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Exchange Interactions and Fluctuations in CeB_6 †

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We report measurements of the low-temperature specific heat of CeB_6 and discuss their significance in the light of earlier studies of this compound. The large specific heat above the antiferromagnetic ordering at 2.31 K is interpreted with the aid of a decorated Ising model. This model permits us to combine exchange and crystal field interactions in a simplified, but exact, calculation of the thermodynamic properties of a magnetic system including the effects of fluctuations. The analysis gives independent support to the proposal by Nickerson and White that the exchange in the crystal field excited state is substantially stronger than the ground-state exchange in CeB_6. We also comment on the possibility of extending such an analysis to other magnetic rare-earth hexaborides.

I. INTRODUCTION

Cerium hexaboride is a metal with an antiferromagnetic transition at 2.3 K. The trivalent Ce ions are in the $4f^1$ configuration, resulting in a $^2F_{5/2}$ ground state, which is further split by a cubic crystal field into a (ground-state) doublet Γ_7 and a quartet Γ_8. With but a single $4f$ electron and a well-known crystal field spectrum, CeB_6 should thus be the simplest of the magnetic rare-earth hexaborides.

The magnetic susceptibility of CeB_6 has been measured a number of times, with consistent results[1,2]: The magnetic susceptibility follows a Curie-Weiss law with a free-ion slope down to 150 K, and rises above the extrapolated Curie-Weiss value below. Nickerson and White[3,4] have given a theoretical interpretation of the magnetic susceptibility. Hull[5] has measured the isothermal magnetization from 1.74 to 7 K, and Fisk obtained the resistivity from 2 to 300 K.[2] The firmest evidence for a Γ_7 crystal field ground-state assignment is in the isothermal magnetization measurements.[5] At the lowest temperature and highest field (60 kOe), the magnetization curve is rather flat and has a value of 0.74 μ_B/atom, in good agreement with the 0.71 μ_B/atom expected from a well-isolated Γ_7 doublet.[6]

We present measurements of the specific heat of CeB_6 from 1 to 22 K and discuss its significance in the context of the earlier work on this compound. Our data were analyzed using a decorated Ising model; the general form of such models has been discussed by Fisher.[7,8] Within this framework we find strong support for the proposal by Nickerson and White[3] that the exchange interactions in the ground and excited states are of different magnitudes, with the excited-state exchange being considerably stronger. The extension of such an analysis to other rare-earth hexaborides, however, is more problematical. We discuss the difficulties further below.

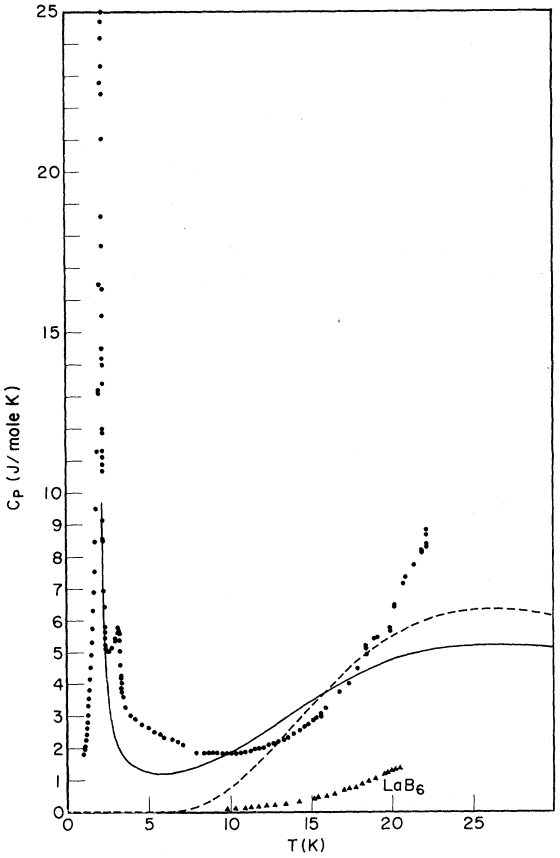

FIG. 1. Specific heat of CeB_6. Broken curve: Schottky anomaly with $\Delta = 70$ K, no exchange; solid curve: fit to the decorated Ising model, $J_7 = 1.39$ K, $J_8 = 12.5$ K, $\Delta = 70$ K.

II. SPECIFIC HEAT

Data were taken using new techniques for measuring heat capacities of small samples. These methods are described elsewhere.[9] The sample was a 24-mg slice cut from an arc-melted ball which had been remelted more than twenty times in an effort to grow large crystallites. Laue x-ray–back-reflection photographs showed that crystallites as large as 1 mm had indeed been grown. Our specific-heat data show, however, that this was something of a Pyrrhic victory, since the sample had also picked up some second-phase contamination.

The data were taken by the heat-pulse method; a few points were also measured by the step method.[9] Data from the two techniques agreed with each other and with earlier data taken (by the step method) on a 54-mg chip of CeB_6 used in a previous investigation[5] (supplied by Hull, Jr. of the Bell Telephone Laboratories). Despite its small size, the sample heat capacity far outweighed that of all the addenda, and no correction for the latter was applied. The scatter in our data (Fig. 1) is typically 2%, and we estimate an absolute accuracy of 5%. The slight oscillation near 15 K is attributed to error in the temperature calibration.

The first striking feature of our data is the presence of two ordering peaks. The higher-temperature one at 3.3 K contains only 5% of the entropy of the large peak at 2.31 K, if one makes a smooth extrapolation of the background due to the large peak. Magnetic-susceptibility measurements at liquid-helium temperatures show a broad peak at 2.4 K, with a shoulder—but no second peak—at about 3.3 K. From the weakness of the magnetic signal and the small entropy enclosed by the satellite peak, we attribute it to a second cerium compound. This interpretation is supported by a microprobe analysis[10] which gives a 6% signal for boron-deficient regions.

Next, consider the total entropy. According to Nickerson and White,[3] the Γ_7 doublet lies about 320 K lower than the Γ_8.[11] We expect, then, an entropy of $R\ln 2$ to be released by the magnetic transition. In accord with this expectation, the entropy under the large peak is $R\ln 2$. The difficulty is in the large specific heat above the ordering peak. By 20 K, in fact, the total entropy is more than $R\ln 4$, only a small part of which can be attributed to the lattice. (Figure 1 also shows the specific heat of LaB_6, to indicate the size of the lattice and conduction-electron contributions.)

The excess specific heat can be interpreted in a number of ways. To begin with, it might be nonmagnetic. Following the procedure of Robinson and Friedberg,[12] we plot the specific-heat data as CT^2 vs T^5 to extract a cubic coefficient which can then be associated with the lattice. Between 11 and 22 K we do indeed find a cubic temperature dependence, corresponding to a Debye temperature $\Theta_D = 135$ K. Both the low value of Θ_D and the high temperature to which the T^3 behavior persists ($0.2\Theta_D$) make an interpretation in terms of phonons rather unlikely. In addition, the magnetic entropy is then approximately $R\ln 3$, requiring a triplet ground state, which is impossible for the $^2F_{5/2}$ configuration. We regard the T^3 behavior as accidental.

Second, one might take the ground state to be the quartet Γ_8. The magnetization measurements[5] show a saturation moment of about 0.7 μ_B, quite far from the 1.57 μ_B expected for the Γ_8; we may regard this possibility as ruled out.

Last, the excess specific heat might be due to fluctuations induced by the excited state, taking Γ_7 to be the ground state. Nickerson and White[3] fitted the magnetic susceptibility data and found a crystal field splitting of 320 K, making this interpretation impossible, too. We have, however, found it possible to reanalyze the susceptibility to give a crystal field splitting of 70 K, a value which al-

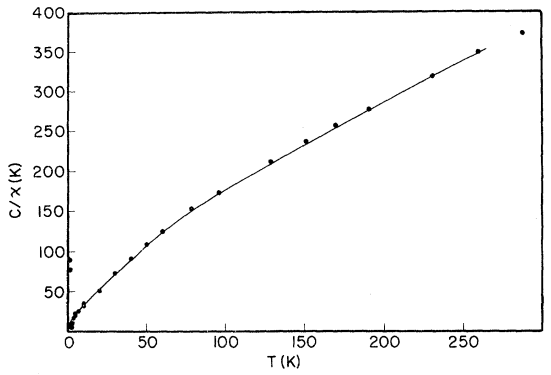

FIG. 2. Inverse magnetic susceptibility of CeB_6. Data from Refs. 2 and 5. Solid curve is the fit described in the text.

lows us to make a qualitative fit to the specific-heat data, as shown by the solid line in Fig. 1. We shall discuss this calculation further below.

III. MAGNETIC SUSCEPTIBILITY

Because of the simplicity of the two-level structure, the crystal-field-only magnetic suceptibility of the $J=\frac{5}{2}$ manifold may be calculated analytically[13]:

$$\chi=(C/T)f(\Delta/T),$$
$$f(x)=(1+2e^{-x})^{-1}[\tfrac{5}{21}+26e^{-x/2}+32(1-e^{-x})/21x], \tag{1}$$

where Δ is the crystal field splitting, defined to be positive when the ground state is the Γ_7. When we introduce exchange in the molecular field approximation, we find

$$C/\chi=T/f(\Delta/T)-\Theta_p\,. \tag{2}$$

The curve of χ^{-1} vs T is simply shifted rigidly by Θ_p. The enhanced magnetic susceptibility of CeB_6 thus cannot be accounted for in this form of the molecular field approximation.

Nickerson and White pointed out that there is no reason to believe that the exchange coupling is the same for the two crystal field levels[3]: The rare-earth hexaborides are thought to be indirect-exchange magnets,[2] and the overlap between conduction-electron and ion wave functions is manifestly different because of the different spatial distributions of ionic charge in the two crystal field levels. They combined this physical insight with the full form of the Heisenberg Hamiltonian

$$\mathcal{H}=\mathcal{J}\textstyle\sum_i(\vec{s}_0\cdot\vec{s}_i+\frac{1}{4}) \tag{3}$$

in the molecular field approximation to obtain a fit to the data on CeB_6 (Fig. 2).

Nickerson and White argued that it was important to retain the constant term $\frac{1}{4}$ in the Heisenberg Hamiltonian, because the exchange differed in the two crystal field levels. In second-quantized form, the constant term becomes proportional to the square of the number operator for the excited state.[14] The presence of this population-dependent term makes the effective crystal field level separation dependent upon the population of the upper level. Using their fitted parameters,[3] we find an effective crystal field splitting of about 700 K at room temperature. With this large a separation, it is hard to see how the slope of the magnetic susceptibility could be the free-ion slope, except by accident. In addition, at low temperatures, the specific heat would not rise to the values we have observed.

On theoretical grounds, moreover, the use of the $\frac{1}{4}$ term in the Heisenberg Hamiltonian seem dubious. In spirit, the Nickerson-White model is a physical approximation to the higher-order exchange Hamiltonian described by Birgeneau *et al.*[15] As Birgeneau *et al.* note, however, the orbital degrees of freedom lead to the possibility of, e.g., off-diagonal exchange. These complications may be expressed by rewriting Eq. (3), including an orbital operator equivalent similar to the well-known operator equivalents of crystal field theory. When the orbital operator is expanded, the constant term is inextricably mixed in with the spin-dependent ones. Thus, it is far from obvious that the constant term has the value $\frac{1}{4}$, nor is it clear that this is the salient term to extract from the expansion.

In the face of these uncertainties, we deemed it worthwhile to adopt a cruder phenomenological procedure. Taking the kernel of the Nickerson-White proposal, we let Θ_p in Eq. (2) be temperature dependent according to

$$\Theta_p=n_7\Theta_7+n_8\Theta_8,\quad n_7=(1+2e^{-\Delta/T})^{-1},\quad n_8=1-n_7\,, \tag{4}$$

where $n_7(n_8)$ is the probability that a given ion is in the $\Gamma_7(\Gamma_8)$ state and Θ_7 and Θ_8 are fitting parameters symbolizing the different exchange interactions of the two levels. This trivially generalized molecular field approximation yields the solid curve in Fig. 2 with $\Delta=70$ K, $\Theta_7=-5$ K, and $\Theta_8=-140$ K. Above liquid-helium temperatures, the curve is quite insensitive to the value chosen for Θ_7. The important result is the much smaller crystal field splitting needed to fit the data.

The question now arises of why CeB_6 does not order at a much higher temperature than observed, since the exchange in the Γ_8 is quite strong. In the molecular field limit, we write

$$T_N=\xi\Theta_p,\quad \xi=-\mathcal{J}(\vec{Q})/\mathcal{J}(0)\,, \tag{5}$$

where $\vec{Q}$ is the wave vector describing the spin arrangement in the ordered phase. In the $J=\frac{5}{2}$ mani-

fold with a Γ_7 ground state, we must have

$$\Theta_8 = 2\Delta/\xi \tag{6}$$

for ordering to occur at a temperature of order Θ_8. For $\xi = 1$, we are at the verge of ordering, with the parameters chosen to fit the magnetic susceptibility. Although crude, this molecular field consideration alerts us to the possibility that CeB_6 might barely miss ordering at some high temperature, and thus that fluctuations and short-range order may be very important.

IV. DECORATED ISING MODELS

The molecular field approximation predicts that the response of a magnetic system to applied fields is different from the no-exchange response at all temperatures. Above the ordering temperature, where there is no long-range order, however, the specific heat in the molecular field approximation is identical to the specific heat in the absence of exchange. In order to calculate a realistic specific-heat curve, then, one needs to include short-range order explicitly. The possibility of a crystal field splitting of 70 K encouraged us to study the influence of short-range order on the Schottky peak shown by the broken line in Fig. 1, since above 10 K the Schottky curve represents the data fairly well. In addition, the simplicity of the $4f^1$ configuration permits the straightforward formulation of a decorated Ising model for simple-cubic cerium lattices such as CeB_6.

Onsager's solution of the two-dimensional Ising problem has stimulated analytic and approximational attacks on the three-dimensional analog, until it is now safe to say that the magnetic Hamiltonian

$$\mathcal{H} = \sum_{\langle i,j \rangle} \mathcal{J}\, s_i^z s_j^z - g\mu_B H \sum_i s_i^z \tag{7}$$

is the best understood of all many-body magnetic models. The spin operators in Eq. (7) are spin $\frac{1}{2}$ operators taking the values ± 1, and the first sum is over all pairs of nearest neighbors.

Moreover, the Ising model can be related to more complex magnetic Hamiltonians, and thus the wealth of knowledge accumulated in the study of the Ising system can be used to shed light on these harder problems. The essential point to be exploited is the simplicity of the diagonal interaction $s_i^z s_j^z$. The joint spin states (s_i^z, s_j^z) can only take the values (+, +), (+, −), (−, +), and (−, −). This restriction to only four states enables one to rewrite the partition function of a complex model system in terms of a modified (or "decorated") Ising partition function. The Ising partition function and the thermodynamic properties derived from it are known as functions of the transformation variables, so that the statistical-mechanical properties of the complex system then become available for study. A further simplification for antiferromagnetic models was discovered by Fisher.[8] For certain kinds of antiferromagnetic coupling, the partition function of the decorated lattice in applied field is related to the partition function of the underlying Ising lattice at zero field. The magnetic susceptibility and magnetization are thus derivable from the zero-field Ising results alone.

A. Decoration

Several kinds of transformations on the Ising lattice have been discovered.[8] We shall discuss here the decoration process schematically illustrated in Fig. 3. The transformation enables one to write the partition function of the total system (ionic and Ising spins) in the form of the partition function of an Ising system with direct bonds between the Ising spins. This technique was apparently discovered by Naya in 1954, used by Syozi and Nakano, and extensively discussed by Fisher[8] in a study of the properties of two-dimensional Ising nets in applied fields.[7]

First, consider the partition function for an Ising-spin system:

$$Z_I = \sum_{\langle s_1, s_2 \rangle} e^{K s_1 s_2 + L_1 s_1 + L_2 s_2}, \tag{8}$$

where

$$K = \mathcal{J}/kT, \quad L_i = \mu_i H/kT. \tag{9}$$

μ_i is the magnetic moment of the ith Ising spin, and the sum is over all nearest-neighbor pairs (s_1, s_2).

Now consider the partition function for an ion interacting with a pair of Ising spins (left-hand side of Fig. 3). The ion energy levels depend on the state of the Ising spins (s_1, s_2), the applied field, and perhaps other variables. We write schematically

$$\begin{aligned} Z_{ION} &= \sum_{s_1, s_2 = \pm 1} \psi_{s_1 s_2}(H), \\ \psi_{s_1 s_2}(H) &= \sum_j e^{-E_j(s_1, s_2, H)/kT}. \end{aligned} \tag{10}$$

We now use the fact that there are only four spin states, and thus only four ψ's for a given applied field. By inspection, the quantities

$$\begin{aligned} f^4 &= \psi_{++}\psi_{--}\psi_{+-}\psi_{-+}, & e^{4K} &= \psi_{++}\psi_{--}/\psi_{+-}\psi_{-+}, \\ e^{4\delta L_1} &= \psi_{++}\psi_{+-}/\psi_{--}\psi_{-+}, & e^{4\delta L_2} &= \psi_{++}\psi_{-+}/\psi_{--}\psi_{+-} \end{aligned} \tag{11}$$

allow us to write

FIG. 3. Decoration transformation.

$$Z_{\mathrm{ION}} = f e^{K s_1 s_2 + \delta L_1 s_1 + \delta L_2 s_2} \tag{12}$$

for each of the four possible spin states.[8] Thus, Z_{ION} is proportional to a term in Eq. (8), if we identify the K's and set

$$L_i = L_0 + \delta L_i = (\mu_0 + \delta \mu_i) H/kT \,, \tag{13}$$

where μ_0 is the undecorated moment of the Ising spin.

With one ion per Ising bond, and N ions in the system, we may now write the total partition function as

$$Z = Z_{\mathrm{ION}}^N = f^N Z_I(K, L) \,, \tag{14}$$

where Z_I is the Ising partition function with exchange coupling $J = kTK$ and magnetic moment $\mu = kKL/H = \mu_0 + \sum_i \delta \mu_1$. The number of Ising spins per ion is determined by the geometry, as we illustrate in Sec. IV B.

We have thus factored the total partition function into a piece f, which depends only on the transformation [Eq. (11)], and an Ising partition function, which depends on the variables K and L, defined by Eq. (11). If we know $Z_I(K, L)$ from, say, a high-temperature series expansion, then we may calculate the thermodynamic quantities from the series.

If there is no exchange, the (E_i) are independent of (s_1, s_2). All the ψ's are equal in this case, and we have $K = \delta L_1 = \delta L_2 = 0$ and (putting $\mu_0 = 0$)

$$Z = f^N \,. \tag{14'}$$

We have now reduced the evaluation of the partition function Z to a pair of discrete problems: (i) We need to find the appropriate underlying Ising lattice, for which we need the appropriate series formulas for the derivatives of Z_I; (ii) we must write a model ion-Ising coupling, in order to find the E_i.

B. Ising Lattice

The magnetic ions in the rare-earth hexaborides form a simple-cubic lattice. The decoration process puts an ion on every bond between Ising spins, and there is a bond between every pair of nearest neighbors in the Ising lattice. Our task, then, is to find an Ising lattice which, when decorated, yields a sc lattice. As Fig. 4 shows, a bcc lattice is the proper starting point. We may check this intuitive guess by computing the number of ions per ionic unit cell: $\frac{1}{8}$ (Ising cell/ionic cell) $\times 2$ (spins/Ising cell) $\times 4$ (bonds/spin) $\times$ (ion bond) $= 1$ ion/ionic cell, the proper number for a sc lattice. Since the primitive vectors of the decorated lattice are those for sc symmetry, we have indeed found the right Ising lattice to decorate. (We have used the fact that each ion corresponds to $\frac{1}{4}$ of an Ising spin. Thus, when there are N ions in the ion lattice, there are $\frac{1}{4}N$ Ising spins in the Ising lattice.)

In general, finding the correct underlying Ising lattice for a given ionic lattice is not easy. The decoration transformation takes a bond, which is associated with a direction in space, and replaces it with a point. The point symmetry of the ions, in consequence, is not necessarily a subgroup of the Ising-lattice point group, as was the case for our sc ion lattice. For example, decorating a sc Ising lattice yields ions which are eightfold coordinated, as in a bcc lattice, but the ion point group is tetrahedral (considering nearest neighbors only).

Having found the proper Ising lattice, we must now look at the magnetic coupling needed to produce antiferromagnetic order. If we alternate the ion-Ising bonds as shown in Fig. 4, we ensure that the ion nearest neighbors will be oppositely oriented at $T = 0$, producing a two-sublattice antiferromagnet. That is, we require that an ion have ferromagnetic (+) coupling to one of its Ising-spin neighbors, antiferromagnetic (−) to the other, in the pattern shown. Reversing the sign of the ion-Ising exchange then leaves the lattice invariant, in contrast to the usual kind of magnetic exchange. This pattern of coupling is the generalization of the model used by Fisher[7] to analyze the two-dimensional Ising net. As Fisher showed, the alternating coupling scheme amounts to assuming that the magnetic moments of the Ising spins are zero; we shall return to this point below in discussing the partition function. In particular, the Ising spins are not coupled to an applied field. It is this feature which permits analysis of the decorated system using only the zero-field properties of the Ising lattice.

C. Partition Function

The E_i are the eigenvalues of the mixed Hamiltonian

$$\mathcal{H} = \mathcal{H}_{\mathrm{CF}} + \mathcal{H}_{\mathrm{ex}} + \mathcal{H}_Z \,, \tag{15}$$

where $\mathcal{H}_{\mathrm{CF}}$ is the crystal field Hamiltonian deduced from some physical model[14]—which may not be related to the Ising-lattice symmetry. $\mathcal{H}_Z$ is the Zeeman Hamiltonian and $\mathcal{H}_{\mathrm{ex}}$ contains the ion-Ising coupling.

A simple form for the exchange energy is the "superexchange" coupling

$$E_{\mathrm{ex}} = \mathcal{J}_{\mathrm{CF}} S^Z (s_1 - s_2) \,, \tag{16}$$

where $\mathcal{J}_{\mathrm{CF}}$ is a coupling parameter which may depend on crystal field level, S^Z is the spin of the ionic crystal field state, and the s_i are the Ising spins. We have explicitly included the alternating coupling needed for antiferromagnetic order. The alternating coupling makes the Ising state $(s_1, s_2) = (-, +)$ the ground state of the system, thus leading

to antiferromagnetic order.

Thus,

$$E_i(s_1, s_2, H) = E_{CF} + \mathcal{J}_{CF} S^Z (s_1 - s_2) - g\mu_B H J_Z \ . \tag{17}$$

The alternating coupling implies that $\psi_{++} = \psi_{--}$, so that $\Delta L_1 = \Delta L_2$ from Eq. (11). If we set $\mu_0 = 0$ so that the Ising spins have no (undecorated) moment, then $L = 0$, and we have

$$Z = f^N Z_{I,\,\mathrm{bcc}}^{N/4}(K) \ . \tag{18}$$

Here $Z_{I,\,\mathrm{bcc}}$ is the zero-field Ising partition function for N Ising spins in a bcc lattice, and we have explicitly accounted for the symmetry.

The thermodynamic functions may be straightforwardly evaluated from Eq. (18). For example, the entropy is

$$\begin{aligned} S &= K \ln Z - K\beta(\partial/\partial\beta) \ln Z \\ &= NK[\ln f + \tfrac{1}{4} Z_I(K)] - NK\beta \\ &\quad \times [(\partial/\partial\beta) \ln f + \tfrac{1}{4} (\partial K/\partial\beta)\omega(K)] \ , \end{aligned} \tag{19}$$

where $\omega = (\partial Z_I/\partial K)/Z_I$ is the internal energy of the Ising lattice. As $\beta \to 0$, the second term vanishes, $f \to 2J+1$, and $Z_{I,\,\mathrm{bcc}} \to 2$, so we see that the magnetic entropy approaches

$$S_{\mathrm{MAG}} = Nk[\ln(2J+1) + \tfrac{1}{4} \ln 2] \ . \tag{20}$$

Thus, the decorated Ising model releases slightly more entropy than the Heisenberg direct-exchange model. The excess for $J = \frac{5}{2}$ is about 10% at infinite temperature.

At finite temperatures, the decorated Ising model gives us a way to calculate the thermodynamics exactly.[16] The model thus trades off intuitive "reasonableness" for precision. In particular, the following physical criticisms may be made:

(i) The energy [Eq. (17)] is certainly only a schematic form for the true eigenvalue. The exchange parameters $\mathcal{J}_{CF}$ are thus meant to be illustrative rather than representative of any true exchange coupling constants.

(ii) The response of the Ising spins to the ions is qualitatively unlike the polarization of the itinerant conduction electrons in the Ruderman-Kittel model. In particular, the Ising spins do not respond to an applied field, and there is no "molecular field" component in the magnetic response. This aspect of the model is discussed further below.

(iii) The geometrical arrangement of the ion-Ising bonds puts first, second, and third ion neighbors on an equivalent footing in the sense that each of these is linked to the ion by two ion-Ising bonds. While this may not be a bad approximation for indirect exchange via conduction electrons, the uniaxial character of the Ising spins, which permits only a two-sublattice antiferromagnet, confines the spin arrangement of the ions more than is actually the case. Spiral ordering cannot be accommodated in the model.

(iv) Higher-degree exchange[15] is also not included, though this is in principle remediable by a more sophisticated form for the energy than Eq. (17).

Point (ii), first noted by Fisher,[7] is important for discussions of the magnetic properties. In the Heisenberg Hamiltonian, the interaction is

$$\textstyle\sum_i \vec{s}_i \cdot (\sum_j \mathcal{J}_{ij} \vec{s}_j - g\mu_B H) \ , \tag{21}$$

so that, in an applied field, the polarization of the system adds to the applied field. The polarization term, when thermally averaged, yields the molecular field approximation. In the present model, the ion-ion coupling occurs via the nonmagnetic (i.e., zero-moment) Ising spins, and the polarization term is absent. Fisher showed that this has a drastic effect on the magnetic susceptibility: In the high-temperature expansion of the susceptibility, the leading term is the Curie law C/T. The first correction is of order $(\mathcal{J}/kT)^2$, instead of $(\mathcal{J}/kT)$, as one finds in the direct-exchange case.[7] This means that to leading order the paramagnetic Curie temperature is zero.

In the case of the rare-earth hexaborides, the anomalously enhanced susceptibility, which we have interpreted as evidence of temperature-dependent exchange interactions, cannot be fitted by a decorated Ising model for this reason.[17] Calculations of the decorated-Ising-model susceptibility show only minor deviations from the crystal-field-only values. We have, therefore, restricted our discussion of the magnetic response to the molecular field scheme. Nonetheless, as we shall see below, the fluctuation effects on the specific heat are quite outstanding, and the decorated Ising model is illuminating in the study of these fluctuations.

V. FLUCTUATION-INDUCED SPECIFIC HEAT

The eigenvectors and eigenvalues given by Wang and Cooper[18] permit us to write down explicit formulas for the E_i in Eq. (17) and compute the ψ functions of Eq. (10). As shown by the discussion above, the problem is then reduced to a computer calculation.

In accord with the Nickerson-White model, we permit the exchange parameters in Eq. (17) to depend on the crystal field level, calling them J_7 and J_8, corresponding to the Γ_7 and Γ_8 levels. J_7 is essentially fixed by the ordering temperature. For $T_N = (2.3 \pm 0.1)$ K, we find $J_7 = (1.39 \pm 0.05)$ K. Using the same criterion of $T_N = (2.3 \pm 0.1)$ K and $J_7 = 1.39$ K, we mapped out the allowed range of J_8 and Δ. The values $J_8 = 12.5$ K, $\Delta = 70$ K fall well within the allowed region, and are taken to be representative.[19]

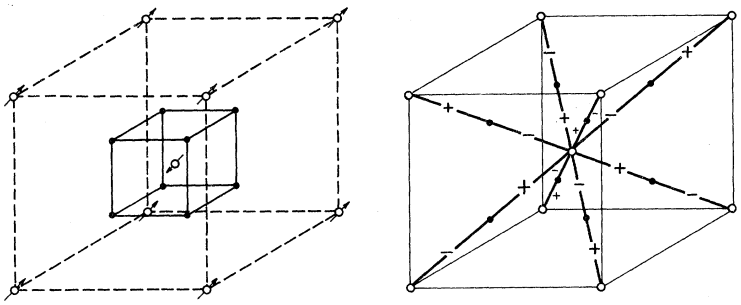

FIG. 4. Bcc Ising lattice for an ion lattice.

A. Phase Diagram

As a preliminary, we follow Fisher[7] and analyze the behavior of the interaction parameter K defined by Eq. (11). Recall that for the undecorated antiferromagnetic Ising lattice $-K$ plays the role of β, the inverse temperature [see Eq. (9)]. Physically, then, $-K$ measures the order—both long range and short range—of the Ising lattice, and thus (roughly) of the system as a whole. The contours of constant $-K$ in Fig. 5 thus serve to delineate the phase diagram of the decorated Ising lattice. At $-K=K_c = 0.221\,716$, the bcc Ising lattice orders. Thus, the heavy contour labeled K_c marks the boundary between antiferromagnetic and paramagnetic phases.[20] The solid triangles mark peaks in the magnetic susceptibility measured at different fields,[5] indicating that in CeB_6 the antiferromagnet-paramagnet phase boundary curves more sharply than the K_c contour in our model. The rapid decrease of the ordering temperature as the field rises is characteristic of spiral magnets, because their magnetic order is not so rigid in applied fields as a two-sublattice antiferromagnet, for example, is. Spiral ordering has also been found in PrB_6 by neutron scattering[21] and inferred for EuB_6.[22]

Now consider the behavior at zero field. As T increases, $-K$ at first decreases, and then has a peak at about 25 K. Although the peak value of $-K$ is too low to produce ordering, it does show the recurrence of significant short-range order, as the Γ_8 state becomes thermally populated. In effect, the Ising lattice cools as the temperature rises to the peak. This behavior is a precise statement of the notion that CeB_6 "barely misses ordering" at higher temperatures, which was expressed in Sec. III.[23]

In an applied field, we see a gradual suppression of the short-range order as the field is raised, as intuitively expected. The short-range order at about 25 K persists to surprisingly large fields because of the strong exchange in the excited state.

B. Specific Heat

In the absence of exchange, $Z=f^N$, and we have

$$C_v = Nk\beta^2 \frac{\partial^2}{\partial\beta^2} \ln f ; \tag{22}$$

the Schottky anomaly is shown by the broken line in Fig. 1. When the exchange is included,

$$C_v = Nk\beta^2 \left[\frac{\partial^2}{\partial\beta^2} \ln f + \frac{1}{4}\omega(K) \frac{\partial^2 k}{\partial\beta^2} \right.$$

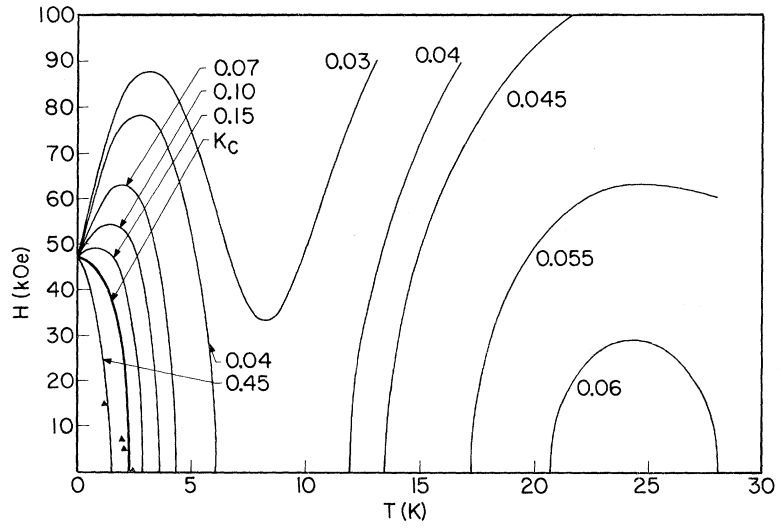

FIG. 5. Contours of constant $-K$ in the H–T plane. Heavy curve marked K_c separates the antiferromagnetic and paramagnetic phases. Triangles mark the peaks in the magnetic susceptibility of CeB_6, as a function of temperature, in different fields. Data due to Hull, Ref. 5.

$$+\frac{1}{4}\frac{c^*(K)}{K^2}\left(\frac{\partial K}{\partial \beta}\right)^2\Bigg], \quad (23)$$

where $c^*(K)$ and $\omega(K)$ are the specific heat and internal energy of the Ising lattice.

Equation (23) with $J_7 = 1.39$, $J_8 = 12.5$, and $\Delta = 70$ K is plotted as the solid curve in Fig. 1. Instead of falling to zero above the ordering temperature, as predicted by both the molecular field approximation and the no-exchange Schottky curve, the specific heat in the decorated Ising model falls to a minimum of above 1 J/mole K near 6 K. At higher temperatures, the Schottky peak is somewhat depressed and broadened, though the curves are similar in magnitude and shape.

Although the calculated curve reproduces the qualitative behavior displayed by the data, the magnitude of the specific heat is still too small, typically by a factor of 2 below 10 K. This is somewhat worrying since the principal contributions to the entropy come from this region. Measurements to higher temperatures in both CeB_6 and LaB_6 (to permit subtraction of the lattice specific heat) would show whether the rapid release of entropy at low temperature signals an anomalously large entropy, or rather an inadequacy in our decorated Ising model.

The exact calculation described above in a footnote shows that same specific-heat curve as the solid line in Fig. 1 when the exchange in the $J_z = \pm\frac{1}{2}$ states in the Γ_8 quartet is strong.

VI. SUMMARY

The bulk magnetization[5] and specific heat provide cogent evidence that CeB_6 would have a Γ_7 ground state in the absence of exchange interactions, with a Γ_8 excited state about 70 K higher in energy. The anomalous enhancement of the magnetic susceptibility below 150 K can be explained in this framework by assuming that the exchange in the Γ_8 is stronger than that in the Γ_7, as pointed out by Nickerson and White.[3] The magnetic susceptibility is not a sensitive quantitative measure of the crystal field splitting, as shown by our reformulation of the Nickerson-White model; rather, it seems to be sensitive primarily to the details of the exchange interaction.

By contrast, the specific heat has a Schottky anomaly whose peak is not appreciably shifted from the no-exchange value of 0.4Δ, even though the peak is slightly decreased in height, and the low-temperature shoulder is strongly smeared by exchange-induced fluctuations. Such smearing, long a part of the experimental folklore, has been explicitly displayed by an exact calculation of the fluctuation-induced specific heat using the decorated Ising model. The striking qualitative feature of the decorated-Ising-model calculation is that it demonstrates that short-range order can be induced by exchange in an excited crystal field state, as that state becomes thermally populated.

In principle, the type of analysis we have used in this discussion can now be extended to PrB_6 and NdB_6. Both compounds have crystal-field-split energy spectra, and for both measurements of the magnetic susceptibility and specific heat have been done.[24,25] The greater complexity of the energy-level schemes of the Pr^{3+} and Nd^{3+} ions, however, precludes quantitative comparison.[26] Qualitatively, both compounds show large specific heat above the magnetic-ordering temperatures, indicating substantial short-range order in the paramagnetic phase.

Deviations from the Curie-Weiss law have also been found in the magnetic susceptibilities of EuB_6[22] and GdB_6.[2,27] The rare-earth ions in these compounds, however, are in the spherically symmetric $^8S_{7/2}$ state, and thus cannot be split by crystal fields. In EuB_6, the specific heat[28] displays only weak short-range-order contributions, and the entropy is in accord with the expected eightfold degeneracy of the ground state. The question remains, then, of whether the anomalous susceptibility below liquid-nitrogen temperatures in these compounds is in fact due to changes in the effective strength of the exchange interaction. We have, in this discussion, assumed a Heisenberg-like form for the exchange; theoretical investigations of the effect of discarding this assumption would be interesting.

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[11]This splitting is in accord with a value of 350 K found by Fisk in $Y_{0.964}Ce_{0.036}B_6$ (see Ref. 2). The crystal field splitting, however, is quite sensitive to details of the conduction band: In $Sr_{0.974}Ce_{0.026}B_6$, for example, where the SrB_6 host is a semiconductor, Fisk finds a splitting of only 20 K. The Nickerson-White theory of the crystal field (see Ref. 4) in the rare-earth hexaborides employs a 5*d*-derived conduction band, while the conduction band in YB_6 is thought to arise from 4*d* orbitals. Thus, a crystal field splitting derived from CeB_6 in YB_6 may not be quantitatively reliable.

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[17]Endowing the Ising spins with nonzero moments—which would restore the molecular field behavior—would, also necessitate knowledge of Ising-lattice properties in applied fields. This, however, is not known for the bcc Ising lattice.

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In the improved model, we take the exchange Hamiltonian to be

$$\mathcal{H}_{EX}=\sum_{ml} \mathcal{J}(m_l) P_{m_l} S^z (s_1 - s_2),$$

where $\mathcal{J}(m_l)$ is an exchange parameter dependent on the orbital state —and thus reflecting directly the shape of the charge distribution [$\mathcal{J}(m_l) = \mathcal{J}(-m_l)$];

$$P_{m_l} = \sum_{m_s} |m_l, m_s\rangle \langle m_l, m_s|$$

is the projection operator which isolates the orbital dependence. We thus neglect off-diagonal exchange. We take as a basis the six eigenstates of J_z. The 6×6 matrix separates into two 2×2 and two 1×1 problems. All may be solved analytically to find the E_i exactly.

[20]One might wonder if the Ising lattice can be ordered when the ion lattice is not, or vice versa. By an explicit consideration of the long-range order Fisher showed that this does not happen in the two-dimensional Ising antiferromagnet (see Ref. 7). The conclusion generalizes to the present case: When $K<K_c$, there is no long-range antiferromagnetic order.

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[23]In the exact calculation, the recurrent short-range order reflects strong exchange in the $J_z=\pm\frac{1}{2}$ states. The other four states are admixed by the crystal field operators and form the doublet Γ_7 and two of the quartet Γ_8 states. Evidence for a strong excited-state exchange is found in the specific heat (see below).

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