Contribution of giant spin clusters to the resistivity, neutron-scattering cross section, and specific heat in alloys: Application to Ni-Cu†*

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A simple model for a nondilute alloy containing giant spin clusters is used to calculate the spin contribution to the resistivity, the neutron cross section, and the specific heat C_V. The model is expected to be applicable to Ni-Cu alloys near the critical concentration for ferromagnetism. Intracluster interactions are treated exactly using a near-neighbor Heisenberg exchange interaction. Intercluster interactions are treated within the molecular-field approximation. It is assumed that in paramagnets there is a weak local field, which derives from the magnetic-anisotropy energy. Reasonable semiquantitative agreement with resistivity, elastic neutron scattering, and low-temperature specific-heat measurements on Ni-Cu for a range of concentrations and temperatures is obtained if the average cluster contains 50 Ni spins and if a Ni atom has a spin when eight or more of its near neighbors are also Ni. It is found that the anomalous temperature dependence of the resistivity, which behavior is common to a variety of alloy systems, can be accounted for using the present theory if the Fermi wave vector times the lattice spacing is less than $\simeq 2$. The previously unexplained behavior of the elastic neutron cross section in paramagnetic alloys can also be understood within this theoretical framework. In contrast to earlier discussions, it is shown that the spin contribution to C_V is not temperature independent; in ferromagnetic alloys this contribution is found to increase with increasing temperature and in paramagnetic alloys it decreases with temperature. It is believed that this temperature dependence has, in the past, been incorrectly attributed to the electronic contribution to the specific heat. The validity of previous suggestions that the specific-heat and neutron-scattering measurements on these alloys probe different spin clusters is also questioned.

I. INTRODUCTION

In the past few years there has been considerable progress toward a theoretical understanding of the electronic properties of nondilute alloys. The coherent-potential approximation[1] which focuses on the configuration-averaged alloy has been particularly useful for calculating some alloy properties such as the electronic density of states[2] and the uniform static spin susceptibility.[3] However, it is not suitable for calculating properties that are sensitive to local inhomogeneities in the alloy concentration. It is believed that these local inhomogeneities may be extremely important in understanding the observed behavior of the resistivity and neutron-scattering cross section in alloys such as Ni-Cu[4] and possibly Ni-Rh in which the magnetic Ni atoms (which are presumably a small fraction of the total number of Ni atoms at Ni concentrations near 50 at.%) appear to be in reasonably well-separated clusters containing roughly 50 spins.[5] The existence of these giant spin clusters is consistent with the interpretation of neutron-scattering[5] and low-temperature specific-heat experiments.[6] The clusters occur in highly Ni-rich regions and presumably originate from local environmental effects: a Ni atom has a magnetic moment if somewhere between 8 and 12 of its near neighbors are also Ni atoms.[4,5,7] This feature makes these Ni-based alloys ideal systems in which to study clustering effects, since the isolated Ni or Ni pairs carry no moment, and the large clusters dominate the magnetic properties of these alloys.

It is the purpose of the present paper to calculate the resistivity, neutron-scattering cross section and specific heat, using a simple model for a nondilute alloy which is composed of giant spin clusters. The results of these calculations are expected to be applicable to Ni_xCu_{1-x} alloys near the critical concentration: $x = 0.44$. The motivation for these calculations is fivefold:

(i) To explain the anomalous temperature dependence of the resistivity in Ni-Cu alloys.[8] This experimental observation has not yet been explained. In paramagnetic alloys the resistivity decreases with increasing temperature T. There is also a Kondo-like minimum in these (paramagnetic) alloys. In ferromagnetic alloys the resistivity increases monotonically with T.[8] This behavior is common to a variety of other alloy systems.[9]

(ii) To explain the behavior of the elastic neutron-scattering cross section in paramagnetic alloys.[5] The elastic neutron-scattering cross section in paramagnets has a peak in the forward direction similar to that observed in ferromagnetic alloys. However, the behavior of the cross section in paramagnets cannot be explained by the usual Marshall[10] formalism, which is applicable only to ferromagnets at temperatures low compared to the Curie temperature, where the spins are pinned

tightly along one direction.

(iii) To correlate the results of specific-heat, neutron-scattering, and resistivity measurements. It has previously been assumed[4,5] (we believe erroneously) that neutron-scattering and specific-heat measurements probe different spin clusters and are thus independent of one another.

(iv) To put the spin-cluster model formulated by Beck,[6,7] Kouvel,[5] and their co-workers on a firmer theoretical basis.

(v) To predict the results of new experiments such as inelastic neutron cross-section measurements and measurements of the temperature dependence of the specific heat and of the elastic neutron-scattering cross section over a wider temperature range than that explored until this time.

The model used to calculate the various experimental quantities is based on that proposed by Beck[6,7] and Kouvel.[5] While in previous descriptions, the internal dynamics of the spin clusters have not been considered, the present paper focuses on a detailed treatment of intracluster interactions, which must clearly play an important role at the higher temperatures. The usual assumption that all the spins within a cluster are parallel is correct only at sufficiently low temperatures and must become invalid when the temperature approaches that corresponding to the intracluster exchange interaction J^{dd}/k_B, where k_B is Boltzmann's constant. Intracluster interactions are described here by a Heisenberg Hamiltonian. Intercluster interactions are treated within the molecular-field approximation in ferromagnets and are neglected in paramagnets. However, as in previous papers,[6] it is assumed that there is a local magnetic field in paramagnets, which derives from the anisotropy energy. While a localized-spin model for Ni-Cu is not entirely appropriate, it is used here in order to get a "handle" on the internal dynamics of the spin clusters. It is relatively easy to diagonalize the cluster Hamiltonian and thus obtain exact results for the spin-spin correlation functions. An itinerant model lends itself most easily to Hartree-Fock calculations which only approximate the static correlation functions and which cannot be applied to investigations of the spin dynamics of the clusters. It should be noted that a localized-spin model for Ni-Cu is purely phenomenological. However, it will be shown later that within this model semiquantitative agreement with experiment is possible. In addition, a localized-spin model has been successful[11] in explaining the temperature dependence of the resistivity near the Curie temperature in pure Ni.

The present model for a disordered spin system should be contrasted with that of Klein and Brout.[12] In the present work local environmental effects play an important role: an isolated Ni atom does not have a moment; the magnetic spins are clustered and the clusters reasonably well isolated from one another.[13] It is then possible to treat the interaction between two spins on a different basis according to whether they are in the same cluster or not. In the model discussed by Klein and Brout (which is appropriate for alloys such as dilute *Cu*Mn) all the spins are treated on an equal basis and interact with one another via a long-ranged interaction which is very much weaker than the short-ranged d-d exchange interactions used here to describe the intracluster spin dynamics.

In comparing the calculated values for the low temperature specific heat, resistivity, and neutron-scattering cross section with experiments on Ni-Cu several other assumptions are made for simplicity only. (i) The Ni atoms are assumed to have a spin of $\frac{1}{2}$. This corresponds to exactly 1 d hole per magnetic Ni atom, which is not too unreasonable if hybridization effects are neglected. (ii) The Ni spins within a cluster are assumed to be in the most closely packed configuration on a face-centered-cubic (fcc) lattice. Thus no cluster configuration averaging is performed. As a result of the tendency to cluster magnetically[7] it is clear that the spins will be distributed rather compactly.[13] (iii) All clusters are assumed to contain exactly 50 atoms. This number is consistent with neutron-scattering measurements.[5] While it is possible to consider fluctuations in the size of the clusters, this is not necessary if only semiquantitative agreement with experiment is expected. In view of the number of simplifications necessary in order to make the problem tractable, it does not seem reasonable to introduce unnecessary complications. (iv) All clusters are assumed to be in the same local magnetic field. Thus, for the same reason as in (iii), fluctuations in the local field are neglected.

The number of Ni near neighbors required for a given Ni atom to have a moment is taken to be eight.[14] This number is consistent with previous estimates[7] and completely determines the concentration of clusters in the alloy. Using assumption (iii) above, it follows that the cluster concentration is $xf(x)/50$, where x is the Ni concentration and $f(x)$ is the probability that at this concentration a Ni atom will have eight or more Ni near neighbors. The cluster concentration is of the order of tenths of a percent near $x = 0.5$, which is in agreement[5] with previous estimates; however, in contrast to previous treatments[5,6] it is not a free parameter of the problem.

It is shown that in paramagnetic alloys the spin-disorder resistivity ρ decreases with increasing temperature providing the Fermi wave vector times the lattice constant ($k_F a$) is less than ≈ 2.0 in fcc lattices and the spin configuration within a cluster is

reasonably compact. The importance of the lattice parameter in determining the behavior of the resistivity is fairly easy to see. In the (rather unphysical) limit $k_F a \ll 1$, when the de Broglie wavelength of the electron is long compared to the separation between the spins, interference effects play an unimportant role in the cross section for the scattering of an electron from a cluster of N spins. For $k_B T \ll J^{dd}$, as the cluster tumbles about, the intracluster exchange interactions keep the spins aligned, and the electron scattering cross section is proportional to $NS(NS+1)$, where S is the spin of a magnetic atom. When $k_B T \gg J^{dd}$ the individual spins move in an uncorrelated way and scatter independently; the cross section is then proportional to $NS(S+1) \ll NS(NS+1)$, if N is large. Thus when $k_F a$ is small, the resistivity will decrease with increasing temperature. In comparing the theory with experiments it is assumed that in the resistivity form factor the quantity $(k_F a)$ is a free parameter. This is reasonable in view of the approximate nature of the model. Good semiquantitative agreement with experiment is obtained for $k_F a = 1.0$ (this should be compared with the value 2.28 obtained in the free-electron approximation with one conduction electron per atom) and for a conduction-electron localized-spin exchange constant J^{sd} of roughly 10 eV Å^3.

It is also shown that if terms of third order in J^{sd} are included in calculating the transition rate for the scattering of conduction electrons from the spin clusters, a Kondo-like[15] minimum in the resistivity can appear at low temperatures. However, as the cluster size increases, this minimum is suppressed relative to that obtained when the cluster is replaced by a single spin of the same magnitude. A low temperature minimum in the resistivity has been experimentally observed.[8]

In analyzing the low-temperature specific-heat C_V experiments on Ni-Cu, it is found that the cluster contribution to the specific heat is probably not temperature independent, as has been assumed previously,[6] but that in ferromagnetic alloys C_V increases slowly with increasing temperature while in paramagnets C_V decreases somewhat more rapidly with temperature. However, the "anomaly" observed by Schroeder,[6] which consists of an upturn in C_V/T at low temperatures, is reproduced in the present theory. Our results may explain why Robbins *et al.*[6] were forced to invoke a rather rapid decrease in the electronic contribution to the specific heat in going from the ferromagnetic to the paramagnetic concentration regimes to explain their C_V experiments. This assumption is not necessary if the spin contribution to C_V is taken to be properly temperature dependent in the manner described here. It should also be remarked that the low-temperature specific heat per cluster is found to be an appreciable fraction of k_B even for clusters which appear to be ferromagnetically pinned (i.e., for which $k_B T/\mu_B H \ll 1$, where $\mu_B H$ is the Zeeman splitting and H is the effective field on the cluster). It is therefore not correct to state that the specific heat measures only the number of free paramagnetic clusters.[4]

In agreement with experiment, the calculated elastic neutron-scattering cross section $d\sigma/d\Omega_\kappa$ in paramagnetic Ni-Cu exhibits a peak in the forward direction. The neutrons are shown to scatter from spin fluctuations in the paramagnetic state and, as in the ferromagnetic alloys, the width of the peak reflects the size of the spin clusters. It should thus be noted that, contrary to previous suggestions,[5] clusters which are *not* ferromagnetically pinned will contribute to the elastic neutron-scattering cross section. It is found, however, that the contribution of spin fluctuations is relatively unimportant at $T = 4$ K in *ferromagnetic* alloys slightly above the critical concentration and that the main contribution in these alloys to the cross section comes from the usual Marshall term,[10] as has been assumed in the analysis of Hicks *et al.*[5]

The remainder of the paper is divided into four sections. In Sec. II the model Hamiltonian is discussed, and the Born approximation used to obtain general expressions for the electrical resistivity ρ and the neutron cross section $d^2\sigma/d\Omega_\kappa d\omega$. An equation for C_V is also given. In paramagnetic alloys the resistivity and neutron cross section can be obtained by summing up contributions arising from scattering by spin fluctuations from each individual cluster. In ferromagnetic alloys there are additional contributions to ρ and $d^2\sigma/d\Omega_\kappa d\omega$ which arise because the average spin in the alloy is nonzero.

In Sec. III the contribution to ρ, C_V, and $d^2\sigma/d\Omega_\kappa d\omega$ arising from a single cluster of N atoms in the absence of a magnetic field is obtained. The discussion in this section is appropriate primarily to paramagnetic alloys at temperatures above ≈ 1 K. Numerical examples are discussed for small N. A perturbation theoretic calculation of ρ which contains terms of third order in J^{sd} is outlined in Sec. III C. In Sec. IV, the contribution to ρ, C_V, and $d^2\sigma/\Omega_\kappa d\omega$ arising from a single cluster in the presence of a field is considered. This discussion is applicable to ferromagnetic alloys and, for the purposes of low-temperature C_V measurements, to paramagnetic alloys. It is shown that, for alloys near the critical concentration and at low temperatures, analytical expressions for the resistivity, neutron cross section, and specific heat can be obtained for arbitrary N. These are evaluated numerically in Sec. IV B. Finally, in Sec. V the results of Secs. III and IV are applied to Ni-Cu alloys. Good semiquantitative agreement with experiment is obtained for a range of concentrations and temperatures.

II. THEORETICAL EXPRESSIONS FOR ELECTRICAL RESISTIVITY, NEUTRON-SCATTERING CROSS SECTION, AND SPECIFIC HEAT

The model Hamiltonian that describes the conduction-electron–localized-spin system in a random alloy containing spin clusters is

$$\mathcal{H} = -2\sum_{i,j} J^{dd}\vec{S}_i\cdot\vec{S}_j - \mu_B\sum_i \vec{H}\cdot\vec{S}_i - \sum_{i,e} J^{sd}\vec{S}_i\cdot s_e\delta(\vec{R}_i-\vec{R}_e), \tag{2.1}$$

where $\vec{S}_i$ denotes the localized (d) spin at the site $\vec{R}_i$ and $\vec{s}_e$ the conduction electron (s) spin. The first term in the Hamiltonian represents the ferromagnetic ($J^{dd}>0$) interaction between two localized near-neighbor spins; the second term represents the interaction between the d spin and a magnetic field $\vec{H}$, which may vary spatially. Here μ_B is the Bohr magneton. Finally, the last term in Eq. (2.1) represents the interaction between the conduction electrons and the localized spins. The exchange constant J^{sd} may have either sign. As a result of local environmental effects, the spins are segregated into separate clusters. Because J^{dd} is a near-neighbor exchange constant, it then follows that the first term describes intracluster interactions only. Intercluster interactions are included in the field $\vec{H}$, which is assumed to be constant within a cluster. This magnetic field which is the sum of the anisotropy field and the internal molecular field which results from ferromagnetic alignment of the spin clusters, will be discussed in detail in Sec. V. For simplicity the d spins are assumed to have a spin magnitude of $\frac{1}{2}$ and potential scattering effects are neglected. The only circumstance under which potential scattering effects are not ignorable, for the present purposes, is in calculations of the resistivity in ferromagnetic alloys. This will be discussed in detail below.

An expression for the contribution to the resistivity from spin-disorder scattering can be obtained[16] from the linearized Boltzmann equation in its variational form. Using the Born approximation to evaluate the transition rate $W(\vec{k}\sigma\rightarrow\vec{k}'\sigma')$ at which conduction electrons of wave vector $\vec{k}$ and spin σ are scattered from the localized spins into final states of wave vector $\vec{k}'$ and spin σ', the resistivity can be shown[16] to be

$$\rho = \frac{A_1}{N'}\sum_{i,j}\int_{-\infty}^{\infty} d\omega\frac{\beta\omega}{(e^{\beta\omega}-1)}\int_{-\infty}^{\infty} dt\frac{e^{i\omega t}}{2\pi} \times(4k_F^4)^{-1}\int_0^{2k_F}\kappa^3\,d\kappa\, e^{i\vec{\kappa}\cdot\vec{R}_{ij}} \times\{\langle\langle\vec{S}_i(t)\cdot\vec{S}_j(0)\rangle\rangle_{av}-\langle\langle\vec{S}_i\rangle\rangle_{av}\cdot\langle\langle\vec{S}_j\rangle\rangle_{av}\}. \tag{2.2}$$

The Born approximation is, in general, expected to be valid whenever J^{sd} is small compared to the Fermi energy E_F. However, as has been shown in Ref. 15 even for $J^{sd}/E_F\ll 1$, this approximation may break down at sufficiently low temperatures when a Kondo anomaly is present. This will be discussed in more detail in Sec. III C. In obtaining (2.2) both elastic and inelastic scattering processes are included. The symbol $\sum_{i,j}$ refers to a sum over all lattice sites i and j and the constant A_1 is given by[17]

$$A_1 = N'\hbar k_F(mJ^{sd})^2(ne^2\Omega 4\pi\hbar^4)^{-1}. \tag{2.3}$$

In Eq. (2.2)

$$\vec{R}_{ij}\equiv\vec{R}_i-\vec{R}_j, \tag{2.4a}$$

$$\vec{\kappa}\equiv\vec{k}-\vec{k}', \tag{2.4b}$$

and N' denotes the total number of atoms, $\beta=1/k_BT$ and k_F is the Fermi wave vector. The angular brackets $\langle\,\rangle$ around the spin operators represent a statistical average over a density matrix for a given spatial arrangement of the spins, while the quantity $\langle\,\rangle_{av}$ denotes that an average is taken over all possible spin configurations. Thus the quantity $\langle\langle\vec{S}_i\rangle\rangle_{av}$ represents the average of the expectation value, $\langle\vec{S}_i\rangle$, of $\vec{S}_i$, over all alloy configurations and is independent of i. The term in Eq. (2.2) involving the product $\langle\langle\vec{S}_i\rangle\rangle_{av}\cdot\langle\langle\vec{S}_j\rangle\rangle_{av}$ will not contribute to ρ. However, as in Refs. 11 and 17, it is written here for convenience. In Eq. (2.3) m is the electron mass, n is the number of conduction electrons per unit volume, and Ω is the crystal volume.

The cross section per atom for the scattering by the localized spins of neutrons of wave vector $\vec{k}$ into states of wave vector $\vec{k}'$ is[10]

$$\frac{d^2\sigma}{d\Omega_\kappa d\omega} = \frac{A_2}{N'}\sum_{i,j}\sum_{\alpha,\beta}(\delta_{\alpha\beta}-\hat{\kappa}_\alpha\hat{\kappa}_\beta)\int_{-\infty}^{\infty}\frac{dt}{(2\pi)}e^{i\omega t} \times e^{i\vec{\kappa}\cdot\vec{R}_{ij}}\{\langle\langle S_i^\alpha(t)S_j^\beta(0)\rangle\rangle_{av}\}, \tag{2.5}$$

where

$$A_2 = [\gamma e^2/(2mc^2)]^2\hbar^{-1}(k'/k)\,|\mathcal{F}(\kappa)|^2. \tag{2.6}$$

In Eq. (2.6) γ is the neutron g factor and $\mathcal{F}(\kappa)$ is the scattering form factor for a single spin. The indices α and β represent Cartesian coordinates.

Finally, the contribution to the specific heat per atom arising from the localized spins is

$$C_V = (N')^{-1}\frac{d\langle E\rangle}{dT}, \tag{2.7}$$

where $\langle E\rangle$ is the expectation value of the energy of the localized spin system.

It is useful to rewrite the quantity in curly brackets in Eq. (2.2) as follows:

$$\{\langle\langle\vec{S}_i(t)\cdot\vec{S}_j(0)\rangle\rangle_{av}-\langle\langle\vec{S}_i\rangle\rangle_{av}\cdot\langle\langle\vec{S}_j\rangle\rangle_{av}\} = [\langle\langle\vec{S}_i(t)\cdot\vec{S}_j(0)\rangle\rangle_{av}-\langle\langle\vec{S}_i\rangle\cdot\langle\vec{S}_j\rangle\rangle_{av}] + [\langle\langle\vec{S}_i\rangle\cdot\langle\vec{S}_j\rangle\rangle_{av}-\langle\langle\vec{S}_i\rangle\rangle_{av}\cdot\langle\langle\vec{S}_j\rangle\rangle_{av}]. \tag{2.8}$$

As discussed in connection with Eq. (2.1), it is assumed throughout this paper that the motion of the spins in different clusters is uncorrelated. Thus $\langle \vec{S}_i(t) \cdot \vec{S}_j(0) \rangle = \langle \vec{S}_i \rangle \cdot \langle \vec{S}_j \rangle$ if i and j are not in the same cluster; the contribution to ρ from the first two terms on the right-hand side of Eq. (2.8) can be obtained by summing up the contributions from each individual cluster. The sum over lattice sites i and j of the first two terms in Eq. (2.8) may then be written as

$$\sum_N \sum_\lambda \int dH\, \mathcal{P}_\lambda(N) Q(H) \sum_{i,j}{}' \times \{ \langle \vec{S}_i(t) \cdot \vec{S}_j(0) \rangle - \langle \vec{S}_i \rangle \cdot \langle \vec{S}_j \rangle \} e^{i\vec{\kappa} \cdot \vec{R}_{ij}}, \quad (2.9)$$

where the factor $e^{i\vec{\kappa} \cdot \vec{R}_{ij}}$ that appears in ρ is also included. Here $\mathcal{P}_\lambda(N)$ represents the probability that a cluster containing N atoms in a configuration specified by λ occurs in the alloy and $Q(H)dH$ is the probability that the cluster is in a local field of magnitude H. Here $\sum'_{i,j}$ refers to a sum over lattice sites within a cluster with parameters N, λ, and H. $\mathcal{P}_\lambda(N)$ is normalized so that

$$\sum_N \sum_\lambda N P_\lambda(N) = N^s, \quad (2.10)$$

where N^s is the number of spins in the alloy and $Q(H)$ satisfies the equation

$$\int dH\, Q(H) = 1. \quad (2.11)$$

The quantity $[\langle \vec{S}_i(t) \cdot \vec{S}_j(0) \rangle - \langle \vec{S}_i \rangle \langle \vec{S}_j \rangle]$ is the spin-spin correlation function for the cluster. The contribution of a single cluster to ρ arising from this term, which represents the scattering by spin fluctuations, is denoted by ρ^{c1} and can be written

$$\rho^{c1} = A_1 Z^{-1} \sum_{i,j}{}' \sum_{m,n} F(2k_F R_{ij}) e^{-\beta E_n} \times [\beta(E_m - E_n)(e^{\beta(E_m - E_n)} - 1)^{-1} \vec{S}_{inm} \cdot \vec{S}_{jmn} - Z^{-1} e^{-\beta E_m} S^z_{inn} S^z_{jmm}]. \quad (2.12)$$

Here Z is the partition function for the cluster, E_m and E_n are the eigenvalues of the cluster Hamiltonian, and the subscript mn on the spin operators refers to matrix elements between the cluster eigenfunctions $|m\rangle$ and $|n\rangle$. Throughout this paper it will be assumed that the direction of the magnetization vector in a ferromagnet is along the $\hat{z}$ axis; hence the z component of $\vec{S}_{inm}$ appears in Eq. (2.12). The resistivity form factor $F(x)$ is defined as

$$F(x) = (4x^{-4})[2x \sin x - (x^2 - 2)\cos x - 2], \quad (2.12')$$

where $F(0)$ is equal to 1. This quantity is obtained by replacing $e^{i\vec{\kappa} \cdot \vec{R}_{ij}}$ by its spherical average $(\sin \kappa R_{ij})/\kappa R_{ij}$ and carrying out the κ integration in Eq. (2.2). The form factor thus obtained is identical to that found in Ref. 11.

The last two terms on the right-hand side of Eq. (2.8) represent an elastic scattering contribution to the resistivity and are nonvanishing only in ferromagnetic alloys where $\langle S_i \rangle \neq 0$. These terms lead also to a finite spin-disorder residual resistivity. In the absence of magnetic clustering they give rise to a Nordheim[18] $c(1-c)\langle S^z \rangle^2 (J^{sd})^2$ term in ρ which decreases to 0 as the temperature approaches the Curie temperature of the alloy T_C from below. Here $\langle S^z \rangle \hat{z} \equiv c^{-1} \langle\langle \vec{S}_i \rangle\rangle_{av}$ is the average z component of the spin of the magnetic atoms and c is their concentration. In ferromagnetic alloys there will be an additional temperature-dependent contribution to the resistivity which arises from the interference between potential and the non-spin-flip portion of the magnetic scattering. When magnetic clustering effects are negligible this yields[19] a term that varies as $-2c(1-c)\langle S^z \rangle^2 \langle J^{sd} \rangle^2$. The net effect of the Nordheim term and ρ^{c1} is a contribution to the resistivity which increases (very slightly for large cluster sizes) as $T \to T_C$. The interference term also increases as $T \to T_C$.

It is useful to rewrite the quantity in curly brackets in the neutron-scattering cross section [Eq. (2.5)] using an equation analogous to Eq. (2.8):

$$\{\langle\langle S^\alpha_i(t) S^\beta_j(0) \rangle\rangle_{av}\} = [\langle\langle S^\alpha_i(t) S^\beta_j(0) \rangle\rangle_{av} - \langle\langle S^\alpha_i \rangle\rangle \langle\langle S^\beta_j \rangle\rangle_{av}] + [\langle\langle S^\alpha_i \rangle\rangle \langle\langle S^\beta_j \rangle\rangle_{av} - \langle\langle S^\alpha_i \rangle\rangle_{av} \langle\langle S^\beta_j \rangle\rangle_{av}] + \langle\langle S^\alpha_i \rangle\rangle_{av} \langle\langle S^\beta_j \rangle\rangle_{av}. \quad (2.13)$$

Since $\langle S^\alpha_i(t) S^\beta_j(0) \rangle = \langle S^\alpha_i \rangle \langle S^\beta_j \rangle$ if i and j are not in the same cluster, the contribution to $d^2\sigma/d\Omega_\kappa d\omega$ from the first two terms in Eq. (2.13) may be obtained by adding up the contribution from each cluster separately. This contribution (for a single cluster) is denoted $d^2\sigma^{c1}/d\Omega_\kappa d\omega$ and can be written

$$\frac{d^2\sigma^{c1}}{d\Omega_\kappa d\omega} = A_2 Z^{-1} \sum_{i,j}{}' G(\kappa R_{ij}) \sum_{\alpha,\beta} (\delta_{\alpha\beta} - \hat{\kappa}_\alpha \hat{\kappa}_\beta) \times \sum_{n,m} e^{-\beta E_n} \{ S^\alpha_{inm} S^\beta_{jmn} \delta(\omega - E_n + E_m) - Z^{-1} \delta_{\alpha z} \delta_{\beta z} e^{-\beta E_m} S^z_{inm} S^z_{jmm} \delta(\omega) \}, \quad (2.14)$$

where the factor $e^{i\vec{\kappa} \cdot \vec{R}_{ij}}$ in Eq. (2.4) has been replaced[10] by its spherical average $G(\kappa R_{ij})$:

$$G(\kappa R_{ij}) \equiv (\sin \kappa R_{ij})/\kappa R_{ij} \quad (2.15)$$

and E_n is the energy of the nth eigenfunction of the cluster.

These terms will play an essential role in the subsequent discussion. They contribute to both the elastic and the inelastic neutron-scattering cross section in ferromagnetic and paramagnetic alloys. It is important to note that any theory which describes the cluster by a Hartree-Fock approximation applied to an itinerant or modified Anderson model[4] will not yield this fluctuation term since such a picture requires the local moments to be

"pinned" along a fixed spatial direction. In paramagnetic alloys and in ferromagnetic alloys at temperatures near the Curie temperature, where the spins are not pinned, it is thus preferable to use a localized- rather than an itinerant-electron-spin Hamiltonian to explain neutron-scattering cross-section measurements.

The third and fourth terms on the right-hand side of Eq. (2.13) are nonvanishing only in ferromagnetic alloys and contribute only to elastic diffuse scattering, i.e., to scattering away from the Bragg peaks. These two terms, which are absent in pure metals, have been studied by Low and Collins[20] and by Marshall.[10] Their contribution to the cross section will be called the Marshall term. In previous analyses[5] of the elastic neutron-scattering cross section, it has been assumed that the entire contribution to the cross section comes from these terms. In the present paper their contribution to $d^2\sigma/d\Omega_\kappa d\omega$ will be analyzed following Ref. 5 and will be discussed in more detail in Sec. V. The last term on the right-hand side of Eq. (2.13) contributes to Bragg scattering. (Note that $\langle\langle S_i^\alpha\rangle\rangle_{av}$ is independent of site index i.) This term which has not been of interest to experimentalists and which contains no information about the detailed structure of the spin clusters will be neglected here.

Because it is assumed that the spin clusters do not interact (except within the molecular-field approximation), the contribution to the energy $\langle E\rangle$ from the clusters is additive. The contribution to the specific heat from a single cluster can be written in terms of the cluster eigenenergies E_n as

$$C_V^{cl} = k_B\left[Z^{-1}\sum_n \beta^2 E_n^2 e^{-\beta E_n} - Z^{-2}\left(\sum_n \beta E_n e^{-\beta E_n}\right)^2\right]. \tag{2.16}$$

III. EXPLICIT RESULTS FOR CLUSTERS IN ZERO MAGNETIC FIELD

A. Some general theoretical results

It is, in general, difficult to obtain analytical expressions for the resistivity, neutron cross section, and the specific heat. However, at very low temperatures ($k_BT \ll J^{dd}$) and at very high temperatures ($k_BT \gg J^{dd}$) some simple exact results can be obtained. Since resistivity measurements have been performed[8] over a wide temperature range, it is of interest to examine in detail the behavior of ρ in the two extreme temperature regimes. A low-temperature limit of $d^2\sigma/d\Omega_\kappa d\omega$ will also be discussed. The special case where the magnetic field H = 0 is examined first. This special case is appropriate to the discussion of the resistivity and neutron cross section above ≈ 1 K in paramagnetic alloys since, as will be shown later, the anisotropy field is expected to be small compared to 1 K. It is also relevant to discussions of the specific heat in paramagnetic alloys for temperatures considerably above the anisotropy field temperature. It follows that in zero field $\langle S^\alpha\rangle = 0$ and therefore the only contribution to the resistivity and neutron-scattering cross section arises from ρ^{cl} [Eq. (2.12)] and $d^2\sigma^{cl}/d\Omega_\kappa d\omega$ [Eq. (2.14)]. Both the Nordheim and the interference terms in ρ are zero, as is the Marshall term in $d^2\sigma/d\Omega_\kappa d\omega$.

As stated in Sec. I, the temperature dependence of ρ in paramagnetic alloys is governed by the parameter k_Fa. The contribution to ρ^{cl} arising from the autocorrelation function $\langle\vec{S}_i(t)\cdot\vec{S}_i(0)\rangle$ [see Eq. (2.2)] increases with increasing temperature and approaches the value $\langle\vec{S}_i^2\rangle = S(S+1)$ as $T\to\infty$. On the other hand, the contribution to ρ^{cl} arising from the cross correlation function $\langle\vec{S}_i(t)\cdot\vec{S}_j(0)\rangle$ with $i\neq j$ will decrease toward 0 with increasing T. These latter correlation functions are weighted by a lattice-parameter-dependent form factor in the expression for the resistivity. Hence the resistivity will decrease with increasing temperature only if the contribution of the cross-correlation terms in the resistivity dominates that of the autocorrelation terms. These remarks will now be made more explicit. In Sec. IV it will be shown that an analytical expression for ρ^{cl} for $k_BT \ll J^{dd}$ in the limit of zero field is $\rho^{cl}(0)$, where

$$\rho^{cl}(0) = (A_1/4)(N+2)N^{-1}{\sum_{i,j}}' F(2k_FR_{ij}). \tag{3.1}$$

This equation can be used to determine the residual spin-disorder resistivity in paramagnetic alloys. For ferromagnetic alloys near the critical concentration it can be used to obtain the value of ρ^{cl} at $T = T_C$ where T_C is the Curie temperature of the ferromagnetic alloy. Here N is the number of spins in the cluster and $F(2k_FR_{ij})$ is defined in Eq. (2.12′). It follows from Eq. (2.12) that as $T\to\infty$, ρ^{cl} approaches $\rho^{cl}(\infty)$, where

$$\rho^{cl}(\infty) = (A_1/4)3N. \tag{3.2}$$

In the high temperature limit, when $k_BT \gg J^{dd}$, the spins within a cluster scatter the electrons incoherently so that the cross section is proportional to $N\langle\vec{S}_i^2\rangle = N\frac{1}{2}(\frac{1}{2}+1)$.[21] In paramagnetic alloys the spin-disorder resistivity will then decrease with increasing temperature, as is the case in Ni-Cu alloys,[8] provided

$$(N+2)N^{-1}{\sum_{i,j}}' F(2k_FR_{ij}) > 3N. \tag{3.3}$$

If this inequality is not satisfied, the resistivity increases with increasing temperature. For the fcc lattice, because the atoms are closely packed, the inequality in Eq. (3.3) is easier to satisfy than for simple-cubic lattices.

Finally, in the absence of a magnetic field the sum over α and β in Eq. (2.14) can be performed to yield

$$\frac{d^2\sigma_{cl}}{d\Omega_\kappa d\omega} = \tfrac{2}{3}A_2 Z^{-1} \sum_{i,j}{}' \sum_{m,n} G(\kappa R_{ij}) e^{-\beta E_n} \vec{S}_{inm} \cdot \vec{S}_{jmn} \times \delta(\omega - E_n + E_m), \quad (3.4)$$

and for $k_B T \ll J^{dd}$, it will follow from the results of Sec. IV that the elastic scattering contribution to the neutron cross section is

$$\frac{d^2\sigma^{cl}(0)}{d\Omega_\kappa d\omega} = 2A_2 Z^{-1}(N+2)(12N)^{-1} \sum_{i,j}{}' G(\kappa R_{ij})\delta(\omega). \quad (3.4')$$

The high temperature ($k_B T \gg J^{dd}$) limit of Eq. (3.4), which can easily be written down, in analogy with Eq. (3.2), is not, in general, obtainable experimentally.

B. Numerical examples

In the paramagnetic case, except when $k_B T \ll J^{dd}$ and $k_B T \gg J^{dd}$, ρ^{cl}, $d^2\sigma^{cl}/d\Omega_\kappa d\omega$, and C_V^{cl} must be numerically evaluated. The contribution of a single cluster of N atoms to the first term in $\mathcal{H}$ [Eq. (2.1)] was diagonalized on a computer for all possible cluster configurations on a simple-cubic (sc) lattice and for $N = 2$, 3, and 4. A simple-cubic lattice was chosen at this stage in order to simplify the calculations. The results of the calculations in this section are qualitatively insensitive to whether an sc or an fcc lattice is used. It should be pointed out that all calculations in Sec. V, which compare the theory with experimental data on Ni-Cu alloys, are appropriately based on an fcc lattice. It was possible to obtain exact expressions for the resistivity, neutron-scattering cross section, and specific heat over the entire temperature range. Because the dimension of the cluster Hamiltonian for spin-$\frac{1}{2}$ particles is 2^N, it is difficult, as well as costly, to obtain eigenfunctions for clusters with $N \gtrsim 6$. The eigenfunctions may easily be grouped into multiplets using the rules of addition of angular momenta; the ground-state degeneracy is $(N+1)$.

Table I lists the eigenenergies for clusters of 2, 3, and 4 atoms in all possible configurations which give distinct eigenenergies. The quantity in parentheses after each energy is the degeneracy of the level. The Roman numerals I, II, and III correspond to the different configurations which will be discussed in connection with Fig. 2.

In Fig. 1 is plotted the spin-disorder contribution to the resistivity divided by $\rho_0 = \frac{1}{4}A_1$ as a function of $k_B T/J^{dd}$ for a cluster of two spins. For $k_F a = 0.5$ the resistivity decreases with increasing temperature. For $k_F a = 1.0$ there is a slight, but almost inappreciable, maximum in ρ. Above this maximum ρ decreases. Finally, if $k_F a = 1.5$ the resistivity increases monotonically with increasing T. As is expected, the resistivity is independent of $k_F a$ for $k_B T/J^{dd} \gtrsim 10.0$. These conclusions are consistent with the analytical expressions for ρ^{cl} at $T = 0$ and $T = \infty$ given in Eqs. (3.1) and (3.2). In contrast to the results for an sc lattice, in an fcc lattice even for values of $k_F a = 1.5$, ρ^{cl} at $T = 0$ is larger than ρ^{cl} at $T = \infty$ because, as noted above, the inequality in Eq. (3.3) is more readily satisfied in the fcc lattice than in the sc lattice.

In Fig. 2, ρ^{cl}/ρ_0 is plotted as a function of $k_B T/J^{dd}$ for several different configurations of four spins (denoted by I, II, and III) and for the same three values of $k_F a$ as in Fig. 1. The three configurations whose eigenvalues are listed in Table I are shown schematically in the figure, where the dots represent the position of a spin; the resistivity in each configuration is represented by a dot-dashed line (I), solid line (II), and a dashed line (III). There are four other distinct configurations for $N = 4$ which give rise to slightly different resistivity curves. However, in each of these four cases the Hamiltonian for the configuration is equivalent to that of one of the three configurations that are explicitly shown. The differences between the resistivity in the various configurations are sufficiently small (as can be seen by comparing the dot-dashed, dotted, and solid lines) so that it is not necessary to exhibit the results for all seven of them. As in the case of $N = 2$, ρ^{cl} decreases monotonically with increasing temperature for $k_F a = 0.5$. For $k_F a = 1.0$, the resistivity has a maximum and then decreases and for $k_F a = 1.5$, ρ^{cl} increases, reaches a slight maximum and then decreases slightly with T. In this last

TABLE I. Energy eigenvalues for clusters of 2, 3, and 4 spins (in the three configurations of Fig. 2) in zero field with intracluster exchange constant J^{dd}. Degeneracy of each energy level is indicated in parentheses.

$N=2$	$N=3$	$N=4$ I	$N=4$ II	$N=4$ III
$E_1 = -J^{dd}$ (3)	$E_1 = -2J^{dd}$ (4)	$E_1 = -4J^{dd}$ (5)	$E_1 = -3J^{dd}$ (5)	$E_1 = -3J^{dd}$ (5)
$E_2 = +3J^{dd}$ (1)	$E_2 = 0$ (2)	$E_2 = 0$ (1)	$E_2 = 1.828J^{dd}$ (3)	$E_2 = -J^{dd}$ (3)
	$E_3 = 4J^{dd}$ (2)	$E_3 = 0$ (3)	$E_3 = -.464J^{dd}$ (1)	$E_3 = -J^{dd}$ (3)
		$E_4 = 0$ (3)	$E_4 = J^{dd}$ (3)	$E_4 = 3J^{dd}$ (1)
		$E_5 = +4J^{dd}$ (3)	$E_5 = 3.828J^{dd}$ (3)	$E_5 = 3J^{dd}$ (1)
		$E_6 = +8J^{dd}$ (1)	$E_6 = 6.464J^{dd}$ (1)	$E_6 = 5J^{dd}$ (3)

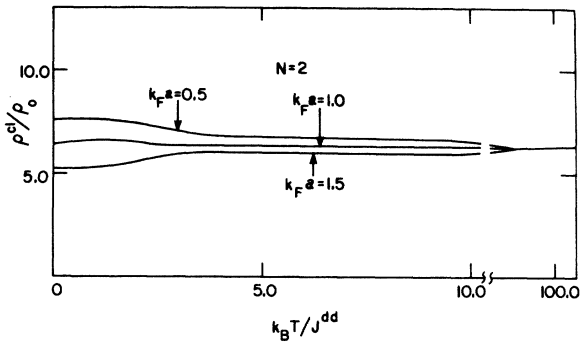

FIG. 1. Contribution of one cluster of 2 atoms to the resistivity in zero magnetic field as a function of temperature, for three values of the parameter $k_F a$. J^{dd} is the intracluster exchange constant and ρ_0 is defined in text. (Note the break in horizontal axis.)

case, as is consistent with Eqs. (3.1) and (3.2), $\rho^{cl}(0)$ is less than $\rho^{cl}(\infty)$. However, for $k_F a = 1.5$ this very slight maximum may be due to computational inaccuracies. For $k_B T/J^{dd} = 6.0$, ρ^{cl}/ρ_0 was found to be 12.3, whereas at $k_B T/J^{dd} = 100.0$, ρ^{cl}/ρ_0 is 12.0. It can be seen from Fig. 2 that for $N = 4$, ρ^{cl}/ρ_0 does not reach the high-temperature limit until $k_B T/J^{dd}$ is greater than 10.0. It can also be seen by comparing Figs. 2 and 4 that as N increases, the resistivity at low temperatures deviates more dramatically from its high-temperature value. This is to be expected on the basis of arguments given in Secs. I and III A, since at low temperatures the scattering of electrons from the cluster is coherent. It should be kept in mind that all of these results for the resistivity are based on the use of the lowest Born approximation, which retains only terms of order $(J^{sd})^2$ in ρ. The Kondo effect for the cluster, if appreciable, will appear first in the terms of order $(J^{sd})^3$ and may modify the behavior of the resistivity at low temperatures. This will be discussed in detail in Sec. III C.

In Fig. 3 is plotted the contribution of a single cluster to the specific heat for $N = 2$ and $N = 4$ as a function of $k_B T/J^{dd}$. The Roman numerals I, II, and III correspond to the same cluster configuration as in Table I. As can be seen, C_V^{cl} has a maximum as a function of $k_B T/J^{dd}$. It should also be noted that for $N = 2$ the peak in C_V^{cl} is much broader and more symmetric than for $N = 4$. However, the qualitative shape of the curves is similar for both values of N.

Because of the difficulty of performing neutron scattering experiments at temperatures of the order of J^{dd} the T dependence of $d^2\sigma^{cl}/d\Omega_\kappa d\omega$ will not be plotted here. The low-temperature ($k_B T \ll J^{dd}$) limit of the cross section is given in Eq. (3.4′) and will be discussed in more detail in Sec. V. The temperature dependence of $d^2\sigma^{cl}/d\Omega_\kappa d\omega$ at arbitrary temperatures can be obtained from Eq. (3.4).

C. Kondo resistivity of a spin cluster

A perturbation theoretic calculation of the transition probability for the scattering of conduction electrons from random noninteracting localized spins contains logarithmically divergent terms at low temperatures.[15] These divergent terms are of third order in the conduction-electron–localized-spin exchange interaction and give rise to a minimum in the resistivity at low temperatures when the exchange constant is negative. Béal-Monod[21] has investigated the way in which the Kondo divergence is modified when the conduction electrons

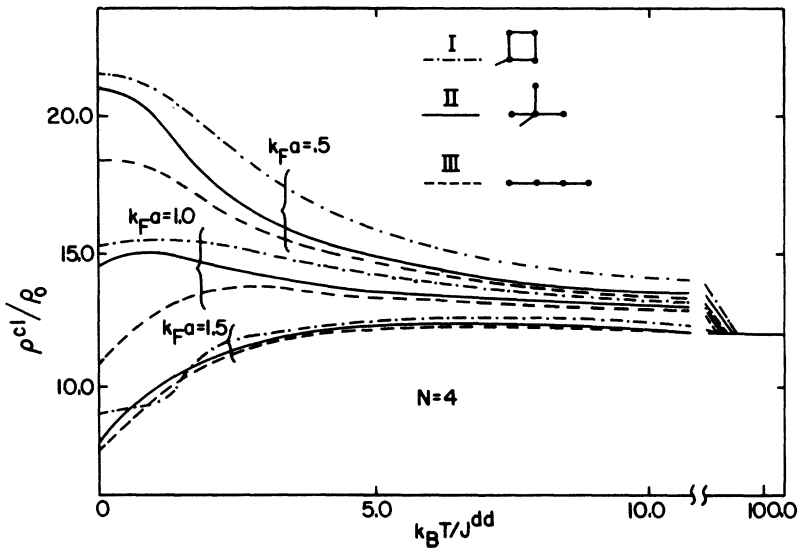

FIG. 2. Contribution of clusters of 4 atoms in zero field to resistivity as a function of temperature, for three values of $k_F a$ and three different configurations (I, II, and III). Horizontal axis is broken above ≈ 10.0 and J^{dd} is intracluster exchange constant.

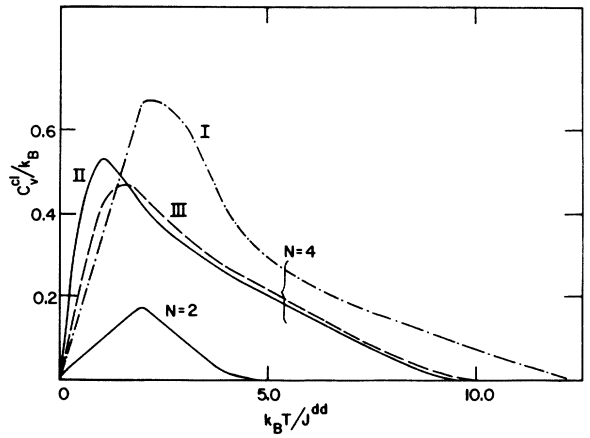

FIG. 3. Temperature dependence of the contribution of clusters of 2 and 4 atoms (in the three configurations of Fig. 2) to specific heat. Clusters are in zero magnetic field and J^{dd} is intracluster exchange constant.

scatter from a pair of interacting localized spins. In this section the transition probability for the elastic scattering of conduction electrons from spin clusters $W(\vec{k}\sigma \to \vec{k}'\sigma')$ is calculated to third order in J^{sd}.[22,23] It will be assumed that $k_BT \ll J^{dd}$. Under these circumstances the spin cluster is in the ground state; all the spins within the cluster are parallel to one another. The conduction electrons scatter elastically from the cluster, which makes transitions from any one of its $(N+1)$-degenerate ground-state energy levels to another. These correspond to rigid rotations of the entire spin cluster.

Following Kondo[15] it can be shown that the transition probability for the scattering of electrons by a cluster of N spins $W(\vec{k}\sigma \to \vec{k}') \equiv \sum_{\sigma'} W(\vec{k}\sigma \to \vec{k}'\sigma')$ is given by

$$\frac{W(\vec{k}\sigma \to \vec{k}')}{\bar{W}(\vec{k}\sigma \to \vec{k}')} = \frac{1}{gN^3} \sum_{i,j}{}' \{ g_{ji}\, e^{i\vec{k}'\cdot\vec{R}_{ij}} e^{i(\vec{k}'-\vec{k})\cdot\vec{R}_{li}} \}\,, \tag{3.5}$$

where $\bar{W}(\vec{k}\sigma \to \vec{k}')$ is the transition probability for the scattering of the conduction electrons by a single (spatially localized) spin of magnitude $S = N(\frac{1}{2})$. This quantity has been calculated by Kondo. The quantity g_{ji} which is the the source of the divergence in ρ at low T is given by

$$g_{ji} = \sum_q f^0(q) e^{i\vec{q}\cdot\vec{R}_{ji}}/(\epsilon_k - \epsilon_q)\,, \tag{3.6}$$

where $f^0(q)$ is the Fermi function, $f^0(q) = \{\exp[\beta(\epsilon_q - \mu)] + 1\}^{-1}$, μ is the chemical potential, and ϵ_q is the energy of a conduction electron of wave vector q; g is defined to be the value of g_{ji} when $\vec{R}_j = \vec{R}_i$.

The quantity g_{ji} has been previously evaluated[21] at temperatures small compared to μ. The contribution of g_{ji} which leads to a divergence in the resistivity is proportional to $[(\sin kR_{ij})/kR_{ij}] \times \ln|k - k_F|$. An order-of-magnitude estimate of the divergent term in ρ can be obtained by replacing $e^{i\vec{k}'\cdot\vec{R}_{ij}}$ and $e^{i\vec{k}\cdot\vec{R}_{ij}}$ by their spherical averages $(\sin k_F R_{ij})/k_F R_{ij}$ and, similarly, $e^{i(\vec{k}'-\vec{k})\cdot\vec{R}_{li}}$ by $(\sin\kappa R_{li})/\kappa R_{li}$ (where $\kappa = |\vec{k} - \vec{k}'|$) in $W(\vec{k}\sigma \to \vec{k}')$. Whenever $j \neq l$ the two exponentials in Eq. (3.5) are averaged separately. When $j = l$ they must be averaged together. It follows that the Kondo resistivity for a spin cluster is approximately given by

$$\rho/\bar{\rho} \approx N^{-3} \sum_{i,j,l} [(\sin k_F R_{ij})/(k_F R_{ij})]^2 \times [F(2k_F R_{li})(1 - \delta_{lj}) + \delta_{ij}]\,, \tag{3.7}$$

where $\bar{\rho}$ is the divergent term in the resistivity (which varies as $\ln T$) arising from a single spin of magnitude $\frac{1}{2}N$ and $F(x)$ is defined in Eq. (2.12′). Equation (3.7) evaluated for the case $N = 2$ is equivalent to the result obtained by Béal-Monod.[21]

The values of the ratio $(\rho/\bar{\rho})$ for several values of N and $k_F a$ for a compact configuration of spins on an sc lattice are shown in Table II. As can be seen, the Kondo minimum arising from a spin cluster is suppressed relative to that arising from a single spin of the same magnitude.[24] This result may be interpreted physically. As in the first Born approximation to the resistivity, there is a suppression of ρ relative to that obtained by scattering from a single point spin. Part of this suppression is represented by the form factor $F(2k_F R_{li})$ (which also appears in the first Born approximation to ρ) and arises because the differential cross section for the scattering of electrons is peaked in the forward direction (for large cluster sizes). Because of the $(1 - \hat{k}\cdot\hat{k}')$ term in the expression for the resistivity [in Eq. (2.2) this term is written in terms of the momentum transfer variable κ] such scattering processes will not contribute to the resistivity. In addition to the form factor $F(2k_F R_{li})$, there is a further suppression of ρ which is contained in the term $[(\sin k_F R_{ij})/k_F R_{ij}]^2$. This term may be viewed as arising partly from the intermediate scattering process in which the conduction electrons are scattered from the incident state $|\vec{k}\rangle$ to the intermediate state $|\vec{q}\rangle$. Because the differential cross section for this scattering process

TABLE II. Ratio of Kondo resistivity of cluster of N spins of magnitude $\frac{1}{2}$ to that of point spin of magnitude $\frac{1}{2}N$ for several values of Fermi wave number k_F times lattice spacing a.

N	$k_F a = 0.5$	$k_F a = 1.0$	$k_F a = 1.5$
10	0.654	0.206	4.9×10^{-2}
20	0.536	0.100	1.63×10^{-2}
30	0.440	5.26×10^{-2}	7.69×10^{-3}
40	0.351	2.93×10^{-2}	4.51×10^{-3}
50	0.294	1.94×10^{-2}	3.15×10^{-3}

is also peaked in the forward direction for large cluster sizes, this leads to an additional suppression of ρ. It can be seen from Eq. (3.5) that as $N \to \infty$, the Kondo divergence of ρ must disappear completely.

IV. EXPLICIT RESULTS FOR CLUSTERS IN FINITE MAGNETIC FIELDS

The expressions for the contribution of a single cluster in a finite magnetic field to the resistivity, neutron cross section, and specific heat have been given in Sec. II. As mentioned in Sec. II, the field is assumed to arise from the magnetic anisotropy and internal molecular fields produced by ferromagnetic alignment of the clusters. In contrast to the zero-field case, the contribution to the various quantities arising from terms involving $\langle S^z \rangle$ are nonvanishing. Hence there will be contributions to the resistivity and neutron cross section in addition to those arising from spin fluctuations. After performing the α and β summations in Eq. (2.14) it follows that[25]

$$\frac{d^2\sigma^{c1}}{d\Omega_\kappa d\omega} = Z^{-1}A_2 \sum_{i,j}{}' \sum_{m,n} G(\kappa R_{ij}) \tfrac{1}{3} e^{-\beta E_n} \times [2S^z_{inm}S^z_{jmn} + 5S^x_{inm}S^x_{jmn}]\delta(\omega - E_n + E_m) - Z^{-2}A_2 \sum_{i,j}{}' \sum_{m,n} G(\kappa R_{ij}) \tfrac{2}{3} e^{-\beta E_n} \times e^{-\beta E_m} S^z_{inn} S^z_{jmm} \delta(\omega) . \quad (4.1)$$

At low temperatures the terms involving $S^x_{inm}S^x_{jmn}$ and $S^z_{inm}S^z_{jmn}$ lead to inelastic and elastic scattering, respectively. As discussed in Sec. II, the latter represents a process for elastic neutron scattering which has not been considered previously in these nondilute alloys.

A. Analytic expressions for the resistivity, neutron cross section, and specific heat at low temperatures

At temperatures low compared to J^{dd} and for fields $\mu_B H \ll J^{dd}$ analytical expressions for ρ^{c1}, C_V^{c1} and $d^2\sigma^{c1}/d\Omega_\kappa d\omega$ can be obtained. Alloys near the critical concentration will satisfy the two conditions $k_B T \ll J^{dd}$ and $\mu_B H \ll J^{dd}$, where H is the molecular field for ferromagnetic alloys and the anisotropy field for paramagnetic alloys. Hence the results presented below will be applicable to ferromagnetic alloys at all temperatures below the Curie temperature of the alloy, T_C, and to paramagnetic alloys at low temperatures. When $k_B T \ll J^{dd}$ the spins within a cluster are parallel and the clusters occupy only the lowest $(N+1)$-nondegenerate levels. If $|l\rangle$ and $|l'\rangle$ are two states within this ground-state manifold which correspond, respectively, to energy eigenvalues of $-(\mu_B H)/2[N+2-2l]$ and $-(\mu_B H)/2[N+2-2l']$ (the zero of energy is unimportant here) then

$$(S^x_{ill'})^2 \equiv (\langle l | S^x_i | l' \rangle)^2 = \tfrac{1}{4}N^{-2}[(N+1)l - l^2]\delta_{|l-l'|,1} \quad (4.2)$$

and

$$S^z_{ill'} \equiv \langle l | S^z_i | l' \rangle = \tfrac{1}{2}N^{-1}[N-(l-1)2]\delta_{l,l'} , \quad (4.3)$$

where $1 \le l \le (N+1)$. In the ground state the eigenvalues of the total z component of angular momentum are given by N times the (diagonal) elements of S^z_i. Substituting these equations in Eqs. (2.12), (2.14), and (2.16), it follows that

$$\rho^{c1} = A_1 N^{-2} \sum_{i,j}{}' F(2k_F R_{ij}) \{ X e^X (e^X - 1)^{-2} \times [N + 2(N+1)(e^{X(N+1)} - 1)^{-1} - 2(e^X - 1)^{-1}] + [e^X (e^X - 1)^{-2} - (N+1)^2 e^{X(N+1)} (e^{X(N+1)} - 1)^{-2}] \}, \quad (4.4)$$

where

$$X = \mu_B H / k_B T . \quad (4.4')$$

In the limit $J^{dd} \gg k_B T \gg \mu_B H$, the expression for ρ^{c1} is given by Eq. (3.1). On the other hand, ρ^{c1} approaches zero when $k_B T \ll \mu_B T \ll \mu_B H$; the clusters are strongly pinned by the magnetic field, and thus the field suppresses scattering from spin fluctuations. The first term in square brackets in Eq. (4.4), which represents inelastic scattering, comes from the x-x and y-y components of the spin-spin correlation function, whereas the second term in square brackets comes from the z-z component and represents elastic scattering. The contribution of each of these three terms can be shown to be equal for $k_B T \gg \mu_B H$.

Similarly, the elastic part of the neutron cross section which derives from the z-z terms in Eq. (4.1) is given by

$$\frac{d\sigma^{c1}}{d\Omega_\kappa} = A_2 N^{-2} \tfrac{2}{3} [e^X (e^X - 1)^{-2} - (N+1)^2 e^{X(N+1)} \times (e^{X(N+1)} - 1)^{-2}] \sum_{i,j}{}' G(\kappa R_{ij}) , \quad (4.5)$$

where the elastic scattering contribution to the cross section is written $d^2\sigma^{c1}/d\Omega_\kappa d\omega = (d\sigma^{c1}/d\Omega_\kappa)\delta(\omega)$. In the limit $J^{dd} \gg k_B T \gg \mu_B H$, Eq. (4.5) may be used to obtain a formula for the elastic neutron cross section for paramagnetic alloys at low temperatures or for ferromagnetic alloys (which are near the critical concentration) near T_C

$$\frac{d\sigma^{c1}}{d\Omega_\kappa} \approx \tfrac{2}{3} A_2 (N+2)(12N)^{-1} \sum_{i,j}{}' G(\kappa R_{ij}) . \quad (4.6)$$

This expression will be compared with experiments on paramagnetic alloys in Sec. V. Using Eq. (4.5) it can be shown that the fluctuation contribution to the elastic cross section is zero for $k_B T/\mu_B H \ll 1$, since in this limit the spins are strongly pinned by the field.

There are two types of contributions to the in-

elastic neutron-scattering cross section: (i) those which arise from processes in which the neutron energy change is $\pm\mu_B H$ and, correspondingly, the z component of angular momentum of the cluster changes by one unit; and (ii) those in which the neutron excites the internal degrees of freedom of the cluster. The latter involve large energy transfers of the order of J^{dd} and carry detailed information about the internal spin dynamics of the cluster. The contribution to the inelastic cross section from small energy transfers derives from the x-x term in Eq. (4.1) and is given by

$$\frac{d^2\sigma^{cl}}{d\Omega_\kappa d\omega} = \tfrac{1}{4}A_2 N^{-2}(e^X-1)\tfrac{5}{3}[N+2(N+1)(e^{X(N+1)}-1)^{-1} - 2(e^X-1)^{-1}]\sum_{i,j}{}'G(\kappa R_{ij}) \times[\delta(\omega-\mu_B H)e^X+\delta(\omega+\mu_B H)]. \quad (4.7)$$

When $\mu_B H$ is small compared to the energy resolution in the neutron beam, the contribution in Eq. (4.7) will appear as a contribution to the elastic scattering. At temperatures $J^{dd} \gg k_B T \gg \mu_B H$ and when $0 < \omega \ll J^{dd}$,

$$\frac{d^2\sigma^{cl}}{d\Omega_\kappa d\omega} \approx \tfrac{5}{3}A_2(N+2)(24N)^{-1}\sum_{i,j}{}'G(\kappa R_{ij}) \times[\delta(\omega-\mu_B H)+\delta(\omega+\mu_B H)]; \quad (4.8)$$

and for $k_B T \ll \mu_B H$,

$$\frac{d^2\sigma^{cl}}{d\Omega_\kappa d\omega} \approx \tfrac{5}{3}A_2(4N)^{-1}\sum_{i,j}{}'G(\kappa R_{ij})\delta(\omega-\mu_B H). \quad (4.9)$$

The last equation suggests that inelastic scattering measurements can provide information about the strength of the molecular fields in the alloy. This will be discussed in more detail at the end of Sec. V. Finally, the specific heat per cluster is

$$C_V^{cl} = k_B X^2[e^X(e^X-1)^{-2} - (N+1)^2 e^{X(N+1)} \times(e^{X(N+1)}-1)^{-2}]. \quad (4.10)$$

In the limit $J^{dd} \gg k_B T \gg \mu_B H$

$$C_V^{cl} \approx k_B[N(N+2)/12]X^2. \quad (4.11)$$

Thus, the specific heat at temperatures high compared to the magnetic field, has the usual T^{-2} tail of a Schottky anomaly. For $k_B T \ll \mu_B H$, $C_V^{cl} \approx 0$. It should be noted by comparing Eqs. (4.4), (4.5), anc (4.10) that the expression for the elastic scattering contribution to the resistivity $(\rho^{cl})_{el}$, the elastic neutron-scattering cross section, and the specific heat are very similar. In particular, $d\sigma^{cl}/d\Omega_\kappa|_{\kappa=0} \equiv \sigma^{cl}$ is related to C_V^{cl} by

$$\frac{\sigma^{cl}}{C_V^{cl}} = \left(\frac{k_B T}{\mu_B H}\right)^2 \frac{1}{k_B} A_2(\tfrac{2}{3}). \quad (4.12)$$

An analogous equation can be obtained for $(\rho^{cl})_{el}/C_V^{cl}$. It is clear from this equation that specific-heat and neutron-scattering measurements are not, in general, independent of one another.

B. Numerical results

The analytical results derived in the preceding section will now be illustrated numerically. These results which follow are expected to describe the temperature dependence of the resistivity, neutron cross section and specific heat in ferromagnetic alloys near the critical concentration and at temperatures $k_B T < k_B T_C \ll J^{dd}$. In addition, they are appropriate to low temperature ($k_B T \ll J^{dd}$) measurements in paramagnetic alloys. In particular, these results will be used in Sec. V to understand the temperature dependence of the specific heat in paramagnetic Ni-Cu alloys between 1 and 4 K. However, as will be shown below, for reasonable cluster sizes, in this temperature range the resistivity and neutron cross section in paramagnetic alloys are already comparatively temperature independent. It can also be seen that the high temperature ($k_B T \gg \mu_B H$) limits of the results obtained in this section correspond to low temperature ($k_B T \ll J^{dd}$) limits of the analogous results obtained in Sec. III B.

The temperature dependence of ρ^{cl} [Eq. (4.4)] for clusters of $N=10$ and $N=30$ spins in the most compact configuration on an sc lattice is illustrated in Fig. 4. As in Sec. III, the quantity ρ_0 is $\frac{1}{4}A_1$ and it is assumed that $k_F a = 1.0$. As is expected, the component of the resistivity which arises from the scattering of conduction electrons from spin fluctuations increases monotonically with $k_B T/\mu_B H$. For arbitrary T, as N increases from 10 to 30, ρ^{cl} also increases. At very low temperatures ($k_B T/\mu_B H < 1$) the main contribution to ρ^{cl} comes from inelastic scattering.

In Fig. 5 is plotted σ^{cl}, the elastic neutron-scattering cross section in the forward direction di-

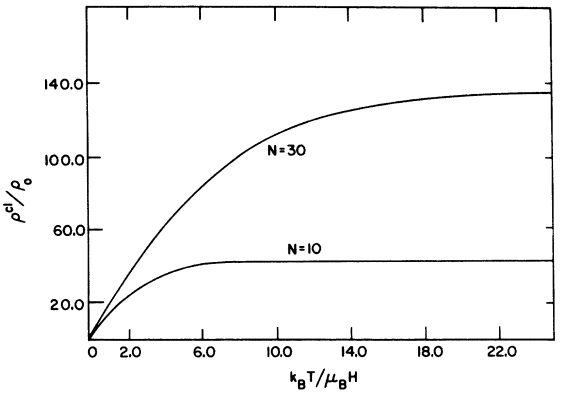

FIG. 4. Temperature T dependence of the contribution to the resistivity of clusters of 10 and 30 atoms in finite field H; $k_B T$ and $\mu_B H$ are small compared to intracluster exchange constant.

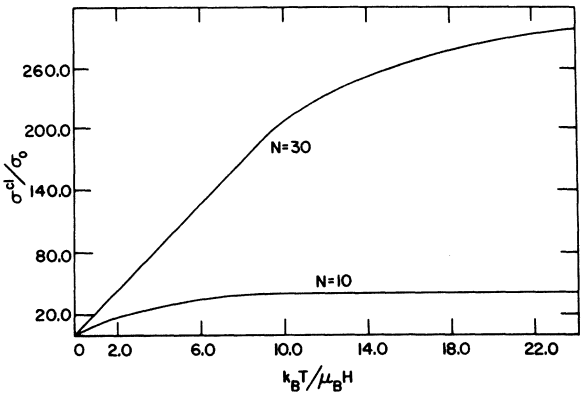

FIG. 5. Temperature T dependence of the contribution of clusters of 10 and 30 atoms to the elastic neutron cross section in forward direction. H is magnetic field and k_BT and μ_BH are small compared to intracluster exchange constant.

vided by $\sigma_0 = \frac{1}{6}A_2$, as a function of k_BT/μ_BH for $k_BT \ll J^{dd}$. As in the resistivity, the fluctuation contribution to the cross section increases monotonically with temperature.

The specific heat as a function of temperature is plotted in Fig. 6 for $k_BT \ll J^{dd}$ and for $N = 10$ and 30. The results found here are equivalent to those obtained by other authors.[6,26] It can be seen for both values of N, that C_V^{cl} reaches a maximum of $\approx k_B$ and falls off like $(1/T)^2$ at high temperatures. The maximum is broadened as N increases and for $N = \infty$, the specific heat is temperature independent and equals k_B above the Einstein temperature $T_E \approx \mu_BH/k_B$. It is important to note that even for clusters as big as 30 atoms C_V^{cl} is equal to k_B only over a relatively narrow temperature range. At very low temperatures C_V^{cl} is roughly independent of N. This follows because the energy level spacing for the cluster is independent of N. At these very low temperatures C_V^{cl} rises rapidly: for $k_BT/\mu_BH = 0.2$, $C_V^{cl} = 0.17\,k_B$.

V. APPLICATION TO Ni_xCu_{1-x} ALLOYS NEAR THE CRITICAL CONCENTRATION

A. Description of model

The results of Secs. III and IV are applied to Ni_xCu_{1-x} alloys to investigate the concentration x dependence of the specific heat and the neutron cross section at low temperatures ($1 \leq T \leq 4$ K) and that of the resistivity at all temperatures.

It is assumed that a Ni atom must have eight or more Ni near neighbors in order to have a spin. This number is consistent with that used in previous analyses[7] and yields semiquantitative agreement with experiment for all three experimental quantities that are studied here. While the critical number of near neighbors required for a Ni atom to have a moment should probably be taken to be concentration dependent, for simplicity, it will be chosen to be a constant as in previous papers.[7] The concentration of magnetic Ni atoms is $N^s/N' = xf(x)$, where $0 \leq f(x) \leq 1$ is the probability that a Ni atom has eight or more Ni near neighbors. The lattice is face-centered cubic and short-range-order effects are neglected, for simplicity.

The intracluster exchange constant J^{dd} is chosen to be the same as in pure Ni. Assuming the Ni atoms have a spin of $\frac{1}{2}$ and using molecular-field theory,[27] J^{dd} is given in terms of the Curie temperature, T_C^{Ni}, of pure Ni,

$$2J^{dd} = \tfrac{1}{3}k_BT_C^{Ni} \approx 210\ \text{K}, \tag{5.1}$$

where the factor of 2 on the left-hand side of this equation comes from the fact that the exchange constant in Eq. (2.1) is $2J^{dd}$. The magnitude of the mean internal field $\overline{H}$ in ferromagnetic alloys is estimated from molecular-field theory[27] to be

$$\mu_B\overline{H} \approx 6[1-(T/T_C)^2]\,k_BT_C/(\overline{N}+2), \tag{5.2}$$

where it is assumed that $\langle S^z\rangle$ varies as $[1-(T/T_C)^2]$, which is a crude approximation to the molecular-field-theory results. Note that this approximation does not reduce to the correct molecular-field-theory results very near the Curie temperature of the alloy, T_C, but should be adequate away from T_C. The spin of the cluster of $\overline{N}$ atoms is $\frac{1}{2}\overline{N}$. This last assumption follows from the fact which will be used throughout this section, that $k_BT_C \ll J^{dd}$ for alloys near the critical concentration. In paramagnetic alloys the internal field is chosen to be roughly equal to the anisotropy field of pure Fe and is given by $\mu_B\overline{H}/k_B \approx 0.05$ K.[6] While there is considerable uncertainty in the size of the internal field in para-

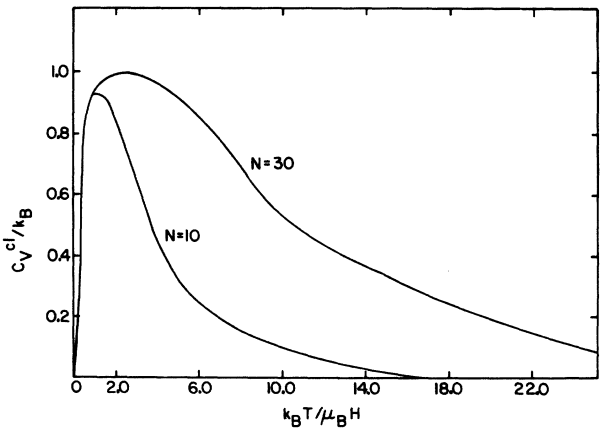

FIG. 6. Contribution of clusters of 10 and 30 atoms in magnetic field H to specific heat as a function of temperature T; k_BT and μ_BH are small compared to intracluster exchange constant J^{dd}.

magnets,[28] this choice of $\overline{H}$ gives reasonable agreement with experiment.

As stated in Sec. I, the clusters are chosen to be in the most compact configuration. Because each Ni atom must have at least eight Ni near neighbors to have a magnetic moment, this assumption is not unreasonable.[13] In the most compact configuration the Ni atoms in the cluster are assumed to have the maximum number of Ni neighbors consistent with the size of the cluster and the crystal structure. Finally, all clusters are chosen to contain 50 spins, as is consistent with neutron-scattering experiments,[5] and fluctuations in the internal magnetic field are neglected, so that

$$\mathcal{P}(N)/N' = (xf(x)/\overline{N})\delta_{N\overline{N}}, \quad \overline{N} = 50 \tag{5.3}$$

and

$$Q(H) = \delta(H - \overline{H}), \tag{5.4}$$

where $\mathcal{P}(N)$ and $Q(H)$ are defined below Eq. (2.9) and the subscript λ is omitted since only one configuration is considered.

Several words about the "spirit" of this approach are in order. While it is possible to allow the distribution functions $\mathcal{P}(N)$ and $Q(H)$ to be free parameters that can be chosen to fit the experimental curves, it seems unreasonable to complicate the calculations in this way. Our estimates show that if $\mathcal{P}(N)$ and $Q(H)$ are taken to be Lorentzian functions centered about $\overline{N}$ and $\overline{H}$, the values obtained for C_V, ρ, and $d^2\sigma/d\Omega_\kappa d\omega$ are fairly insensitive to the half-widths of these distribution functions for all reasonable values of the half-widths. Similarly, changes in the configuration of the spin clusters (providing the configurations are reasonably compact) will not alter the values obtained for the various quantities by more than a factor of 2 or 3. Many of the calculations in this section were repeated using a linear chain configuration for the cluster. In comparing the results obtained from this (least compact) configuration with those obtained from the most compact configuration, it was found that the calculated values of the specific heat and neutron cross sections were qualitatively unchanged. However, for some values of the parameter $(k_F a)$, the temperature dependence of the resistivity was significantly altered. In particular the value of $k_F a$ above which the calculated resistivity increases with increasing temperature (rather than decreasing with temperature) was found for the linear chain configuration to be smaller than for the most compact configuration. Hence these noncompact configurations will be more likely to lead to a spin-disorder resistivity which increases with increasing temperature than will the more compact configurations. Once the assumptions, which have been outlined above, are made, there are no adjustable parameters in the theory. At most, semiquantitative agreement with experiment is to be expected. It will be shown, in Sec. V B, that for all three experiments considered, reasonable agreement between theory and experiment is obtained over a range of concentrations and temperatures. The qualitative trends observed in the behavior of C_V, ρ, and $d\sigma/d\Omega_\kappa$ with varying concentrations are all reproduced in the present theory.

In paramagnets, the bulk resistivity, neutron cross section, and specific heat are obtained by adding up the contribution from each cluster. Thus $\rho = C\rho^{\mathrm{cl}}$, $d^2\sigma/d\Omega_\kappa d\omega = C\, d^2\sigma^{\mathrm{cl}}/d\Omega_\kappa d\omega$, and $C_V = CC_V^{\mathrm{cl}}$, where $C = xf(x)/\overline{N}$ and ρ^{cl}, $d^2\sigma^{\mathrm{cl}}/d\Omega_\kappa d\omega$, and C_V^{cl} are evaluated as in Secs. III and IV for clusters of $\overline{N} = 50$ atoms and for a mean field of $\overline{H}$. As discussed in Sec. II, in ferromagnets there are additional contributions to the resistivity and the elastic neutron cross section because $\langle S^z \rangle$ is finite. For the neutron cross section this extra contribution, which is called the Marshall[10] term, can be written as[5]

$$\tfrac{2}{3} A_2 C(1-C)[\tfrac{1}{2}(1-(T/T_C)^2)]^2 \sum_{i,j}{}' G(\kappa R_{ij}), \tag{5.5}$$

where it is again assumed, for simplicity, that $\langle S^z \rangle$ varies as $[1-(T/T_C)^2]$. It follows by analogy with Eq. (5.5) that the Nordheim contribution to ρ, which arises from the last two terms on the right-hand side of Eq. (2.8) can be written as

$$A_1 C(1-C)[\tfrac{1}{2}(1-(T/T_C)^2)]^2 \sum_{i,j}{}' F(2k_F R_{ij}). \tag{5.5a}$$

Similarly, the interference term is expected, on the basis of Ref. 19, to be given by

$$-2A_1 C(1-C)[\tfrac{1}{2}(1-(T/T_C)^2)]^2 \sum_{i,j}{}' F(2k_F R_{ij}). \tag{5.5b}$$

Finally the constants A_1 and A_2 which are defined in Eqs. (2.3) and (2.6) may be easily estimated. The density of atoms N'/Ω and of conduction electrons n is taken to be the same as in pure Cu, which is[29] $\approx 8.55 \times 10^{22}$ cm^{-3}. It follows that $A_1 = 4.35(J^{sd})^2$ $\mu\Omega$ cm for J^{sd} in units of 10 eV Å^3. The constant A_2 was evaluated in Ref. 20 and found to be 72.9 mb.

B. Numerical examples

In this section our model for Ni_xCu_{1-x} is compared with experiment. The predictions of the model for the electrical resistivity, the elastic neutron cross section, and the specific heat are compared with measurements on these alloys for a range of concentrations in Figs. 7–9. The experimental curves for ρ and $d\sigma/d\Omega_\kappa$ that are presented here are approximate reproductions of those presented in Refs. 8 and 5, respectively. The experimental curves for C_V were reconstructed using the parameters of Robbins *et al.*[7] No raw data were easily available. It is important to note that the theoretical results presented here represent the spin cluster contributions only. Thus the phonon contributions to ρ and C_V (which are included in the experimental curves) are

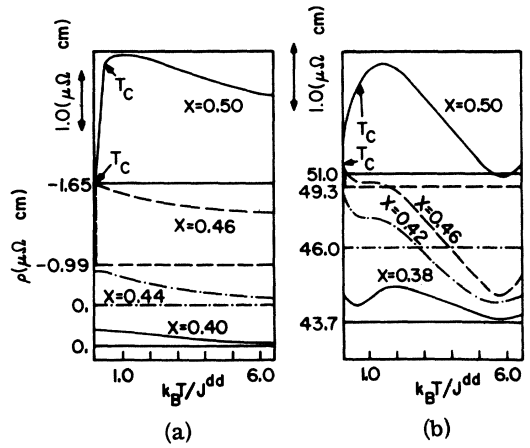

FIG. 7. Theoretical [Fig. 7 (a)] and experimental (after Ref. 8) [Fig. 7 (b)] curves for resistivity in Ni_xCu_{1-x} as a function of temperature for four Ni concentrations. T_C is the Curie temperature of an alloy and J^{dd} is the intracluster exchange constant. Potential scattering effects are *not* included in estimating the residual resistivity in the theory.

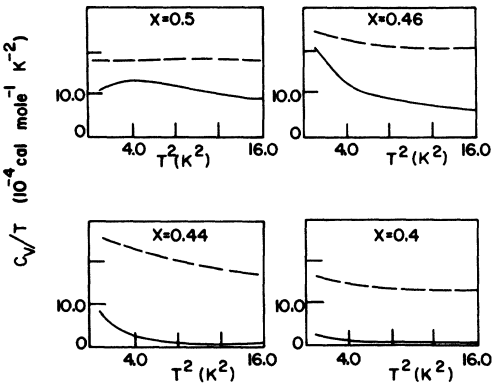

FIG. 9. Specific heat divided by temperature T in Ni_xCu_{1-x} as a function of T^2 for same four alloy concentrations as in Figs. 7 and 8. Solid lines are theoretical results (which include spin contribution only) and dashed lines are experimental results (after Ref. 6) which also include electronic contribution.

not included in the theoretical ones. In addition, the electronic contribution to C_V is omitted in the theoretical curve, but not in the experimental results. With two exceptions the experiments were performed for the same four alloy concentrations near the critical concentration $x = 0.4$, 0.44, 0.46, and 0.5. The theoretical curves are therefore computed for these same four concentrations. The rapid changes in the calculated resistivity, specific heat, and elastic neutron-scattering cross section for small changes in x result from two factors: the concentration dependence of $f(x)$ and that of T_C.

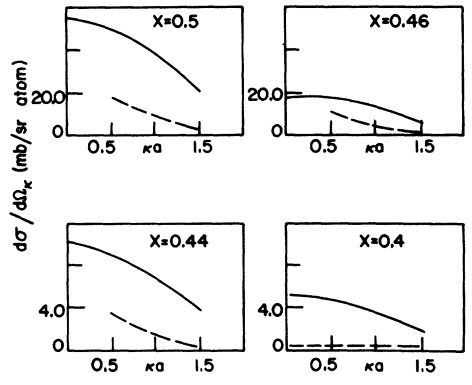

FIG. 8. Elastic neutron cross section in Ni_xCu_{1-x} as a function of momentum transfer κ times the lattice spacing a for the same four Ni concentrations as in Fig. 7 (a). Solid lines are theoretical and dashed lines are experimental results (after Ref. 5).

In Fig. 7, the theoretical [Fig. 7(a)] and the experimental [Fig. 7(b)] resistivity curves are plotted as a function of temperature for four different alloy concentrations. The experiments were performed for $x = 0.50$, 0.46, 0.42, and 0.38. However, the theory is computed for $x = 0.50$, 0.46, 0.44, and 0.40, which are the same concentrations that are used in Figs. 8 and 9. The origin of the resistivity curve for each concentration in both Fig. 7(a) and Fig. 7(b) is indicated by a horizontal line which is solid, dashed, or dot-dashed in the same way as the resistivity curves. The scale is constant within each figure, but it differs slightly between Fig. 7(a) and Fig. 7(b). The residual resistivity in the experimental curves includes the large potential scattering contribution which is not included in the theoretical curves. This contribution is temperature independent and is, therefore, of no interest here. In the theoretical curves the residual resistivity comes entirely from spin-disorder scattering and, in the case of the ferromagnetic alloys, includes the (negative) term which arises from the interference between potential and magnetic scattering [Eq. (5.5b)]. The upper two curves in both Figs. 7 correspond to alloys which undergo a ferromagnetic phase transition below a Curie temperature T_C that is 40 K for $x = 0.5$ and 9 K for $x = 0.46$. Using Eq. (5.1) it follows that the upper limit of the temperature axes is $k_BT = (6.0J^{dd}) \approx k_BT_C^{Ni}$. As discussed in Sec. III, it is difficult to obtain the exact temperature dependence of ρ above T_C for clusters containing as many as 50 spins. However, the value of the resistivity at $T = T_C$ (in the paramagnetic alloys T_C is assumed to be 0) and $T = \infty$ can be found from Eqs. (3.1) and (3.2). The theoretical curves presented in Fig. 7(a) are obtained by drawing a

smooth curve between ρ at T_C and ρ at T_C^{Ni}. It is assumed that ρ at T_C^{Ni} is roughly $\{\rho(T_C) - \frac{2}{3}[\rho(T_C) - \rho(\infty)]\}$, which is consistent with Figs. 1 and 2. It is clear from these figures that the high-temperature limit of the resistivity $\rho(\infty)$ [which can be obtained from Eq. (3.2)] is not attained at $k_B T/J^{dd} = 6.0$. However, ρ at this temperature is considerably reduced from its value at T_C. The value of $k_F a$ which appears in the form factors is taken to be 1.0. The low-temperature maximum which is present in Figs. 1 and 2 for this value of $k_F a$ is not included in Fig. 7(a). In addition, a low-temperature Kondo minimum which is believed to be present (see Sec. III C) is not drawn in the theoretical curve because of difficulties in calculating the exact coefficient of the $\ln T$ term. (Crude estimates suggest that this coefficient is roughly 25% of the resistivity at T_C.)[30] However, it may be seen that in all paramagnetic alloys (except for $x = 0.50$) such a minimum is found experimentally. The possibility that this minimum may arise from Fe contamination rather than from a spin cluster Kondo effect should not be overlooked. In calculating the resistivity it was assumed that J^{sd} is 10 eV Å^3, which is consistent with estimates of J^{sd} in gadolinium.[17] However, it is difficult to obtain reliable independent estimates of J^{sd} in Ni. Small changes in J^{sd} will have a large effect in ρ, since ρ is proportional to $(J^{sd})^2$ and a better fit to the experimental data in the paramagnetic alloys can be obtained by increasing J^{sd} slightly.

It may be seen that for all four concentrations, the qualitative behavior of the experimental curves is reproduced by the theory. The resistivity of the two ferromagnetic alloys increases up to T_C, reaches a maximum and then decreases.[31] In the $x = 0.5$ alloy the maximum in ρ is found experimentally at a temperature above T_C, while the theoretically determined maximum is at T_C. It is possible that the two maxima would coincide if some of the structure in the theoretical ρ-vs-T curve which was found numerically to be present for clusters of 2 and 4 atoms were included in the plot. For $x = 0.5$ the measured resistivity above T_C appears to fall off more rapidly with increasing temperature than the calculated resistivity. This decrease would be even more apparent if phonon effects are subtracted from the experimental curve. However, it is believed that the experimental curves may be somewhat inaccurate above room temperature ($k_B T/J^{dd} \approx 3$) because of a miscibility gap that has been reported in these alloys.[32]

As the concentration is decreased to $x = 0.46$ the maximum in ρ is decreased relative to that at $x = 0.50$. However, the calculated resistivity curve is qualitatively the same as for $x = 0.46$. Above T_C the experimental curve falls more rapidly with increasing temperature than the theoretical curve and continues to decrease until the phonon contribution dominates the spin-disorder contribution at $k_B T \approx 6J^{dd}$. In the two alloys which are paramagnetic at all temperatures, the calculated resistivity curves decrease with increasing temperature. In the experimental curves there is a low-temperature Kondo-like minimum, which was discussed earlier, but otherwise the theoretical and experimental results are in reasonable agreement. It is important to note that the broad qualitative trends that appear in the experimental curves as x and T vary are also found in the theory.

In Fig. 8 is shown the elastic neutron-scattering cross section at $T = 4$ K as a function of κa for the same four alloy concentrations as in Fig. 7(a).[33] The solid line represents the theoretical, and the dotted line the experimental, results.[5] The lattice constant a is taken to be 2.5 Å, which corresponds to that of pure Ni and pure Cu. It may be seen that both the experimental and theoretical curves have a maximum at $\kappa = 0$. The experimental values are roughly a factor of 2 smaller than the theoretical ones. There are several reasons for this, not unreasonable, discrepancy. One, in the theoretical calculation the magnitude of all the spins within a cluster have the same value, which is consistent with a localized-spin model. In previous analyses[5] of the neutron cross section (which have focused only on ferromagnetic alloys using an itinerant spin model) the spin magnitude within a cluster has been allowed to vary spatially. Two, the analysis of the experimental results was based on the assumption that a magnetic field of 4.0 kOe will saturate the magnetization. The spin contribution to the cross section was then obtained by subtracting the cross section in the presence of the external field with $\vec{\kappa}$ along the field direction, from that in zero field. Because saturation in a field of this magnitude does not occur,[34] this difference in the cross section should underestimate the magnetic contribution to $d\sigma/d\Omega_\kappa$. This could account for most, if not all, of the difference between the theoretical and experimental curves for all values of x.

For $x = 0.5$ and 0.46 the fluctuation contribution to $d\sigma/d\Omega_\kappa$ [Eq. (4.5)] is dominated by the Marshall term represented in Eq. (5.5), and hence the former contribution can be neglected as in previous analyses.[5] The reason that the fluctuation contribution is small is that $k_B T/\mu_B \overline{H} = \mathcal{O}(1)$; as can be seen from Fig. 5 and Eq. (5.5), the fluctuation contribution to the cross section at $\kappa = 0$ for $k_B T/\mu_B \overline{H} < 1$ is negligible compared to that of the Marshall term. It follows from Eq. (5.2) that this would not be true at higher temperatures or for alloys for which $T/T_C \approx 1.0$, since the fluctuation contribution becomes more important as $k_B T/\mu_B \overline{H}$ increases. The present analysis of the elastic cross section for ferromagnetic alloys differs from that of Hicks *et al.*[5]

in several important ways. In Ref. 5 the cluster concentration C, which appears in Eq. (5.5), was taken to be a free parameter. Furthermore the shape of the $d\sigma/d\Omega_\kappa$-vs-κ curve was fitted to a Lorentzian curve with two additional free parameters. It should be remarked that the fit obtained in this way is excellent. However, in the present paper there are no adjustable parameters in this sense. The emphasis here is in fitting several different experiments within the same model. While the agreement between theory and this particular experiment is not as impressive as Ref. 5, it is important to note that the present model is consistent with three rather different types of measurements.

For the paramagnetic alloys [$x = 0.44$ and $x = 0.40$], the theoretical and experimental cross sections are considerably smaller than for the ferromagnetic case. Note the different scales on the vertical axis of the top two and bottom two sets of curves. The contribution to $d\sigma/d\Omega_\kappa$ comes entirely from fluctuations [Eq. (4.5)] and because $k_BT/\mu_B\bar{H} \gg 1$ in the paramagnetic alloys, Eq. (4.6) can be used to approximate the cross section. The shape of the elastic scattering cross section is determined by the cluster form factor $\sum'_{i,j} G(\kappa R_{ij})$ defined in Eq. (2.15). It is clear from this equation that there will be a maximum in $d\sigma/d\Omega_\kappa$ at $\kappa = 0$. It should be noted that there has previously been no detailed theoretical explanation offered for the behavior of the cross section in these nondilute paramagnetic alloys. The theory of Refs. 10 and 20 is applicable only to ferromagnetic alloys. It is therefore believed that the present theory represents the first semiquantitative explanation for these experiments.

In Fig. 9, the specific heat divided by the temperature T is plotted as a function of T^2 for the same four alloy concentrations as in Figs. 7(a) and 8. The dotted line represents the experimental results of Robbins *et al.*[6] between 1 and 4 K; the solid line represents the theory given by Eq. (4.10). The "anomaly" reported by Schroeder,[6] which consists of an upturn in C_V/T at low temperatures, is apparent in both the theoretical and experimental curves for all concentrations except $x = 0.5$. It was proposed[6] that the experimental C_V curve could be described by the equation

$$C_V = A + \gamma T + \beta T^3, \tag{5.6}$$

where γT and βT^3 represent the electronic and lattice contribution to C_V and the constant A the spin cluster contribution. However, the present calculations show that the spin contribution to C_V is not temperature independent. In ferromagnetic alloys it follows from Eq. (5.2) that $k_BT/\mu_B\bar{H} \approx 0.25$ at 1 K for $x = 0.5$ and $k_BT/\mu_B\bar{H} \approx 0.97$ at 1 K for $x = 0.46$. Using Fig. 6, it can be seen that this temperature region is on the rising portion of the Schottky anomaly and that, therefore, the spin contribution to C_V will contain a term that increases with increasing temperature for both these ferromagnetic alloys. On the other hand, for the paramagnetic alloys $k_BT/\mu_B\bar{H} \approx 20.0$ at 1 K and it follows from Fig. 6 that the spin component of C_V will decrease with increasing temperature. This temperature region corresponds to the high-temperature tail of the Schottky anomaly. If a constant $\gamma \approx 10.0 \times 10^{-4}$ cal mole^{-1} K^{-2} is added to the theoretical curves, which represent only the spin contribution to C_V, experiment and theory can be brought into reasonable agreement for all four alloy concentrations. The βT^3 term plays a relatively unimportant role at these low temperatures and need not be considered in this analysis. For the $x = 0.5$ alloy the experimental curve is nearly constant, whereas the theoretical curve decreases slightly at the low- and high-temperature ends. For the $x = 0.46$ alloy the theoretical curve drops more rapidly with increasing temperature than the experimental one and for $x = 0.44$ and 0.40 the upturn at low temperature is more pronounced in the experimental than theoretical curves.

In order to fit the experimental curve to Eq. (5.6), it was found earlier[6] that γ must decrease by roughly a factor of 2 as the alloy concentration is decreased from the ferromagnetic concentration regime ($x > 0.44$) to the paramagnetic regime ($x < 0.44$). It is believed here that the electronic contribution to the specific heat represented by the γT term is not strongly concentration dependent in this range and that a reasonable fit to experiment can be obtained by making the constant A in Eq. (5.6) increase with increasing T for ferromagnetic alloys and decrease with T for paramagnetic alloys. In this connection, it would be particularly useful to have measurements of the specific heat in these alloys over a wider range of temperatures. In particular, below 1 K in the paramagnetic alloys it may be possible to see the broad maximum in the Schottky anomaly which is illustrated in Fig. 6.

No detailed discussion has yet been given of inelastic neutron-scattering experiments. It was mentioned in Sec. IV that for alloys near the critical concentration for ferromagnetism, the low-frequency portion of the cross section provides information about the internal magnetic fields in the alloy and that the high-frequency portion will give information about the energy levels of the cluster and thus about the intracluster exchange constant J^{cl} and the number of spins within a cluster. For clusters of 2, 3, and 4 atoms the energies at which high-frequency inelastic scattering takes place are listed in Table I. While they have not been done as yet, inelastic neutron experiments appear to be feasible and, providing the distribution of internal fields $Q(H)$ and that of the cluster sizes and con-

figurations $\Phi_\lambda(N)$ are sufficiently narrow, they should furnish valuable information about spin clusters in these alloys. Additional information about the cluster energy levels can be obtained from high temperature C_V experiments. As can be seen from Fig. 3 the shape of the C_V-vs-T curves depends on the size and configuration of the spin clusters and the magnitude of J^{dd}.

Note added in proof. After this paper was submitted for publication we became aware of a paper by R. L. Falge and N. M. Wolcott.[35] As in the present paper, they have successfully fitted the specific-heat versus temperature curve in Cu-Ni systems to a Schottky function. They also measured the specific heat over a wider temperature range than that examined in previous experiments. In contrast to the present work they considered only Cu-rich samples and chose the anisotropy field and the cluster size to be adjustable parameters.

ACKNOWLEDGMENTS

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[23]While there are third-order contributions to the cross-section which come from the interference between potential and magnetic scattering, they will not be considered here. See Ref. 21 for a treatment of the interference terms.

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[30]Whether a Kondo minimum is obtained or not depends on both the sign of J^{sd} and the low-temperature behavior of the second-order (in J^{sd}) term in ρ plus the lattice contribution. As can be seen from Figs. 1 and 2, depending on the value of $k_F a$ the second-order terms will increase or decrease with T at low temperatures. A necessary, but not sufficient, condition for a minimum to occur is that the sign of the *slope* of the

second-order terms at low temperature and the sign of J^{sd} must be opposite.

[31]It has been shown by R. W. Houghton and M. P. Sarachik [Solid State Commun. 10, 369 (1972)] that the resistivity of paramagnetic Ni-Rh alloys, near the critical concentration does not decrease with increasing temperature. If the same model can be used for Ni-Rh as for Ni-Cu alloys it could be argued that this behavior may be due to one of three things: (i) the Ni clusters are much smaller, (ii) they are considerably less compact, or (iii) the parameter $(k_F a)$ that appears in the resistivity form factor is larger than in Ni-Cu alloys. While the phonon contribution to ρ in these alloys is larger than that in Ni-Cu alloys, our estimates do not indicate that the spin-disorder contribution to ρ is decreasing with temperature above T_C in Ni-Rh.

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[33]It is assumed here that inelastic and elastic contributions to $d^2\sigma/d\Omega_k d\omega$ can be distinguished. Since the Zeeman splitting in paramagnetic alloys $(\mu_B H)$ is small, this may not be the case for these alloys. It follows from Eqs. (4.5) and (4.6) that the errors resulting from this assumption could increase the theoretical results in paramagnetic alloys by at most a factor of 3.5.

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