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Spin-Density-Wave Fluctuations in Copper Nuclear Spins

P. Kumar[a] and M. T. Loponen[b]
Low Temperature Laboratory, Helsinki University of Technology, SF-02150 Espoo 15, Finland

and

L. H. Kjäldman
Department of Technical Physics, Helsinki University of Technology, SF-02150 Espoo 15, Finland

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A spherical-model calculation of the spin-density-wave fluctuations in copper nuclear spins is presented. The results are compared with an experiment where copper nuclear spins have been cooled to below 0.1 μK. The agreement, with no adjustable parameters, is found to be satisfactory for spin susceptibility, entropy, and internal energy. A considerable depression of the transition temperature from its mean-field value, in qualitative agreement with the experiments, is also found.

The thermodynamic properties of nuclear spins cooled to temperatures of the order of tenths of a microkelvin become interesting for two reasons.[1] On the one hand, the spin-spin interaction energy becomes comparable to temperature and one might expect the nuclear spins to undergo a phase transition into an ordered state. Such a condensed state would be the lowest-energy many-body state reached so far. On the other hand, since the interaction between nuclear spins is known, one expects their thermodynamic properties to be predictable. In other words, these systems become "ideal systems" on which theoretical techniques can be examined for thier quantitative accuracy.

Copper nuclear spins interact via the magnetic dipole-dipole interaction and via the conduction-electron-mediated Ruderman-Kittel (RK)[2] exchange interaction. Whereas the former interaction is overall ferromagnetic, the latter is oscillatory and in copper, overall antiferromagnetic. The resulting ground-state spin arrangement has been studied by Kjälman and Krukijärvi[3] for varying strength of the exchange interaction. For the strength appropriate for copper, they find a spin-density wave (SDW) state. This paper is an account of the thermodynamic effects of the SDW fluctuations. We calculate the susceptibility, the entropy, and the internal energy of the copper nuclear spins. We also discuss the depression of the transition temperature caused by the same fluctuations. The calculations have been done within the spherical model[4] which is known to be exact for a large coordination number[5] or a large number of the components of the order parameter.[6] Copper nuclear spins interact with

long-range forces (practically infinite coordination number) and are expected to condense into an $n=4$ state.[3] To our knowledge, this calculation is the first test of the spherical model on a real system.

The experimental results were obtained by Ehnholm *et al.*[7] In their double nuclear-demagnetization cryostat, copper nuclear spins were cooled to a temperature of about 0.10 μK. No transition was seen. However, large fluctuation effects were observed. The magnetic susceptibility follows a Curie-Weiss-Néel form down to 0.25 μK. At lower temperatures it begins to saturate. The high-temperature behavior yields a Curie-Weiss Θ of 0.15 μK, which is somewhat smaller than the value of about 0.24 μK deduced from NMR measurements.[8] The nuclear-spin entropy decreases by 40% over a temperature range 0.1–1.0 μK. The internal energy of the system decreases even more rapidly over the same temperature range. In this paper, we present an explanation of these results in terms of SDW fluctuations.

The Hamiltonian we use consists of the Zeeman term and the two interactions between nuclear spins; the magnetic dipole-dipole and the RK exchange interactions. The space dependence of the latter has been taken to be of the free-electron form and its strength in copper has been taken from the measurements of Ekström *et al.*[8] The numbers are different only by small amounts from the earlier measurements of Andrew, Carolan, and Randall.[9] In the units of the gyromagnetic ratio $\hbar\gamma=1$,

$$H=-\sum_{\substack{ij\\ \mu\nu}} S_\mu{}^i G_{\mu\nu}{}^{ij} S_\nu{}^j-\sum_{i\mu} S_\mu{}^i H_\mu, \tag{1}$$

where

$$G_{\mu\nu}{}^{ij}=-\frac{1}{2r_{ij}{}^3}\left\{[1+2k_F r_{ij} f(2k_F r_{ij})]\delta_{\mu\nu}-\frac{3(r_{ij})_\mu (r_{ij})_\nu}{r_{ij}{}^2}\right\}, \tag{2}$$

$$f(x)=\cos x-\sin x/x, \tag{3}$$

$r_{ij}=r_i-r_j$, and k_F in the Fermi wave vector. The Greek subscripts refer to the spin components, the index i runs over the lattice vector $\vec{r}_i$, and $\vec{H}$ is the external field. In the spherical model, the partition function $Z=\int D[S]\exp(-H/k_BT)$ is calculated by inserting, as a delta function, the requirement $\sum_i S_i{}^2=NS(S+1)$. The measure of the functional integral $D[S]$ is usually taken to be the $3N$-dimensional unit volume. Strictly speaking it should be fixed in such a way as to give the correct high-temperature (free-spins) limit of the entropy. After going through these, and other manipulations, the final results can be written[4,10] for the free energy F (in zero magnetic field), the internal energy E, the entropy S, and the susceptibility χ ($\beta=1/k_BT$):

$$-\beta F=\ln(2S+1)+\beta S(S+1)(t_0-t_0{}^\infty)-I, \tag{4}$$

$$\beta E=\tfrac{3}{2}[1-t_0/t_0{}^\infty], \tag{5}$$

$$S=k_B[\ln(2S+1)-I], \tag{6}$$

$$\chi^{-1}=2[t_0 1-\lambda(q=0)], \tag{7}$$

$$I=\frac{1}{2N}\sum_{q\mu}\ln\frac{t_0-\lambda_q{}^\mu}{t_0{}^\infty}, \tag{8}$$

where $\lambda_q{}^\mu$ are the $3N$ eigenvalues of the matrix G_{ij}. In real space, the matrix can be diagonalized by Fourier transformation. In spin space, the diagonalization has to be carried out explicitly. The temperature-dependent function t_0 is a solution of the equation

$$\beta S(S+1)=(1/2N)\sum_{q\mu}(t_0-\lambda_q{}^\mu)^{-1}. \tag{9}$$

In the high-temperature limit $t_0>>\max(\lambda_q{}^\mu)$ it becomes $t_0{}^\infty=3k_BT/2S(S+1)$.

The eigenvalues $\lambda_q{}^\mu$ have been calculated for 512 discrete values in the first Brillouin zone using the tabulated dipolar sums of Cohen and Keffer.[11] The exchange constant, as mentioned earlier, has been taken from the measurements of Ekström *et al.*[8] The calculations involve no adjustable parameters.

In Fig. (1) we show the results for the temperature dependence of the magnetic susceptibility χ. The fluctuations affect χ via the Curie constant which can be studied separately by subtracting the zero-temperature intercept of χ^{-1} vs T and comparing it with the theoretical results for t_0. The calculations clearly show the low-temperature curvature in χ^{-1} caused by fluctuations. In spherical-model calculations, the presence of a phase transition is indicated by saturation of t_0 at the largest eigenvalue [T approaches T_c in Eq. (9) when $t_0=\lambda_{\max}$]. In our calculations, perhaps because of the finite grid of points used in the evaluation of the k-space integrals, t_0 approaches $\lambda_{\max}$ only at $T=0$. However, the temperature dependence consists of three distinct regions. At high temperatures $\partial t_0/\partial T$ approahces a constant value, the inverse of the Curie constant. It decreases rapidly near a characteristic temperature but does not reach zero; rather

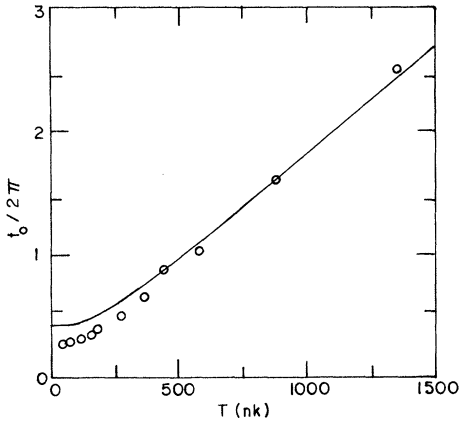

FIG. 1. The magnetic susceptibility of copper nuclear spins [the function $t_0(T)$, see Eq. (7)]. Circles, experimental data from Ref. 7. Solid line, spherical model.

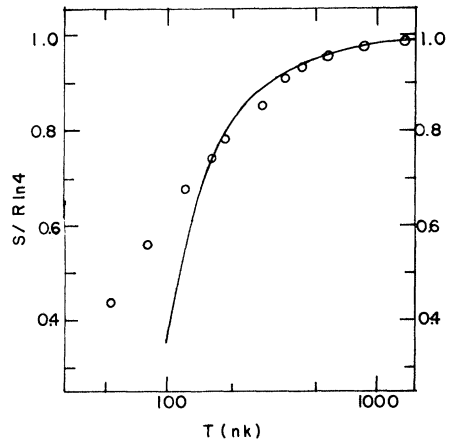

FIG. 2. The entropy vs temperature diagram of the copper nuclear spins. Circles, data from Ref. 7. Solid line, spherical model.

the actual decrease happens smoothly. If the last slow decrease is a result of numerical uncertainties, we can extrapolate the intermediate $\partial t_0/\partial T$ to zero yielding a measure of T_c. Other less precise measures of T_c yield the same value. We have determined T_c for different values of J. The resulting dependence on J roughly amounts to a constant shift of 0.135 μK from the mean field T_c leading to a T_c of 0.1 μK for copper nuclei ($2k_F J = 2.8$). While the lowest temperatures reached so far are a little lower than this value, the experiments cannot rule out the possibility of a phase transition at these temperatures. The estimated T_c at $J=0$ is found to be 0.045 μK.[12] It decreases with increasing J until $2k_F J = 1$ ($T_c = 0.01$ μK) and then begins to increase rapidly.

The $T_c(J)$ dependence can be further studied in terms of the fluctuation density of states $N(\lambda)$ where

$$\beta S(S+1) = \tfrac{1}{2}\int d\lambda [N(\lambda)/t_0 - \lambda];$$
$$N(\lambda) = (1/N)\sum_{q\mu} \delta(\lambda - \lambda_q{}^{\mu}). \qquad (10)$$

The transition temperature β_c is determined by $t_0 = \lambda_{max}$. This requires[10] the $N(\lambda)$ to approach λ_{max} as $(\lambda - \lambda_{max})^{\delta}$ with $\delta > 0$. Within the accuracy of our calculations, this condition is satisfied. However, if the system chose a different ground state, the result would not appear in the spherical model. The eigenvalues (or the eigenfunctions) that determine the ground-state spin configuration are the same as those used in mean-field calculations. For each value of J, we have the same ground state as the one obtained in Ref. 3, only T_c has changed.

In Fig. 2, we display the temperature dependence of the nuclear spin entropy. Again the role of fluctuations in reducing the spin entropy is brought out semiquantitatively by the calculations. Finally, in Fig. 3, we show a third measure of the temperature dependence of this calculation the internal energy as a function of entropy. The results differ widely from the mean-field theory and are in much better agreement with the experiments.

For temperatures below $T_c = 0.10$ μK, the calculations have to be done differently because of the presence of the ordered spin state. In the dis-

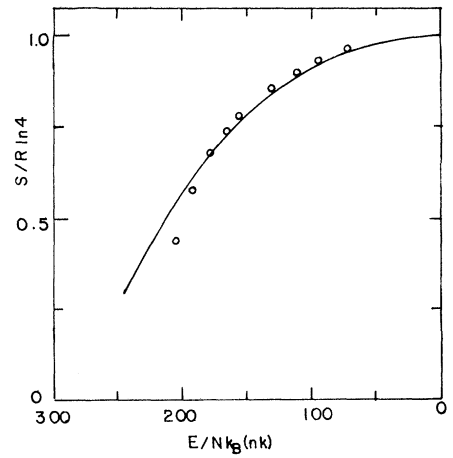

FIG. 3. The entropy vs energy diagram of the copper nuclear spins. Circles, calculated from the data of Ref. 7. Solid line, spherical model.

ordered state, in the absence of any adjustable parameters, the agreement is satisfactory. There are small quantitative differences for $T < 0.15$ μK. The experimental susceptibility while following the predicted saturation, appears a little higher. The spin entropy apparently settles into a $(\ln T)$-type temperature dependence. Another possible source of fluctuations is the presence of the two isotopes ^{63}Cu and ^{65}Cu (abundance ratio of 7:3) with different gyromagnetic ratios (difference of ~7%). In a cubic lattice, the dipolar field is zero only for a uniform environment. The spatially isotope distribution corresponds to a random magnetic field. We plan to study this effect later in some detail.[13]

In conclusion, metallic copper nuclei, at low temperatures, become the first example of the nuclear spin-density waves.

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[a]Present address: Department of Physics, University of Florida, Gainesville, Fla. 32611.

[b]Present address: Bell Laboratories, Murray Hill, N. J. 07974.

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Extended Appearance-Potential Fine-Structure Analysis: Oxygen on Al(100)

M. L. den Boer,[a] T. L. Einstein,[b] W. T. Elam,[c] Robert L. Park, and L. D. Roelofs
Department of Physics and Astronomy, University of Maryland, College Park, Maryland 20742

and

G. E. Laramore
Department of Radiation Oncology, University of Washington, Seattle, Washington 98195

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To measure O-Al separation at Al(100) surfaces disordered (low-energy electron-diffraction beams extinguished) by reaction with oxygen, the extended appearance-potential fine structure was analyzed above the threshold for electron-bombardment excitation of the O 1*s* core. Calculation shows that the outgoing electron has angular momentum $l = 0$, allowing simple Fourier inversion of the fine structure. The separation, 1.98 ± 0.05 Å, suggests that oxygen lies under the top layer, a result undetectable in extended-x-ray-absorption fine-structure measurements on thicker films.

The reaction of a (100) single-crystal aluminum surface with oxygen suppresses completely the low-energy electron-diffraction (LEED) pattern, once oxygen coverages exceed roughly a monolayer.[1] This loss of long-range order renders techniques such as LEED and ion backscattering incapable, even in principle, of determining the oxygen-metal distance. In a recent paper, however, Stöhr, Denley, and Perfetti[2] demonstrated that surface extended x-ray absorption

