

## Thermodynamic Properties of Transition-Ion Impurities in Noble Metals

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The low-temperature specific heat and magnetization of dilute magnetic impurities in noble metals are studied using a simple model in which a Ruderman-Kittel-Yosida (RKY) interaction is assumed between the magnetic impurities. The method used is based on, and is an extension of, the theory developed by Klein and Brout (KB) for the treatment of the  $T=0$  specific heat of dilute Cu-Mn. Departures from the KB treatment for the case when  $T \neq 0$  are considered. The magnetic impurities are considered to be randomly and uniformly distributed over the whole solid. The thermodynamic properties of the system are obtained by performing a statistical average over the positions of the particles and an ensemble average over their spins in an Ising model. The effective field  $H_0$  about an impurity is defined by the relation  $H_0 = \sum v_{0j} \mu_j$ , where  $v_{0j}$  is the RKY interaction and  $\mu_j$  is the spin of an impurity located at site  $j$ . The probability distribution of this effective field as a function of the impurity concentration, the strength of the RKY interaction, and the temperature is obtained. Use of this probability distribution gives the low-temperature specific heat of magnetic impurities in noble metals over a range of temperatures and concentrations in good agreement with experiment. For each class of impurities the strength of the RKY interaction is found from the low-temperature specific-heat data. A connection between the probability distribution of  $H_0$  and the hyperfine field at the nucleus, as measured by a Mössbauer experiment, is made. The recently reported Mössbauer, specific-heat, and magnetic-susceptibility measurements on gold-rich Au-Fe seem to be consistent with our model. We thus conclude that no long-range magnetic order exists in dilute Au-Fe for concentrations of less than about 5% iron.

### 1. INTRODUCTION

A GREAT deal of experimental data have recently been obtained on the low-temperature specific heat and magnetization of transition-ion impurities in noble metals. These materials show anomalous low-temperature specific heat and magnetic properties. The purpose of this paper is to explain the essential features of some of these experiments using a simple model. In this model, we assume a Ruderman-Kittel-Yosida<sup>1,2</sup> (henceforth abbreviated RKY) interaction between the magnetic impurities, and use an extension of the statistical theory for dilute ferromagnets developed by Klein and Brout<sup>3</sup> (henceforth referred to as KB). We find that the RKY potential between the magnetic impurities explains, to a first approximation, the low-temperature cooperative phenomena of localized transition-ion impurities in noble metals. A brief communication to this effect has already been published.<sup>4</sup>

A summary of the experimental specific-heat results is given in Table I. A feature common to all these materials is that they exhibit a large excess low-temperature specific heat  $\Delta C_v$  compared to the pure-host materials. We find that in each case (except possibly Au-Co) in which the experiment was performed at sufficiently low temperatures,  $\Delta C_v/T$  is large and approximately independent of the impurity concentration.  $\Delta C_v/T$  decreases with temperature and becomes concentration dependent for higher temperatures.<sup>5</sup>

Experiments are also available on the low-tempera-

ture magnetic susceptibility of Cu-Mn,<sup>6-9</sup> Ag-Mn,<sup>6</sup> and Cu-Co.<sup>10,11</sup> More recently, susceptibility measurements were performed on dilute concentrations of Cr, Mn, and Fe in gold.<sup>12</sup> A feature common to these data is a maximum in the susceptibility as a function of the temperature. The temperature at which the susceptibility is a maximum,  $T_{max}$ , is approximately proportional to the impurity concentration. This behavior is not shared by cobalt impurities in gold.<sup>12</sup>

In addition to the anomalies mentioned above, these materials exhibit low-temperature-resistivity anomalies,<sup>13,14</sup> remanent magnetizations which vary as a function of temperature,<sup>15</sup> and large anomalous thermoelectric powers.<sup>16</sup> In this paper we only discuss the thermodynamic properties of these systems, relegating the treatment of the nonequilibrium properties to a future publication.

An outline of this paper is as follows. In Sec. 2 we summarize the theory for dilute ferromagnets developed by Klein and Brout,<sup>3</sup> carefully pointing out some of the approximations involved. We discuss the consequences

<sup>6</sup> J. Owen, M. Browne, W. D. Knight, and C. Kittel, *Phys. Rev.* **102**, 1501 (1956).

<sup>7</sup> J. Owen, M. Browne, V. Arp, and A. F. Kip, *Phys. Chem. Solids* **2**, 85 (1957).

<sup>8</sup> I. S. Jacobs and R. W. Schmitt, *Phys. Rev.* **113**, 459 (1959).

<sup>9</sup> R. W. Schmitt and I. S. Jacobs, *Phys. Chem. Solids* **3**, 324 (1957).

<sup>10</sup> R. Tournier and L. Weil, *J. Phys. Radium* **23**, 522 (1962).

<sup>11</sup> R. Tournier, J. J. Veyssie, and L. Weil, *J. Phys. Radium* **23**, 672 (1962).

<sup>12</sup> O. S. Lutes and J. S. Schmit, *Phys. Rev.* **134**, A676 (1964).

<sup>13</sup> Tineke Van Peski-Tinbergen and A. J. Dekker, *Physica* **29**, 917 (1963). This paper contains an excellent set of references on this subject.

<sup>14</sup> G. J. Van den Berg and J. de Nobel, *J. Phys. Radium* **23**, 665 (1962).

<sup>15</sup> J. S. Kouvel, *Phys. Chem. Solids* **24**, 795 (1963). This paper contains a set of references on the experimental data.

<sup>16</sup> D. K. C. MacDonald, *Thermoelectricity* (John Wiley & Sons, Inc., New York, 1962), and references therein.

<sup>1</sup> M. A. Ruderman and C. Kittel, *Phys. Rev.* **96**, 99 (1954).

<sup>2</sup> K. Yosida, *Phys. Rev.* **106**, 893 (1957).

<sup>3</sup> M. W. Klein and R. Brout, *Phys. Rev.* **132**, 2412 (1963) (henceforth referred to as KB).

<sup>4</sup> M. W. Klein, *Phys. Rev. Letters* **11**, 408 (1963).

<sup>5</sup> R. R. Hake and J. A. Cape, North American Science Center Report, February 1964. Also see W. M. Klein, *J. Appl. Phys.* **35**, 944 (1964).

TABLE I. The summary of the experimental low-temperature specific-heat results on dilute magnetic impurities on noble metals.

Material	Temperature range (°K)	Concentration range (%)	Approximate concentration dependence $\Delta C_v/T$	Reference
Cu-Mn	1.5-4	0.35-10	$c^0$	Zimmerman & Hoare <sup>a</sup> Crane & Zimmerman <sup>b</sup>
Cu-Fe	0.4-1.5	0.05, 0.1, 0.2	$c^1$	Franck, Manchester and Martin <sup>c</sup> Crane & Zimmerman <sup>d</sup>
Cu-Co	3-5	2.2-2.5	$c^1$	Tournier & Weil <sup>e</sup> Tournier <i>et al.</i> <sup>f</sup>
Cu-Co	3-5	0.5-2	$c^2$	Ref. d, e, and f
Au-Fe	1.5	0.1, 0.2, 0.5	$c^0$	L. T. Crane <sup>g</sup>
Au-Fe	2-4	0.1, 0.2, 0.5	$c^1$	Ref. g
Au-Co	3-5	~0.5-2	$c^{3/2}$	L. T. Crane <sup>h</sup>
Ag-Mn	~2	0.28, 0.40	~ $c^0$	DeNoble & DuChatenier <sup>i</sup>
Ag-Mn	~3	0.28, 0.40	~ $c^1$	Ref. i

<sup>a</sup> J. E. Zimmerman and F. E. Hoare, Phys. Chem. Solids 17, 52 (1960).

<sup>b</sup> See Ref. 31.

<sup>c</sup> See Ref. 33.

<sup>d</sup> L. T. Crane and J. E. Zimmerman, Phys. Rev. 123, 113 (1961).

<sup>e</sup> See Ref. 10.

<sup>f</sup> See Ref. 11.

<sup>g</sup> See Ref. 24.

<sup>h</sup> L. T. Crane, Phys. Rev. 125, 1902 (1962).

<sup>i</sup> See Ref. 32.

of the correlation length derived in the KB treatment and extend the theory to higher temperatures. Since the thermodynamic functions for the system are obtained from the probability distribution of the effective fields, this probability distribution is discussed extensively in Sec. 3. We find that if we fix a spin at an arbitrary origin, the few spins close to the one fixed at the origin determine the behavior of the probability distribution, and the fields from the far-away spins contribute in an unimportant way. This is because the effective fields from the far-away spins are screened by the alternating RKY potential. We also discuss briefly a possible connection between our theory and a Mössbauer experiment. In Sec. 4 we discuss the specific heat and the magnetization of these dilute systems. We find that the low-temperature specific heat and magnetization of localized magnetic impurities in noble metals are explained by this model. An exception to this appears to be dilute impurities of cobalt in gold. In Sec. 5 we discuss the behavior of gold-iron in detail, and point out that the recently reported specific-heat, magnetization, magnetic susceptibility, and Mössbauer experiments on gold-iron seem to be consistent with our model.

## 2. THEORETICAL CONSIDERATIONS

We propose to examine the thermodynamic properties of a system of dilute magnetic impurities in a nonmagnetic host lattice. We assume that a RKY potential is the interaction mechanism between the magnetic impurities and discuss the behavior of the system, first for the case in which the temperature is zero, and then for  $T \neq 0$ . To do this, we first briefly review the  $T=0$  case discussed previously,<sup>3,17</sup> thereby

<sup>17</sup> That a Ruderman-Kittel interaction explains the low-temperature specific heat of Cu-Mn was first pointed out by W. Marshall, Phys. Rev. 118, 1520 (1960).

introducing the background for a further extension of the theory.

We consider a crystal having  $N$  magnetic impurities distributed over  $N_0$  sites such that  $N/N_0=c$ , where  $c$  is the fractional impurity concentration and  $N_0$  is the total number of lattice sites in the crystal. The position coordinate  $r$  of each impurity is an independent random variable uniformly distributed over the volume of the crystal  $V$  with probability  $1/V$ . With an impurity at position  $i$ , we have associated the random spin variable  $\mu_i$ . We use an Ising model, a model in which  $\mu_i$  may take the values of  $\pm 1$  only.<sup>18</sup> The probability that  $\mu_i$  has a definite orientation is, in general, a function of the temperature. The free energy for the system is given by

$$\log Z = \log \sum_{\text{all states}} \exp[-\beta \sum_{i < j} v_{ij} \mu_i \mu_j], \quad (2.1)$$

where  $Z$  is the partition function for the system and  $\beta=1/kT$ , where  $T$  is the temperature.  $v_{ij}$  is the spatial part of the RKY potential given by

$$v_{ij} = a[(x \cos x - \sin x)/x^4], \quad (2.2)$$

where  $x=2k_F r_{ij}$ , where  $k_F$  is the Fermi momentum and

<sup>18</sup> It has been argued that it is incorrect to use an Ising model for the treatment of the low-temperature specific heat. The reasoning goes as follows. Consider the far-away spins. Since these are, in our model, approximately uncorrelated to the spin at the origin, any direction of orientation is permissible for the spins. Hence, the probability distribution of the field is three dimensional, and the low-temperature specific heat is proportional to  $T^3$  instead of  $T$ , and our conclusions on the low-temperature specific heat are incorrect. We would like to remark that the above argument would be correct if all spins were classical vectors. However, since in the region  $r < R_c$  the spins are strongly correlated to the spin at the origin, we expect that the Ising model is valid for this region. From the discussion in Sec. 2, we find that the behavior of the probability distribution is governed by the fields from the "inside" region. Therefore, the Ising model should have reasonable validity at low temperatures, except possibly at  $T$  equal to zero where a Heisenberg model would give a  $T^3$  dependence of the specific heat.

$r_{ij}$  the distance between the impurities at sites  $i$  and  $j$ .  
For use below, we also define

$$a \equiv JS^2(2k_F)^3, \quad (2.3)$$

where  $a$  is the coefficient of Eq. (2.2) and  $J$  is an interaction energy which may be obtained from Yosida's paper,<sup>2</sup> and  $S$  is the magnitude of the impurity spin. The value of  $JS^2$  will be given in units of degrees Kelvin divided by the cube of a lattice constant. Note: Henceforth, all lengths will be measured in dimensionless units of the lattice constant unless explicitly stated otherwise. The spin average in Eq. (2.1) is performed using the condition that no long-range order exists in the solid (as discussed in KB). The partition function is expanded diagrammatically using the semi-invariant method of Brout,<sup>19</sup> and the diagrams are summed according to a power series in the impurity concentration. The partition function is evaluated exactly up to and including the fourth virial coefficient (3rd power in the concentration), and the contribution from higher virial coefficients is approximated. With an impurity fixed at an arbitrary origin 0 and another at position  $j$ , Eq. (2.1) is differentiated with respect to  $-\frac{1}{2}\beta v_{0j}$  to give the two-particle spin correlation function  $\langle \mu_0 \mu_j \rangle$ ,

$$\lim_{\beta \rightarrow \infty} \langle \mu_0 \mu_j \rangle \approx \lim_{\beta \rightarrow \infty} \left\{ -\tanh \beta v_{0j} + 2 \sum_{n=3}^{\infty} c^{n-2} \times \sum_{i_3 \dots i_n} \langle [1 + \sum_{k=2 \dots n} \exp(2\beta \{ |v_{0j}| - |v_{k,k+1}| \})]^{-1} \rangle \right\}, \quad (2.4)$$

where the indices  $i_3, i_4, \dots, i_n$  run from 1 to  $N_0$ , the brackets  $\langle \rangle$  denote an average over the coordinates of all spins other than 0 and  $j$ , and  $c$  is the fractional concentration.  $k$  denotes the bonds in the  $n$  vertex diagram, as outlined in KB. In the limit as  $\beta \rightarrow \infty$ , we observe that whenever  $|v_{0j}| > |v_{k,k+1}|$ , the second term in Eq. (2.4) is zero. Thus, at  $T=0$ , the summation in Eq. (2.4) is restricted to sites within an approximate radius of  $r_{0j}$  from the origin. Evaluating Eq. (2.4) in the limit as  $T \rightarrow 0$  gives

$$\langle \mu_0 \mu_j(T=0) \rangle \equiv g(r,0) \approx 1 - 2 \sum_{n=3}^{\infty} \alpha_n (cz)^{n-2}, \quad (2.5)$$

where  $z$  is the total number of sites within a volume of the solid of radius  $r_{0j}$  and  $\alpha_n$  is a number of order unity. Using Eq. (2.5) and a self-consistent calculation of the spin-correlation function for spins at large distances from the origin,<sup>3</sup> we find that the spin-correlation function  $g(r,T)$  at  $T=0$  is

$$g(r,0) \approx \begin{cases} [1 - (r^3/R_c^3)] \operatorname{sgn}[v(r)] & r < R_c \\ 0 & r > R_c \end{cases}, \quad (2.6a)$$

where  $\operatorname{sgn}[v(r)] = \pm 1$ , depending on the sign of the

RKY potential, and  $R_c$  is the correlation length, which at  $T=0$  is

$$R_c(0) \approx 0.51c^{-1/3}d, \quad (2.6b)$$

where  $d$  is the lattice constant.  $R_c$  is determined from the condition that Eq. (2.5) equals zero. We find that as the concentration decreases, the correlation length increases in such a fashion that the average number of spins within a volume with radius  $R_c(0)$  stays fixed. This number is, on the average, about 3.3. We also find that an impurity located close to the spin at the origin  $\mu_0$  will be strongly correlated to it, whereas one located far away ( $r > R_c$ ) will have a spin orientation that is approximately random with respect to  $\mu_0$ . This summarizes the major conclusions of the KB theory.

The correlation length is important to the solution of the random ferromagnet and describes what we may call a magnetic screening behavior of the system. Because of the alternating sign of the RKY potential as a function of position, the intermediate spins tend to screen the correlation between the magnetic impurities. However, the screening mechanism described here is not unique to the RKY potential, but exists for other spin-dependent potentials of the form given by Eq. (2.2), provided that the interaction potential alternates in sign as a function of position with a period that is not commensurate with the lattice, and provided the potential converges rapidly enough.

Since the correlation length given by Eq. (2.6b) is the central result of our theory, we make a few remarks about its validity. The result of Eq. (2.4) is derived from the partition function, and thus the length  $R_c$  also results from the partition function. The correlation length divides the system into an "inside," or strongly correlated region, and an "outside," or weakly correlated region. This division is again derived from the partition function. In our approximation we consider the two-particle spin-correlation function only (and neglect higher spin correlations); thus the spins in the "outside region" are approximately randomly oriented with respect to the spin placed at the origin of the "inside" region. We call one of these regions of strong spin correlation a "cluster." However, it is not proper to associate a domain wall or any other physically well-defined boundary with one of these clusters. Also, it is equally valid to consider the position of any one magnetic impurity in the solid as an origin as it is any other. The screening in the dilute ferromagnetic case treated here is, in principle, no different from the screening behavior of the charged particles in an electron gas, where one chosen origin is just as good as any other origin. Admittedly, the problem becomes more complicated because of the discrete sites in the solid.

To extend our theory to temperatures other than zero, we have to reevaluate the derivations which resulted in Eq. (2.4). This is very difficult. Therefore, instead of evaluating the spin-correlation function as a function of the temperature from the partition function,

<sup>19</sup> R. Brout, Phys. Rev. **115**, 824 (1959).

we use a reasonable physical approach which follows from the following approximation. The spins within the correlation length finds themselves in a field which is approximately proportional to  $1/r^3$ . Thus, the spins close to the edge of the correlation length are only weakly coupled to the one at the origin. As the temperature is increased, it is reasonable to assume that these weakly coupled spins at the edge of the correlation length, and then the spins closer to the origin, are decoupled from  $\mu_0$ . For very small, but nonzero, temperatures we obtain the spin correlation function from Eqs. (3.2), (3.9), and (3.11) of KB to be [no approximation is involved in going from Eq. (3.11) of KB to Eq. (2.7)]

$$g(r, T) \equiv \langle \mu_0 \mu_j(T) \rangle \approx [1 - (r^3/R_c^3)] \tanh \beta v_{0j}, \quad (2.7)$$

where  $\beta = 1/k_B T$ . Using Eq. (2.7) with the previous discussion, we now find an approximation to the correlation length as a function of temperature. For this purpose we distribute the spins over the correlated volume with a density  $\rho(r)$ . Since the impurities are uniformly distributed in the solid,  $\rho(r)$  may be assumed to be a constant. At  $T=0$ , the number of spins correlated to the spin at the origin,  $n(0)$ , is

$$n(0) = \int_0^{R_c} \rho(r) |g(r, 0)| d^3r, \quad (2.8)$$

where the vertical bars indicate the magnitude of  $g(r, 0)$ . Let  $n(T)$  be the number of spins correlated to  $\mu_0$  at temperature  $T$ ; then

$$n(T) = \int_0^{R_c} \rho(r) |g(r, T)| d^3r. \quad (2.9)$$

The ratio of Eq. (2.9) to Eq. (2.8) gives the fraction of the spins that are still correlated to  $\mu_0$  at a temperature  $T$ . Upon equating this fraction to the ratio of the correlated volumes at temperature  $T$  to that at temperature zero, we get

$$R_c^3(T) \approx R_c^3(0) \left[ \frac{\int |g(r, T)| \rho(r) d^3r}{\int |g(r, 0)| \rho(r) d^3r} \right]^{-1}. \quad (2.10)$$

We should remark that except for the fact that Eq. (2.7) follows from the partition function, Eqs. (2.8) to (2.10) have not been rigorously justified. We now let

$$\begin{aligned} \tanh \beta x &= \beta x, & \beta x < 1 \\ &= 1, & \beta x > 1, \end{aligned} \quad (2.11)$$

and substitute Eq. (2.11) into Eq. (2.10) to obtain

$$R_c(T) \approx R_c(0) [-2y \ln y + y^2]^{1/3}, \quad (2.12)$$

where  $y = T_c/T$ ,

$$T_c = JS^2/[R_c(0)]^3, \quad (2.13)$$

and  $JS^2$  is defined in Eq. (2.3). Equation (2.12) is the important result of this section and is derived for the case when  $y \leq 1$ , i.e.,  $T > T_c$ .

### 3.1 Probability Distribution of the Field About an Impurity

We define an effective field  $H_0$  at the impurity spin  $\mu_0$ , located at the origin by the relation

$$H_0 = \sum_j v_{0j} \mu_j = H_1 + H_2, \quad (3.1)$$

$$H_1 = \sum_{(r_{0j} < R_c)} v_{0j} \mu_j; \quad H_2 = \sum_{(r_{0j} > R_c)} v_{0j} \mu_j.$$

Since  $r_j$  and  $\mu_j$  are random variables,  $H_0$  is also a random variable whose probability distribution is determined by the probabilities associated with the random variables  $r_j$  and  $\mu_j$ . We found, in the previous section, that the spins giving rise to  $H_1$  are strongly correlated to  $\mu_0$ , whereas those giving rise to  $H_2$  are approximately randomly oriented with respect to  $\mu_0$ . Thus, the fields  $H_1$  and  $H_2$  will be *approximately* independent random variables, and the probability distribution of the total field  $P(H_0)$  will be given by the convolution of the probability distributions  $P(H_1)$  and  $P(H_2)$ .  $P(H_1)$  can be found for any impurity concentration by enumerating the possible positions of the impurities within the correlated volume and the probabilities that the particular sites are occupied. The magnitudes of the various fields are calculated using  $v_{ij}$  in Eq. (2.2). For the details of the  $P(H_1)$  calculation, the reader is referred to Appendix 1.

To obtain the probability distribution of the field  $H_2$ , we use the statistical model of Margenau<sup>20</sup> in conjunction with the previously derived result that the spins in this region are randomly oriented with respect to the spin at the origin. As in KB, we obtain

$$P(H_2) \sim \frac{1}{(2\pi\sigma^2)^{1/2}} \exp\left[-\frac{1}{2}\left(\frac{H}{\sigma}\right)^2\right] + 0(\exp - 5.16), \quad (3.2)$$

where

$$\sigma(T=0) \approx \left[ \frac{16\pi}{3(cR_c^3(0))} \right]^{1/2} \frac{JS^2c}{\sqrt{2}} \approx 7.8JS^2c. \quad (3.3)$$

To obtain the probability distribution of  $P(H_2)$  as a function of temperature, we use Eq. (2.12) and find that for values of  $T/T_c < 5$ ,  $P(H_2)$ , then, is still *approximately* Gaussian;  $R_c(0)$  in Eq. (3.3) is replaced by  $R_c(T)$  given in Eq. (2.12). To find the probability distribution  $P(H_0)$ , we convolve Eq. (3.2) with the discrete probability distribution of  $H_1$  from the inside region.

### 3.2 Qualitative Aspects of the Probability Distribution

The calculation of the probability distribution  $P(H_0)$  for a particular strength of interaction and concen-

<sup>20</sup> H. Margenau and W. Watson, Rev. Mod. Phys. 8, 22 (1936).

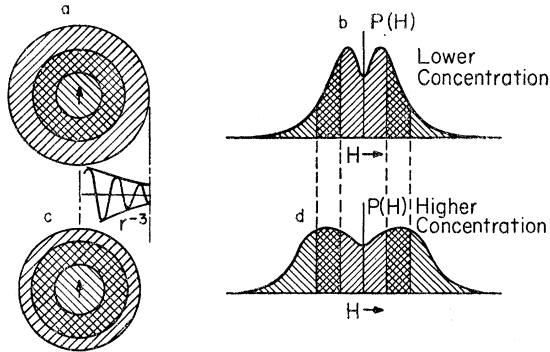


FIG. 1. Qualitative behavior of the probability distribution as a function of the impurity concentration. (a) The volume of the sphere with a correlation radius  $R_c$ . This volume is divided into a near region, intermediate region, and far region shown by different crosshatchings. The qualitative behavior of the RKY potential is shown below (a). (b) The corresponding three regions of the probability distribution of  $P(H_0)$ . (c) The correlated volume for a higher concentration. (d) The corresponding probability distribution for this higher concentration. A comparison of (b) and (d) shows that the effect of an increased concentration is to remove some probability from the center of  $P(H_0)$  and place it into the wings.

tration becomes complicated and is most conveniently done with a computer. However, the characteristic behavior of  $P(H_0)$  is obtained from simple physical considerations. The discussion of  $P(H_0)$  will be centered about the two important results derived previously. These are: (a) the existence of the correlation length, (b) the random orientation of the spins located at large distances from the spin at the origin.

#### Consequences of the Correlation Length $T=0$

Since the fields from the spins located within the correlated volume have a normalized probability distribution, and since these spins contribute a large spread (rms deviation) in effective fields (compared to the spread in the fields from the far-away spins) about the spin at the origin, the character of the probability distribution is primarily determined by the spins from the "inside" region. The "outside" region plays an unimportant role in our model, provided the spread in the fields arising from the far-away spins is sufficiently large to make  $P(H_0)$  continuous. (The sites in the lattice are discrete; thus the values of  $H_1$  are also discrete.) Once this latter condition is satisfied, the specific-heat results are not sensitive to the treatment of the far-away spins. This result may be an additional justification for the treatment of the "outside" region by an Ising model, instead of the presumably more correct isotropic Heisenberg model. We should point out that our present argument differs somewhat from that used by Marshall<sup>17</sup> and by Klein and Brout<sup>3</sup> to explain the low-temperature specific heat of dilute Cu-Mn, where it was believed that *only* the spins that are very far from the origin determine the low-temperature specific-heat behavior of Cu-Mn. However, the previously obtained results for Cu-Mn are still correct;

only the physical interpretation of the behavior of  $P(H_0)$  has changed in a significant way.

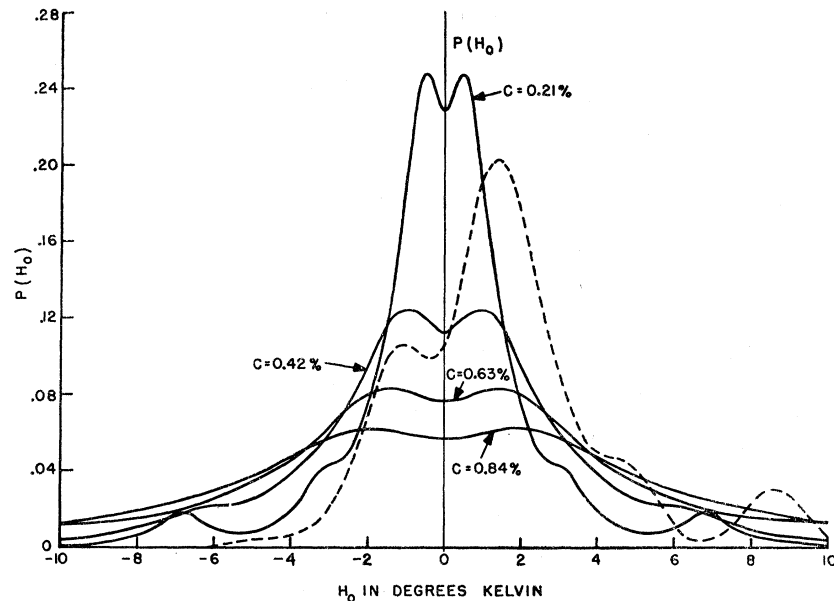
We now discuss the qualitative behavior of the probability distribution of the field  $P(H_0)$  as a function of the concentration, the strength of the RKY interaction  $JS^2$ , and the temperature.

To obtain the concentration dependence of  $P(H_0)$  we subdivide the correlated volume about the origin into three regions as shown in Fig. 1 (a). Since the RKY potential from the origin varies, approximately like  $r^{-3}$ , the spins that are farthest away from the origin contribute small fields, and the spins close to the spin at the origin contribute large fields. The distribution of the fields from the three regions is drawn qualitatively in Fig. 1 (b). Next, consider the probability distribution of  $H_0$  for a larger concentration. The correlation length decreases in accordance with Eq. (2.6b). The correlated volume for this case is shown in Fig. 1 (c). Since  $P(H_0)$  is normalized to unity, the central region, which gives the large fields, now has a higher probability associated with it. Thus, the effect of an increase in the concentration is to remove some probability from the center portion (small fields) of  $P(H_0)$  and to place it into the wings, as shown in Fig. 1 (d). Therefore, the probability of having small fields will be inversely proportional to the concentration, whereas the probability of having large fields is proportional to the concentration.

We should also note from Fig. 1 that the probability distribution has a maximum about some value other than  $H_1=0$ . The reason is as follows. The probability of having a certain field between  $H_1$  and  $H_1+\Delta H_1$  is proportional to the volume which gives the value of  $\Delta H_1$  divided by the total "correlated volume." Since the volume is proportional to  $r^3$ , the most probable fields are those obtained from the spins near the edge of the correlation length. This value of the field is not zero but is approximately given by  $H_1^0 \approx JS^2/R_c^3$ . Therefore,  $P(H_1)$  is peaked about the value  $H_1 \approx H_1^0$ . Since  $R_c^{-3}$  is proportional to the concentration, the value of the  $H_1^0$  is also approximately proportional to the concentration.

Also note that  $P(H)$  in Fig. 1 is symmetric about  $H=0$ . The reason for this is that, on the average, there are just as many spins oriented up as there are oriented down, and a specific-heat measurement does not distinguish between an up-spin or a down-spin. However, if one considers the probability distribution in the presence of an external field, one has to include the asymmetry introduced into  $P(H_0)$  due to the polarization of the spins surrounding the one located at the origin. A sketch of this probability distribution is shown in Fig. 2. The behavior of  $P(H_0)$ , where  $H_0$  is given by Eq. (3.1), was calculated by a computer for a fixed value of  $JS^2$  and for several concentrations. The results are shown in Fig. 2. Note the detailed concentration dependence of  $P(H_0)$  and that  $P(H_0=0)$  is inversely proportional to the concentration in agreement with the qualitative arguments presented.

FIG. 2. The probability distribution as a function of the concentration for a fixed value of interaction strength  $JS^2$ .  $JS^2$  is the strength of the Ruderman-Kittel-Yosida potential at a distance of one lattice constant, and is approximately  $26^\circ\text{K}$  for the case shown in the figure. The various concentrations  $c$  are indicated on each graph. The value of  $P(H_0)$  at  $H_0=0$  is inversely proportional to the concentration in each case. The wiggles in the wings of  $P(H)$  arise from the finite number of values of  $H_1$  used in the calculation. The dashed line shows an approximation to the nonsymmetrized probability distribution actually experienced by the impurity. The curves were obtained using a computer.



#### Variation of the Probability Distribution with the Interaction Strength $JS^2$

From our previous discussion, it follows that as the strength of the interaction increases, so does the probability for having larger fields. Thus, in general, the height of  $P(H_0)$  near  $H_0=0$  will be approximately inversely proportional to  $JS^2$ . In Appendix 1, Eqs. (A1.4) and (A1.5), we derive the expression for the probability distribution of the effective field and find that the shape of  $P(H_0)$  depends only on the product of the strength of the RKY interaction and the concentration. Thus,  $P(H_0)$  for an impurity concentration of  $\alpha c$  and interaction strength of  $JS^2$  is the same as  $P(H_0)$  for a concentration of  $c$  and interaction strength of  $\alpha(JS^2)$ , where  $\alpha$  is any number. Therefore, Fig. 2 is also the representation of the probability distribution of a 0.21% impurity concentration with the interaction strength of 26, 52, 78, and  $104^\circ\text{K}$ .

#### Variation of the Probability Distribution with Temperature

The approximate variation of  $P(H_0)$  as a function of  $T$  is found by relating the variation of the correlation length with temperature, given by Eq. (2.12), to the probability distribution. Since the correlation length, in our approximation, decreases as a function of temperature, the effect of increasing the temperature will be similar to that of increasing the concentration. The physical reason for this can be understood by the following consideration. The spins that are located near the edge of the correlation length are only weakly correlated to the spin at the origin. As the temperature is decreased, these weakly correlated spins become randomized, thereby reducing the effective correlation

length. This results in an increased probability of finding the spin at the origin in large fields.

The value of  $H_1^0$  at which  $P(H_0)$  is a maximum also changes with temperature and is a function of  $T_c/T$  given by Eq. (2.12). For  $T_c/T$  not too small (roughly  $T_c/T$  between 1/5 and unity) we make the approximation

$$H_1^0(T=0)/H_1^0(T=T_0) = R_c^3(T_0)/R_c^3(0), \quad (3.5)$$

where  $R_c^3(T)$  is again given by Eq. (2.12). Since  $T_c = JS^2/R_c^3$ , and is thus proportional to the concentration, we find that the value of  $H_1^0$  at which  $P(H_0)$  is a maximum increases as a function of the temperature. This appears to be in qualitative agreement with a Mössbauer experiment on dilute copper-iron.<sup>21</sup>

We find that  $P(H_0)$  has a local minimum at  $H_0=0$ . For a subsequent discussion of the Mössbauer experiment, it is of interest to find the variation of this local minimum with various quantities. We observe that if  $\sigma \gg H_1^0 \approx [JS^2/R_c^3]$ , then  $P(H_0)$  has a maximum instead of a local minimum at  $H_0=0$ . The magnitude of the dip at  $H=0$  depends upon the ratio  $\xi \equiv H_1^0/\sigma$ . From Eq. (3.3) and the value of  $R_c$  from Eq. (2.7), we find that  $\xi \approx 1$ . However, we have not evaluated the estimated errors in the quantities  $H_1^0$  and  $\sigma$ . In order to see the variation of the dip of the probability distribution and the specific heat with  $\xi$ , we have calculated the central portion of  $P(H_0)$  and the low-temperature specific heat as a function of  $\xi$ , keeping the strength of the interaction  $JS^2$  a constant. We find that the specific heat is quite insensitive to the variation of  $\xi$ , whereas the dip in  $P(H_0)$  depends more strongly on  $\xi$ .

<sup>21</sup> W. Marshall, T. E. Cranshaw, C. E. Johnson, and M. S. Ridout, Rev. Mod. Phys. 36, 199 (1964).

TABLE II. I represents the Zimmerman and Hoare<sup>a</sup> data in the temperature region of 2 to 5°K, II represents the Franck, Manchester, and Martin<sup>b</sup> data in the temperature region of 0.4 to 5°K, III shows the Crane and Zimmerman<sup>c</sup> result in the temperature region of 3 to 5°K, and IV shows Crane's<sup>d</sup> data on Au-Fe.

	Substance	Major contribution to the specific heat	Specific heat	$JS^2/JS^2_{\text{Cu-Mn}}$
I	Cu-Mn	$P(H_0)$ near $H_0=0$	$c[1/c]=c_0$	1
II	Cu-Fe	middle portion of $P(H_0)$	$c[c^0]=c^1$	$\sim 1.4$
III	Cu-Co	wings of $P(H_0)$	$c[c]=c^2$	$\approx 0.5$
IV	Au-Fe	center and middle portion of $P(H_0)$		$\sim 1.1$

<sup>a</sup> See Ref. a, Table I.

<sup>b</sup> See Ref. 31.

<sup>c</sup> See Ref. d, Table I.

<sup>d</sup> See Ref. 24.

### 3.3 Possible Verification of $P(H_0)$ Using a Mössbauer Experiment

It has recently been pointed out by Marshall *et al.*<sup>21</sup> that, in principle, a Mössbauer experiment gives a measure of the probability distribution of the effective field about an impurity in a dilute ferromagnet. Marshall's discussion for spin- $\frac{1}{2}$  goes as follows. The hyperfine field  $h$  at the iron nucleus is a function of the effective molecular field  $H_0$  and is given by

$$h = b \tanh H_0 \mu / kT, \quad (3.6)$$

where  $b$  is the magnitude of the maximum hyperfine field at the nucleus.  $b$  is of the order of  $10^5$  G for iron. For a discussion of the hyperfine field at the nucleus the reader should consult one of several articles on this subject.<sup>22,23</sup> We consider a system like Cu-Fe or Au-Fe, where the results derived in this paper should be applicable. From Eq. (3.6) we find that all the spins with fields  $\mu H \gg kT$  have a maximum splitting associated with their hyperfine spectrum, and those with fields  $\mu H \leq kT$  will have a hyperfine splitting somewhere between zero and maximum. Therefore, the spins in low fields will tend to increase the background noise. A hyperfine spectrum will be observed whenever the number of spins with fields  $\mu H \gg kT$  is sufficiently large so that the six-finger spectrum can be resolved from the background noise. It was reported by Marshall *et al.*<sup>21</sup> that  $P(H_0)$  for Cu-Fe has a local minimum at  $H_0=0$ . This is in qualitative agreement with our results shown in Fig. 2. However, at present we cannot comment on whether this minimum is sufficiently deep to explain the experimental observations of Marshall *et al.* It is encouraging, however, that the experimentally observed maximum in  $P(H_0)$  moves to higher fields with increasing temperature which is in agreement with our theoretical predictions.

#### 4. SPECIFIC HEAT

In the presence of the effective field  $H_0$ , the single-particle energy is

$$E^1(\beta) \approx -\frac{1}{2} \int H_0 \tanh \beta H_0 P(H_0, \beta) dH_0. \quad (4.1)$$

<sup>22</sup> R. C. Preston, S. S. Hannah, and J. Heberle, Phys. Rev. **128**, 2207 (1962).

<sup>23</sup> Also, see A. J. F. Boyle and H. E. Hall, Rept. Progr. Phys. **25**, 441 (1962).

The factor  $\frac{1}{2}$  arises from counting each pair interaction twice in the expression for the energy. The specific heat is

$$C_v = \frac{N_0 c}{k_B T^2} \frac{\partial E^1(\beta)}{\partial \beta} = \frac{N_0 c}{2k_B T^2} \left[ \int P(H_0, \beta) H_0^2 \operatorname{sech}^2 \beta H_0 dH_0 + 0 \left( \frac{\partial P(H_0)}{\partial \beta} \right) \right], \quad (4.2)$$

where  $N_0$  is Avogadro's number and  $c$  the impurity concentration. The term containing  $\partial P(H_0)/\partial \beta$  arises from the change in the probability distribution and is small near  $T=0$ . Using Eq. (A1.6) of Appendix 1, Eqs. (3.3), (2.12), (2.13), and (3.1), we obtain for the second term of Eq. (4.2),  $C_v^{(2)}$ :

$$C_v^{(2)} \approx \frac{N_0 c (1 - T_c/T)^2}{4k_B T^2 \sigma \beta^3} \sum_s a_s \int_{-\infty}^{\infty} \exp \left[ -\frac{1}{2} \left( \frac{x}{\beta \sigma} - b_s \right)^2 \right] \times x \tanh x \left[ 1 - \frac{x^2}{\beta^2 \sigma^2} \right] dx, \quad (4.3)$$

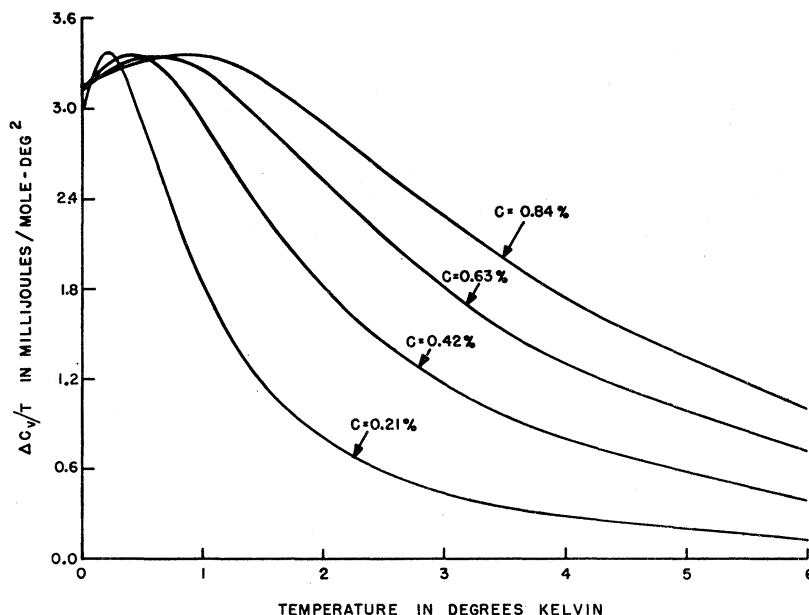
where  $b_s$  is defined in Appendix 1,  $\beta H_0 = x$ , and  $T > T_c$  in the above equation. However, to facilitate the calculation, we shall approximate the specific heat by the first term of Eq. (4.2). The effect of this approximation is that the theoretically obtained specific heat is presumably too low for temperatures greater than  $T_c = JS^2 [k_B R_c(0)^3]^{-1}$ .

Using the first term of Eq. (4.2) with the form of  $P(H_0)$  shown in Appendix 1, we obtain

$$C_v \approx \frac{N_0 c k_B}{2(2\pi)^{1/2} (\sigma \beta)} \sum_s a_s \int_{-\infty}^{\infty} \exp \left[ -\frac{1}{2} \left( \frac{x}{\beta \sigma} - b_s \right)^2 \right] \times x^2 \operatorname{sech}^2 x dx = \frac{N_0 c k_B}{2(2\pi)^{1/2}} f(\sigma \beta). \quad (4.4)$$

Thus we find that the specific heat calculated from the zero-temperature probability distribution is a function of  $\sigma \beta$ , and  $\sigma \beta \propto JS^2 c/T$ . For  $(\sigma \beta) \gg 1$ , we use Eq. (A1.5)

FIG. 3. The excess low-temperature specific heat  $\Delta C_v$ , divided by the temperature  $T$ , as a function of temperature for a fixed value of  $JS^2$  ( $\approx 26^\circ\text{K}$ ), and four different concentrations  $c$ . The very low-temperature specific heat is approximately independent of the concentration. At intermediate temperatures,  $\Delta C_v/T$  is proportional to the concentration; and at even higher temperatures,  $\Delta C_v/T$  is proportional to  $c^2$ .



from Appendix 1 to obtain

$$\lim_{T \rightarrow 0} C_v \approx [N_0 k_B T / 2(2\pi)^{1/2}] (0.25)(c/\sigma). \quad (4.5)$$

Since  $\sigma$  is proportional to  $c$ , the low-temperature specific heat is independent of the concentration and varies linearly with the temperature. This has already been shown.<sup>3</sup> We also find from Eq. (4.5) that the very low-temperature specific heat is inversely proportional to the strength of the interaction  $JS^2$ . Thus, if very low-temperature specific-heat experiments are available, we can determine the value of  $JS^2$  from the  $T=0$  intercept of the  $\Delta C_v/T$  data. We thus obtain the one single parameter necessary to determine the detailed behavior of the system. Equation (4.4) permits us to obtain the specific heat for a particular concentration and temperature once the specific heat as a function of  $T$  is known for one particular value of  $JS^2$  and  $c$  (at least for low temperatures).

The qualitative behavior of  $\Delta C_v$  is found from Eq. (4.4) as follows: We find that the integral is multiplied by a factor of  $c$ ; therefore, the concentration dependence of the specific heat will be  $c$  times the concentration dependence of the probability distribution. The interaction strength  $JS^2$  and the concentration determine which part of the probability distribution gives the major contribution to the specific heat in a particular temperature region. Using the values of  $JS^2$  determined from Eq. (4.5) and the experimental low-temperature specific heat, we obtain that the major contribution to the specific heat for Cu-Mn in the 2 to 4°K range comes from the center of the distribution function which is proportional to  $c^{-1}$ . Thus, the specific heat is independent of the impurity concentration. The major contribution of the specific heat for Cu-Fe in the region

of 0.4 to 1.5°K comes from the middle portion of the probability distribution, which is approximately independent of the concentration. Therefore, the excess specific heat of Cu-Fe is proportional to the concentration. The major contribution to the specific heat of copper cobalt at about 5°K comes from the wings of the distribution function, and thus the specific heat is proportional to the square of concentration. The results are summarized in Table II. The value for  $JS^2$  used for Cu-Mn is about 26°K, and all other values of  $JS^2$  are compared to that of copper-manganese and are listed in the last column of Table II. The low-temperature specific heat was calculated for a fixed value of  $JS^2$  and several concentrations. The results are shown in Fig. 3. The calculations were performed using the  $T=0$  probability distribution. However, using both terms in Eq. (4.2) would result in a somewhat larger specific heat at higher temperatures. The comparison between theory and experiment in Cu-Fe has been made previously,<sup>4</sup> showing good agreement in the low-temperature low-concentration range. For higher temperatures, the Cu-Fe excess specific heat is not proportional to the square of the iron concentration as predicted from the simple  $T=0$  probability distribution. At this point, we cannot make any definite comments on why this discrepancy occurs. One possible reason is that there is an additional contribution to the specific heat arising from a different mechanism, which may be greater than the cooperative magnetic specific heat for these very low concentrated alloys, particularly since the temperature is such that little spin entropy remains in the magnetic system.

The data on gold-iron<sup>24</sup> are again in agreement with

<sup>24</sup> L. T. Crane (private communications). I am grateful to Dr. Crane for communicating his data to me prior to publication.



our theory. At  $T=1.5^\circ\text{K}$ ,  $\Delta C_v/T$  is independent of the concentration and is proportional to the concentration for somewhat higher temperatures. The Cu-Co data for low concentrations are proportional to the square of the concentration; however, a detailed quantitative comparison of the experimental and theoretical results for Cu-Co, over the whole temperature range, becomes difficult for the following reasons: (a) The value of  $JS^2$  has to be estimated from the  $T=0$  intercept of  $\Delta C_v/T$ , and for this case the experiments were not performed at sufficiently low temperatures to get a good estimate of  $JS^2$ . (b) The  $T=0$  probability distribution should be corrected for these higher temperatures using Eq. (4.4). (c) The specific heat of Cu-Co is quite sensitive to the particular treatment to which the material is exposed, as was pointed out previously.<sup>10,11</sup>

Up to the present time, we have considered the Ising model, i.e., only up and down orientations of the spins. The specific-heat results obtained in Fig. 4 are therefore valid for a spin- $\frac{1}{2}$  system. For a spin  $S$ , there may be  $2S+1$  orientation of the impurity in its effective molecular field  $H_0$ . As a result of this,  $\tanh\beta H_0$  in Eq. (4.1) should be replaced by a Brillouin function in Eq. (4.2). The  $T=0$  intercept of  $\Delta C_v/T$  is still inversely proportional to  $JS^2$ ; however, a larger value of  $JS^2$  is necessary to obtain the *same intercept* in  $\Delta C_v/T$  as in the Ising case. Also, for a fixed intercept of  $\Delta C_v/T$ , the specific heat has a smaller decrease as a function of temperature than for the spin- $\frac{1}{2}$  case. This introduces an additional parameter into the specific-heat calculations and results in a quantitative change in  $\Delta C_v$  as a function of  $T$ .<sup>24a</sup> However, all the previous qualitative arguments are still valid.

The magnetic susceptibility of these dilute ferromagnets is discussed in Sec. 5 of KB. The important result found there is that the susceptibility exhibits a maximum as a function of temperature. The temperature at which this maximum occurs is approximately proportional to the strength of the  $R$ - $K$  interaction and the concentration. The latter result is in agreement with experiments on iron, manganese, and chromium in gold<sup>12</sup> and manganese in copper.<sup>6</sup>

## 5. MAGNETIC PROPERTIES OF GOLD-IRON

Having discussed the thermodynamic behavior of dilute ferromagnets, we address ourselves to the case of iron impurities in gold. We single out this system since a great deal of interest exists as to its magnetic state. We find that the experiments, which have been hitherto given conflicting interpretations, seem to be consistent with our theory of dilute ferromagnets and our model. The experimental results are as follows.

<sup>24a</sup> Note added in proof. One should use such an argument for the Ag-Mn<sup>22</sup> data where  $\Delta C_v/T$  versus  $T$  for Ag-Mn drops off at a much slower rate than that of Cu-Fe. However, until more experimental data is available a detailed comparison of experiment with theory is not warranted.

Borg, Booth, and Violet<sup>25</sup> (BBV) have described a Mössbauer experiment on gold-rich Au-Fe alloys. They found that the paramagnetic component of the Mössbauer spectrum disappears at temperatures of 2.2 to  $4^\circ\text{K}$ , even at as low a concentration as 0.84% iron in gold. The spectrum also exhibits the typical six-finger hyperfine splitting.<sup>22</sup> At much higher temperatures the paramagnetic component of the spectrum reappears again. Henry<sup>26</sup> has measured the approach to saturation of a 5% concentrated iron in gold at several temperatures. BBV and Henry both concluded that long-range magnetic effects predominate in dilute Au-Fe. Interpreting his result according to a Curie-Weiss law, Henry also indicated that the ordering seems to be ferromagnetic. However, at very low temperatures (1.5 to  $4^\circ\text{K}$ ), his data exhibited a characteristic anti-ferromagnetic behavior in that the magnetization increased with increasing temperature. Others<sup>27</sup> have interpreted BBV's results to indicate that dilute Au-Fe is antiferromagnetic. More recently, however, an alternative point of view was presented by Crangle and Scott.<sup>28</sup> They have measured the magnetization  $M$  of Au-Fe, in applied fields  $H$  up to 17 kG for different temperatures and plotted  $H/M$  versus  $M^2$  for various constant temperatures to find the Curie temperature by a previously derived method.<sup>29,30</sup> Crangle and Scott conclude that no long-range order exists for iron concentrations less than about 11%. Thus, they conclude that short-range effects dominate in dilute gold-iron but give no reason for their origin.

We would like to correlate the above experiments with the specific heat<sup>24</sup> and magnetization<sup>12</sup> measurements on Au-Fe using our model. As outlined before, the very low-temperature specific heat of these systems is inversely proportional to the strength of the RKY potential  $JS^2$ . Thus, we can deduce the value of  $JS^2$  using the  $T=0$  intercept of  $\Delta C_v/T$  in conjunction with Eq. (4.5). This intercept, for Au-Fe, is found from Crane's<sup>24</sup> result to be approximately  $4\text{mJ/deg}^2\text{-mole}$ . Comparing this intercept with that for Cu-Mn<sup>31</sup> gives the value of  $JS^2$  for Au-Fe to be about 1.1 times that of Cu-Mn. The temperature at which the susceptibility is a maximum,  $T_{\text{max}}$ , is proportional to  $JS^2$ , and the impurity concentrations  $c$ . For Cu-Mn,  $T_{\text{max}} \approx 660c^\circ\text{K}$ . Since  $JS^2$  for Au-Fe is about 1.1 times that of Cu-Mn, we roughly estimate that  $T_{\text{max}} \approx 7.2^\circ\text{K}$  for each percent of iron. The experimental value found by Lutes and Schmit<sup>12</sup> is  $8^\circ\text{K}$  for each percent iron.

If we consider  $P(H_0)$  in Fig. 2, and use the value of  $JS^2$  obtained from the low-temperature specific-heat

<sup>25</sup> R. J. Borg, R. Booth, and C. E. Violet, Phys. Rev. Letters **11**, 469 (1963).

<sup>26</sup> W. E. Henry, Phys. Rev. Letters **11**, 468 (1963).

<sup>27</sup> A. Arrott, Bull. Am. Phys. Soc. **9**, 114 (1964).

<sup>28</sup> J. Crangle and W. R. Scott, Phys. Rev. Letters **12**, 126 (1964).

<sup>29</sup> K. P. Belov and A. N. Goryaga, Fiz. Metal. i Metalloved **2**, 3 (1956).

<sup>30</sup> A. Arrott, Phys. Rev. **108**, 1394 (1957).

<sup>31</sup> L. T. Crane and J. E. Zimmerman, Phys. Chem. Solids **21**, 310 (1961).

experiment<sup>24</sup> to calculate  $P(H_0)$  for iron, we find that with 0.8% iron in gold at  $T \approx 2.2^\circ\text{K}$ , about 20% of the impurities are in effective fields  $\mu H < kT$  and 80% in fields  $\mu H \gg kT$  (this latter percentage increases with concentration). Thus, we will observe the six-finger hyperfine spectrum provided the background noise (including that from the 20% of the spins) is not sufficiently large to smear out the hyperfine spectrum. (See Sec. 3.3 for a discussion of this point.) Also, since at  $2.2^\circ\text{K}$  very few spins are in zero-effective fields, the model gives the complete disappearance of the paramagnetic component of the spectrum. We conclude, therefore, that neither the complete disappearance of the paramagnetic spectrum nor the appearance of the six-finger hyperfine-splitting necessarily indicate long-range order. Thus we feel that BBV's experimental results may be consistent with this theory, except that we differ with their conclusion that long-range order exists in very dilute (less than 5% iron) Au-Fe. However, to compare BBV's result with our model in detail, one should analyze the relative intensities associated with the six fingers and compare it to that associated with the noise spectrum.

## 6. DISCUSSION

From the results presented here we conclude that a RKY potential between the magnetic impurities is, to a first approximation, the important interaction in determining the low-temperature cooperative phenomena in localized transition-ion impurities in noble metals. We take exception to this conclusion for the case of Au-Co, where no maximum occurs in the low-temperature magnetic susceptibility,<sup>12</sup> and it is not yet clear whether the anomalous specific heat is of the same nature as that described by our model. Some interesting experiments should further clarify the validity, as well as the shortcomings of the model in the very low-temperature region. Copper-cobalt<sup>11</sup> and Ag-Mn<sup>32</sup> exhibit a dip in  $\Delta C_v/T$  in going towards very low temperatures. It is likely that this dip arises from the dip of  $P(H_0)$  near  $H_0=0$ , as indicated in Fig. 2. However, it is not yet clear whether the dip predicted by our model is sufficient to explain the low-temperature dip in the specific heat. Therefore, it would be very useful to perform low-temperature specific-heat measurements starting from as low a temperature as is practical to higher temperatures, for impurity concentration from 0.1% up to several percent.<sup>32a</sup> At the same

<sup>32</sup> J. De Nobel and F. J. Du Chatenier, *Physica* **25**, 969 (1959).

<sup>32a</sup> Note added in proof. Such a very low-temperature specific-heat measurement should also indicate the behavior of  $P(H)$  near  $H=0$ , and thus give an indication on the validity of the Ising versus Heisenberg model. This point is sufficiently important that we shall examine the validity of the Ising model in the immediate future. Also, a detailed experimental determination of the total entropy of each of these systems would give a useful comparison with theory. Up to now we have only made a rough comparison of the entropy of Cu-Co [L. T. Crane and E. Zimmerman, *Phys. Rev.* **123**, 113 (1961)] as obtained from the integrated area under the specific-heat curve. We used the Ising model and the disagreement between theory and experiment is less than a factor of 2.

time, it would be of interest to find whether  $\Delta C_v$  is proportional to the square of the impurity concentration for more highly concentrated iron impurities in gold (up to several percent). Iron impurities in gold are convenient to study since the solubility of Fe in Au is larger than some other transition-ion impurities in noble metals. It would also be useful to extend the Cu-Co and Au-Fe measurement to  $0.4^\circ\text{K}$ , the lowest temperature at which Franck *et al.*<sup>33</sup> have performed their experiments.

Another set of experiments of interest from the point of view of this model would be a systematic set of Mössbauer experiments on iron impurities in gold, silver, and copper. The interpretation of the Mössbauer experiment in terms of the probability distribution of the effective field is given briefly in Secs. 3 and 5. Correlating the Mössbauer experiments with specific-heat and magnetization measurements is useful for interpreting the magnetic state (order versus disorder) of magnetic impurities in noble metals. Again, we wish to emphasize that a well-defined six-finger hyperfine spectrum from a Mössbauer experiment does not necessarily indicate long-range order.

Also, according to this model, a maximum in the low-temperature magnetic susceptibility in these materials with a positive (or negative) temperature intercept  $T_c^0$  in the inverse magnetic susceptibility does not indicate ferromagnetism (or antiferromagnetism). This is very well demonstrated by the measurement of Kaufman, Pan, and Clark,<sup>34</sup> where the susceptibility intercept changes with the concentration.

## ACKNOWLEDGMENTS

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## APPENDIX 1

In the appendix we show how to calculate the probability distribution of the field  $P(H_0)$  for a particular concentration at  $T=0$ , and the change in  $P(H)$  as a function of temperature. We should keep in mind that the division of the field into  $H_1$  and  $H_2$  given by Eq. (3.1) follows from the partition function. The calculation of  $P(H_2)$  and result (3.3) follow from the statistical model of Margenau.<sup>20</sup> But it is by no means clear how to calculate  $P(H_1)$ , the probability distribution of the field from the "inside" region. In KB, the calculation was made by permitting 0, 1, 2, 3, etc., spins to be located within a radius  $R_c$  from the origin, but in KB we were only interested in the behavior of

<sup>33</sup> J. P. Franck, F. D. Manchester, and D. L. Martin, *Proc. Roy. Soc. (London)* **A263**, 494 (1961).

<sup>34</sup> A. R. Kaufman, S. T. Pan, and J. R. Clark, *Rev. Mod. Phys.* **17**, 87 (1945).

$P(H_0)$  near  $H_0=0$ . In this paper the detailed shape of  $P(H_0)$  over all  $H_0$  is of interest; therefore, more care has to be exercised in the treatment of  $P(H_1)$ . Fortunately, the treatment outlined in KB and the one used here give the specific-heat results which we estimate to be in an agreement with each other to better than 20%. Thus, for the specific-heat calculation, it is not very critical how one treats the "inside" region, provided one adjust the strength of the interaction accordingly. The method outlined below for the treatment of the inside region is consistent with the statistical model<sup>20</sup> and is also easier to handle.

We recall that there are, on the average, about 3.3 spins within the correlation length, one spin at the origin, and 2.3 more. We therefore allow either 1 or 2 or 3 spins to be within the correlation length, each with probability  $\frac{1}{3}$ . (Allowing 3 spins to be within the correlated volume is somewhat arbitrary. Fortunately, the quantitative behavior of  $\Delta C_v$  is not very sensitive to this assumption.) The value of the field at  $r=R_c$  is given by  $H(R_c)=JS^2/R_c^3\equiv T_c$ ; we incorporate the Boltzmann constant in  $T_c$ . We let the impurity be uniformly distributed over the correlated volume. However, for convenience (for machine-calculational purposes) we let the field from a single spin within the correlation length take  $n$  possible values, where the  $k$ th field  $H_k$  is calculated according to the relation  $H_k=JS^2/r_k^3$ , where we take  $r_k$  to be  $(k/n)R_c$ ; thus,  $H_k=[n/k]^3T_c\equiv b_kT_c$ . The probability for the value  $H_k$  is  $P(H_k)=(3r^2\Delta r)/R_c^3$ . But  $\Delta r\approx R_c/n$ , thus  $P(H_k)=(3/n)(r_k/R_c)^2=3k^2n^{-3}$ . However,  $H_k$  may be positive or negative with a probability given by Eq. (4.11) of KB, and  $P(H_k)=l_k(3k^2n^{-3})=a_k$ , where  $l_k=1-\frac{1}{2}(r_k/R_c)^3$  when  $H_k$  is positive and  $\frac{1}{2}(r_k/R_c)^3$  when  $H_k$  is negative. Thus, we calculated the elementary probabilities with a single spin within the correlated volume.

Next, we allow two spins to be located within the

correlation length; then

$$\begin{aligned} a_j &\equiv P(H_j=H_{k_1}+H_{k_2})=(3n^{-3})^2k_1^2k_2^2, \\ H_j &=n^3[k_1^{-3}+k_2^{-3}]T_c\equiv b_jT_c. \end{aligned} \quad (\text{A1.1})$$

For 3 spins we obtain

$$\begin{aligned} a_l &\equiv P(H_l=H_{k_1}+H_{k_2}+H_{k_3})=(3n^{-3})^3k_1^2k_2^2k_3^2, \\ H_l &=n^3[k_1^{-3}+k_2^{-3}+k_3^{-3}]T_c\equiv b_lT_c. \end{aligned} \quad (\text{A1.2})$$

Convolving the probability distribution from the inside region with that of the outside region using Eq. (3.3) gives

$$P(H_0)=\frac{1}{3(2\pi)^{1/2}}\sum_{s=k,j,l}\frac{a_s}{\sigma}e^{-\frac{1}{2}[(H_0-H_s)/\sigma]^2}, \quad (\text{A1.3})$$

and using Eq. (3.4) gives

$$P(H_0)=\frac{1}{3(2\pi)^{1/2}}\sum_{s=k,j,l}\frac{a_s}{\sigma}e^{-\frac{1}{2}[H_0/\sigma-b_s]^2}, \quad (\text{A1.4})$$

where  $k$ ,  $j$ , and  $l$  take values from 1 to  $n$ . Note that  $a_s$  and  $b_s$  are independent of the strength of the interaction, the concentration, and the temperature. We find that, for any concentration,

$$P(H_0=0)\approx[1/(2\pi)^{1/2}\sigma](0.25). \quad (\text{A1.5})$$

The change in  $P(H_0)$  as a function of temperature is approximately

$$\begin{aligned} \frac{\partial P(H_0)}{\partial \beta} &\approx \frac{1}{3(2\pi)^{1/2}\sigma}\left(\frac{\partial \sigma}{\partial \beta}\right) \\ &\times \sum_{s=k,j,l} a_s \{e^{-\frac{1}{2}(H/\sigma-b_s)^2} \\ &\times [(H/\sigma)(H/\sigma-b_s)-1]\}, \end{aligned} \quad (\text{A1.6})$$

where  $\sigma(\beta)$  is given by Eq. (3.3) with  $R_c$  replaced by  $R_c(\beta)$  as given by Eq. (2.12).