kind $I_a^+ I_b^+$ and $I_a^- I_b^-$ have a similar effect, but are even less important. However, in the AFM phase both the isotropic and dipolar parts develop effective anisotropic interaction terms when viewed from the local, canted coordinate systems; see Fig. 1. For example, the isotropic interaction Hamiltonian has the form, for relatively canted spins, $\mathcal{H}_{\text{int}} = J[I_a^x I_b^x - \cos(2\theta) I_a^{y'} I_b^{y'}]$. This Hamiltonian can both move a spin flip from site to site, and simultaneously flip two adjacent spins against the local molecular fields. The latter process is similar to local crystal-field transitions and should be included before considering the former, low-energy spin-wave-type excitations which do not contribute at $T = 0$. Two important features can now be noted: (a) The interactions bring in a field dependence of the thermodynamic quantities in the ordered region, where there was none in the mean-field theory, and (b) the structures I, II, and III differ qualitatively because of the different relative cantings. The pair interactions can therefore determine the phase diagram and distinguish between the various structures I, II, and III.

Let us evaluate the effect of two-spin-flip terms $(I_a^+ I_b^+ + I_a^- I_b^-)$ using second-order perturbation theory for a cluster of the four sublattice spins; see Fig. 1. The

ground state with energy 0, say, has a wave function $|0\rangle = |I_1, I_2, I_3, I_4\rangle$ with the maximum moment $I_a = \frac{3}{2}$ along the local fields of strength $J'M$ and direction z_a'. This state is coupled to states with energy $2J'M$ having two spins flipped and wave functions of the type $|2\rangle = |I_1 - 1, I_2 - 1, I_3, I_4\rangle$, and various permutations. There is no coupling to the one-spin-flipped cluster states $|1\rangle$ at energy $J'M$. Second-order perturbation theory shifts the cluster levels of energies $(0, J'M, 2J', M)$ by $(-\Delta_n, 0, +\Delta_n)$, where n = I, II, or III. The lowest three levels therefore remain equidistant so that the relative population of the levels remains unchanged at a given temperature. The perturbed wave functions are of course mixed. The state n with the largest Δ_n is the ground state; Δ_n is found to be of the order of 10% of $J'M$. The cluster calculation is similar in spirit to Anderson's randomly distributed singlet-cluster theory.[3] All possible 1-**k** and 2-**k** structures and the 3-**k** structures III of the type shown on Fig. 1 were investigated. It was found that only the structures with the spin projections in the high symmetry directions in the x-y plane are relevant. The relative stability of the four-sublattice, simple type-I antiferromagnetic multi-**k** structures are shown on the phase diagram Fig. 3. At $H = 0$ the results agree with a recent spin-wave calculation[7]; however, there the 3-**k** structure III was not investigated. The strength of the Ruderman-Kittel interaction[4] in Cu is measured by a quantity R defined in Ref. 1. From first-principles calculations[5] one finds $R = -0.34$. Using this value gives, for Cu, $3D/J' = 0.9$ in Fig. 3, and I predict a transition between the I, II, and III structures as a function of the magnetic field along (001). The experimental value[1] for Cu is $R = -0.42$, yielding $3D/J' = 0.8$. For this value the stable phase for intermediate fields fluctuates between the 2-**k** and 3-**k** structures. For the field along the (101) direction one finds a simpler phase diagram involving a smooth transition at $H \sim 0.3H_c$ between two high-symmetry 1-**k** phases. An incommensurate ΓK phase will penetrate from higher D values along this phase separation line. This may be the reason for the observed low neutron-scattering intensity for intermediate fields.[2] The conclusion is that for a relevant range of R values the magnetic structure of Cu is predicted to show at least three phases as a function of magnetic field. This is in agreement with the experimental results.[1,2]

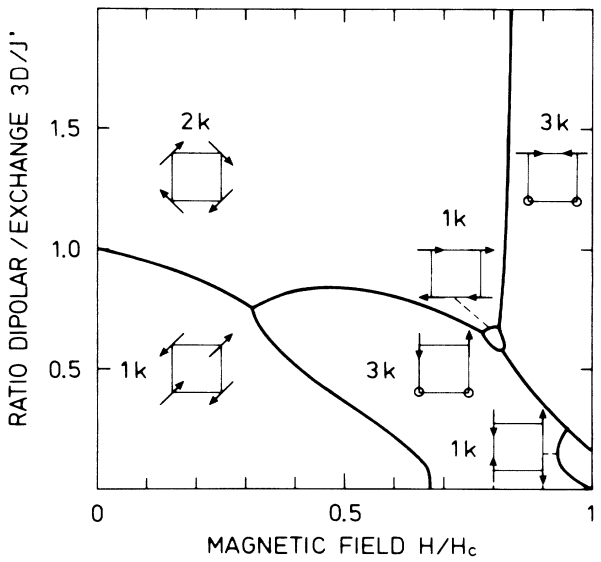

FIG. 3. The calculated regions of stability at $T = 0$ of various multi-**k** structures as a function of field along (001) and the relative strength of the dipolar and exchange interaction indicated by $3D/J'$. For Cu the latter is between 0.9 and 0.8. For fields along the (101) direction there is a smooth transition between two 1-**k** structures at $H \sim 0.3J'$. For $3D/J' > 1.1$ a mean-field calculation (Ref. 5) shows that an incommensurate structure with ordering vector along ΓK is more stable than the type-I AFM structures considered here. Quantum fluctuations will make the ΓK phase penetrate to lower D values along the phase separation lines. The various structures are depicted by their projections onto the x-y plane; see Fig. 1.

For finite T the effect of spin-wave excitation terms $I_a^+ I_b^-$ in all phases I, II, and III is to lower the transition temperature T_N relative to the mean-field value $T_N(\mathrm{MF})$. However, from a recent Monte Carlo computer simulation study on a two-dimensional model system for Cu,[8] it was found that, although the phase separation line to the paramagnetic phase was much reduced in temperature, the entropy $S(T)$ versus temperature remained quite accurately the same as calculated by the mean-field theory and the isentrops were not reduced significantly in temperature. It is therefore expected that the fluctuation-reduced phase boundary approximately follows a temperature-renormalized curve, marked R in Fig. 2, as the true phase boundary to the paramagnetic state. The arguments given above for the relative stability of the structures I, II, and III should remain valid since they are based on the angular variation of the moments, but not the temperature. From renormalization-group theory[9] it has been argued that at $H = 0$ the phase transition is a fluctuation-induced first-order transition, and it was shown above that the transition to phase III is of first order at high T. The phase diagram R is in very good agreement with that found experimentally by Huiku *et al.*[1] In fact, if the theoretical phase line is adjusted to match the experimental phase transition found at one field H and entropy S, all other experimentally found transitions coincide with the theoretical phase diagram.

The off-diagonal terms give rise to a field dependence of the entropy. Taking into account the perturbation of the cluster levels, one can find the perturbed population factors p and expand to first order in Δ_n. The constant-entropy lines are then bent to higher temperatures for $H \to 0$. The shift is proportional to $\int \Delta_n(H) dH$, yielding $k\Delta T = 0.1J'$ at $H = 0$ and $kT/J' > 0.3$. Consider now a slow demagnetization process which permits the system

to attain thermodynamic equilibrium, followed by a fast switch-on of a large magnetic field. At increasing fields it is not possible to decrease the temperature (increase the magnetization) corresponding to the mixing effect of the off-diagonal terms. If we assume instead a simple canting of the moments with the $H=0$ values, the isentrop follows the vertical, mean-field isentrop until it reaches the phase boundary. The entropy increase then corresponds, from Fig. 2, to $0.1/k$ ln4. The calculated entropy increase is in agreement with the nonadiabatic entropy increase $0.12/k$ ln4 found experimentally.[1]

The magnetic phase diagram for Cu has been discussed with use of a simple model. It is concluded that the nearest-neighbor antiferromagnetic fcc lattice with Heisenberg and dipolar interactions exhibits several distinct multi-**k** ground states as a function of a magnetic field. A similar behavior was previously found[10] for a simple linear antiferromagnet at intermediate fields. There it was found that the antiferromagnetic short-range ordered structure was further modified by a long-wavelength modulation. It is likely that such a behavior can also occur for the fcc intermediate-field case. Nonadiabaticity caused by off-diagonal spin-spin interactions was also discussed and estimated to be of the same order of magnitude as found experimentally. Finally, it is emphasized that the simple model has general applicability, for example, also to the resonating-valence-bond problem.

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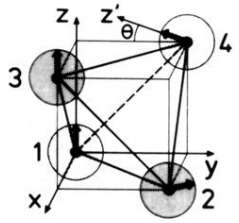

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