PHYSICAL REVIEW B VOLUME 49, NUMBER 21 1 JUNE 1994-I

Calculation of nuclear-spin entropy in silver and rhodium at positive and negative temperatures using Monte Carlo simulations

P. J. Hakonen
Low Temperature Laboratory, Helsinki University of Technology, 02150 Espoo, Finland
(Received 4 January 1994)

A cluster of four rhodium or silver spins interacting with their nearest and next-nearest neighbors is investigated. Randomly generated spin configurations are employed to calculate the density of states $N(E)$ and the entropy $S(E)\propto \ln N(E)$. The second law of thermodynamics, $T=dE/dS$, allows the determination of the entropy as a function of temperature. As in recent experimental data, the calculated $S(T)$ is bigger for positive than for negative spin temperatures.

Magnetic ordering of nuclear spins has been investigated in copper, silver, and rhodium during the past decade.[1] Recently, these studies of nuclear magnetism have been extended to negative spin temperatures as well.[2,3] The basic difference between positive and negative temperatures is that the system maximizes its energy at $T<0$ instead of minimizing it as usual. This leads to ferromagnetic ordering in antiferromagnetic systems as observed in silver.[2]

In recent experiments on rhodium,[3,4] nuclear-spin-lattice relaxation was found to be slower at $T<0$ than at $T>0$. This observation was attributed to a change in the magnetic scattering rate owing to the large negative susceptibility of the nuclear spins.[4] These results could, however, be explained with intrinsic properties of Rh if the nuclear specific heat $c_{T>0}$ at positive temperatures would be larger than $c_{T<0}$ by a temperature-dependent factor up to 2. Experiments indicate, however, that an opposite inequality, $c_{T>0}<c_{T<0}$, is valid. The purpose of this paper is to examine the relationship between these two specific heats theoretically.

In copper, where the Ruderman-Kittel exchange and the dipolar interactions are of comparable size, the spin entropy has been calculated with several series-expansion methods, and good agreement between experimental and theoretical results has been found.[5] Since the nearest-neighbor Ruderman-Kittel interaction dominates strongly in silver, the high-temperature series expansions for the Heisenberg model[6] can be employed in the determination of entropy in this metal. However, problems in evaluating the series expansion arise in silver because the transition temperature $T_c=560$ pK is much lower than the magnitude of the Curie-Weiss parameter $\theta=-4.5$ nK, and because the series expansions converge very slowly when $T\lesssim|\theta|$. The spin system of rhodium has, when compared with silver, the additional problem[3] that the next-nearest-neighbor exchange force is of comparable magnitude as the nearest-neighbor interaction. This complicates the evaluation of series expansion and renders the application of Monte Carlo simulations a more attractive starting point for calculations.

Monte Carlo simulations require a large amount of computing time if the specific heat $c(T)$ is calculated directly.[7] In this paper, I use a microcanonical scheme for Monte Carlo simulations and derive the entropy of the rhodium or silver spins both at positive and negative temperatures. The main idea is that randomly generated spin configurations can be employed to calculate the density of states $N(E)$, which then yields the classical entropy according to the equation

$$S_N=k_B\ln N(E)\ , \tag{1}$$

where k_B is the Boltzmann constant. The connection between entropy and energy in Eq. (1) can, in turn, be employed to calculate the temperature using the thermodynamic identity

$$T=dE/dS\ . \tag{2}$$

Thus, $S(T)$ is obtained by plotting the logarithm of the density of states as a function of its inverse derivative.

The spin-spin interactions in rhodium and silver are approximated by the Hamiltonian

$$H=-\sum_{\mathrm{NN}}J_{\mathrm{NN}}\mathbf{S}_i\cdot\mathbf{S}_j-\sum_{\mathrm{NNN}}J_{\mathrm{NNN}}\mathbf{S}_i\cdot\mathbf{S}_j\ , \tag{3}$$

where only the isotropic nearest- (J_{NN}) and the next-nearest-neighbor (J_{NNN}) exchange interactions have been included; anisotropic forces, which may play a role in rhodium, have been omitted. Table I lists the values of J_{NN} and J_{NNN} employed in the calculations for these two metals. The value of J_{NN} in silver was taken from the experiments of Poitrenaud and Winter,[8] while J_{NNN} was fixed using the ratio $J_{\mathrm{NNN}}/J_{\mathrm{NN}}=0.12$, obtained from the band-structure calculations of Harmon, Wang, and Lindgård.[9] For rhodium, both values were taken from the experimental results of Ref. 3.

As in the calculations of Lindgård,[10] a basic unit of four nuclear spins was investigated in this work. This is

TABLE I. Parameters for nearest- (J_{NN}) and next-nearest-neighbor (J_{NNN}) interactions employed in the Monte Carlo simulations.

	Silver	Rhodium
J_{NN}	-26.5 Hz	-17 Hz
J_{NNN}	$+4$ Hz	$+10$ Hz

sufficient to bring up the inherent frustration of antiferromagnetic nearest-neighbor (NN) interactions in an fcc lattice; at negative temperatures frustration vanishes when ferromagnetic structure is preferred.[2] In order to take into account all of the NN- and NNN- interactions of the four spins, a total of 40 spin sites are needed in the simulation.

The density of states was calculated by repeatedly evaluating the energy of randomly generated spin configurations. The energies were grouped into small intervals (of the total of 4800 about 2000 were in use effectively) and their rate of occurrence was summed up. The resulting density of states after 1.34×10^8 cycles is depicted in Fig. 1 for rhodium; the quantity shown is $\ln N(E)$, where E is the energy of the basic unit divided by four. According to Eq. (1), Fig. 1 illustrates also a quantity proportional to the entropy of the spin system $S(E)$. The curve is clearly asymmetric with respect to $E=0$, which reflects the fact that frustration of the antiferromagnetic interactions limits the spread of energies at positive temperatures. In the case of silver, the calculated density of states (after 0.33×10^8 cycles) is even more asymmetric.

The calculations were performed on a PC-486 (66 MHz) using compilable QuickBasic (Microsoft, version 4.5). There were slight problems with the poor quality of the random number generator but it seemed to work fine up to statistical accuracies of $\Delta N/N\approx1\%$. This limit was reached after one week of computing and was considered sufficient. The quality of the results with this accuracy, however, is not good enough to try to locate the critical entropy for the expected first-order magnetic transition which would be detected as a plateau in dS/dE.

The entropy for a classical system, given by Eq. (1), is determined only within a constant and, therefore, only differences of entropies are meaningful. Since both silver and rhodium have spin-$\frac{1}{2}$, the densities of states have been scaled so that the resulting entropy curves $S(E)$ are normalized to a maximum of $R\ln2$ where R is the gas constant. Only small differences from $R\ln2$ were investigated which means that only a fraction of the calculated density of states is relevant.

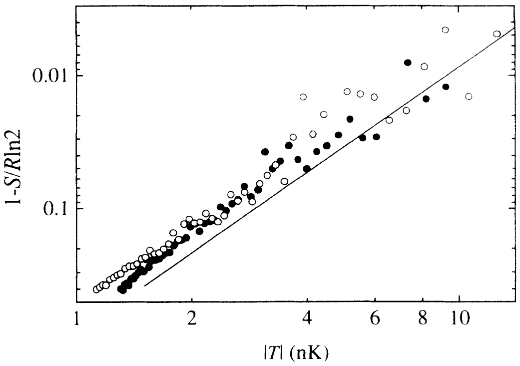

FIG. 2. Reduced entropy $1-S(T)/R\ln2$ as a function of the absolute value of spin temperature $|T|$ for rhodium. Open and filled symbols correspond to $T>0$ and $T<0$, respectively. The solid line gives the leading $1/T^2$ term of the high-temperature entropy expansion.

Temperature was obtained from $S(E)$ according to Eq. (2). Owing to statistical noise, the calculation was performed by fitting a sixth-order polynomial to $S(E)$ in the range $(0.5-1.0)\ S_{\max}$, and the temperatures were calculated from the polynomial for each value of the energy. Note that the left side of the curve in Fig. 1 yields $T>0$, while the right side, with $dS/dE<0$, corresponds to negative temperatures.

Figures 2 and 3 display the calculated entropies, $1-S(T)/R\ln2$, for rhodium and silver over the range $(0.6-1.0)\ S_{\max}$. For comparison, we have included the leading term of the high-temperature entropy expansion, $C(B_{\text{loc}}/T)^2/2\mu_0$ (per molar volume), which agrees with the calculated points unexpectedly well considering the approximate nature of the theoretical scheme (especially the neglect of quantum effects for $S=\frac{1}{2}$). Here the Curie constant $C=1.3$ and 2.0 nK for rhodium and silver, while the local internal field $B_{\text{loc}}=34$ and 35 μT, respectively. The values of the local fields contain small contributions from nuclear dipolar moments which have not been taken into account in the simulations.

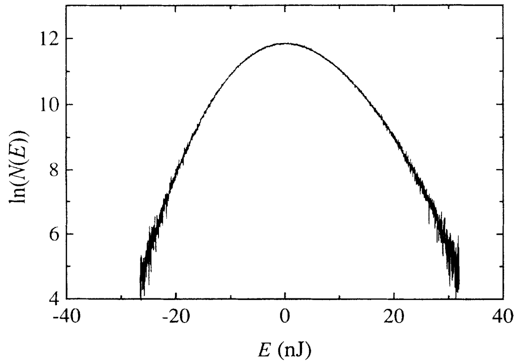

FIG. 1. Logarithm of the calculated density of states $N(E)$ for rhodium; the energy scale is per one mole. The left side of the curve yields $T>0$, while the right-hand side, with $dS/dE<0$, corresponds to negative temperatures.

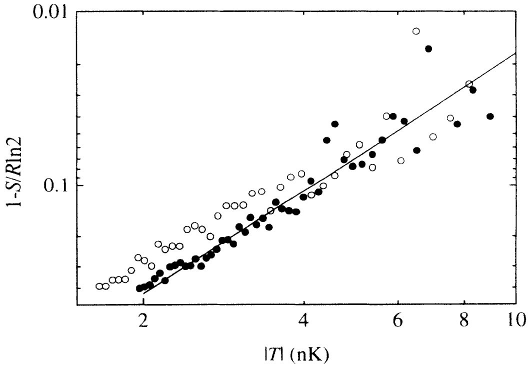

FIG. 3. Reduced entropy $1-S(T)/R\ln2$ vs $|T|$ for silver. Open and filled symbols correspond to $T>0$ and $T<0$, respectively. The solid line displays the leading $1/T^2$ term of the high-T series expansions.

The calculated entropy curves at $T > 0$ for both silver and rhodium in Figs. 2 and 3 are higher than the curves obtained at $T < 0$. This is consistent with recent experimental results[4] on rhodium which indicate that $c_{T>0} < c_{T<0}$. In silver, where the calculated difference in entropy between $T > 0$ and $T < 0$ is larger, the experimental data on $S(T)$ (Ref. 11) are, unfortunately, not good enough to allow any quantitative comparisons.

In rhodium, the experimentally measured susceptibility[9] indicates antiferromagnetic tendency both at $T > 0$ and $T < 0$. This means that the values for the interaction coefficients between rhodium nuclei, leading to ferromagnetic ordering at $T < 0$ according to molecular field calculations,[12] do have some uncertainty. If the antiferromagnetic nature were "stronger" at $T < 0$ than at $T > 0$ then it would become possible that $c_{T>0} > c_{T<0}$. This, however, would require quite large modifications in the experimentally determined interaction parameters.

In conclusion, I have presented a simple method to calculate the approximate entropies of nuclear-spin systems at ultralow temperatures. The procedure inherently yields $S(T)$ at positive and negative temperatures and, therefore, is suited for investigations of the observed differences between $T < 0$ and $T > 0$.[2–4] By using the experimentally determined interaction coefficients between nuclei, I find that the specific heat for rhodium is larger at $T < 0$ than at $T > 0$, in accordance with recent experimental results.[3,4]

Useful discussions and comments by J. Kurkijärvi, O. V. Lounasmaa, and A. S. Oja are gratefully acknowledged. This work was financially supported by the Academy of Finland.

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