Superconducting phase transitions in rare-earth compounds

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The superconducting transition temperature T_c and the upper critical field H_{c2} in the rare-earth (R) compounds $R_xMo_6S_8$, $R_xMo_6Se_8$, and RRh_4B_4, are theoretically studied within a model in which the superelectrons mainly originate from the 4*d* electrons of Mo and Rh atoms. The fluctuation of local spins inside a Cooper pair weakens the BCS coupling. Thus, the quantities T_c and H_{c2} are strongly influenced by the fluctuation. These quantities are obtained as functions of the intra- and interatomic exchange interactions and the concentration of the spins. The theoretical results explain the existence of the upper and lower superconducting transition temperatures T_{c1} and T_{c2} in $ErRh_4B_4$ and $Ho_{1.2}Mo_6S_8$, and the concentration dependence of T_c in $La_{1-x}Gd_xMo_6Se_8$ and $Sn_{1.2(1-x)}Eu_xMo_{6.35}S_8$. The suppression of the spin fluctuation by application of a magnetic field causes an increase of the BCS coupling. In calculating H_{c2}, this fact is taken into account as well as the spin splitting of conduction bands and spin-orbit scattering. Our theory explains the anomalous behavior of the temperature dependence of H_{c2} observed in $Sn_{1.2(1-x)}Eu_xMo_{6.35}S_8$. It is proposed that in certain compounds a superconducting state may appear only in the presence of a magnetic field.

I. INTRODUCTION

The interplay of superconductivity and magnetism has attracted the attention of many solid state physicists.[1-4] The effect of a single magnetic impurity on the superconductivity has been well understood.[3,4] However, the effect of highly concentrated or stoichiometic magnetic ions on the superconductivity is still open to question in spite of considerable research efforts.[1,2] This is partly because there existed no stoichiometric compound suitable for studying this problem.

The recent discovery of the superconducting compounds RRh_4B_4 (Ref. 5) and RMo_6X_8, R being rare-earth ions and X being S (see Ref. 6) or Se (see Ref. 7), has brought about an amazing number of examples concerning the problem. Superconductivity in[8,9] $ErRh_4B_4$ and[10] $Ho_{1.2}Mo_6S_8$ is quenched by a magnetic-ordering transition and, thus, these compounds provide the first examples of superconducting-to-magnetic phase transition. However, superconductivity in $Tb_{1.2}Mo_6S_8$, $Dy_{1.2}Mo_6S_8$, and $Er_{1.2}Mo_6S_8$ is quenched by a magnetic-ordering transition only under a magnetic field.[11] It is also surprising that some of these compounds such as $PbGd_{0.2}Mo_6S_8$,[12,13] $La_{0.8}Eu_{0.2}Mo_6Se_8$,[14] and $Sn_{1.2(1-x)}Eu_xMo_{6.35}S_8$,[12,13] are ultra-high-field superconductors; the upper critical field H_{c2} of these compounds is much higher than 300 kG. Particularly interesting is the temperature and Eu-concentration dependence of H_{c2} in $Sn_{1.2(1-x)}Eu_xMo_{6.35}S_8$.[12,13] With increasing Eu concentration, H_{c2} at absolute zero increases although the superconducting transition temperature T_c decreases. Furthermore, the H_{c2} temperature dependence of the compounds with a considerable amount of Eu ions is quite different from that of usual superconductors. The objective of this paper is to study theoretically the magnetic and superconducting properties of the above rare-earth compounds. We discuss the effects of magnetic ions on T_c and H_{c2}, taking into account the collective nature of the motion of local spins.

As is well known, an impurity spin acts on a Cooper pair as a pair breaker and suppresses T_c.[15] In calculating T_c, elastic scattering of electrons due to a local spin is assumed by taking the local spin as a static potential. At very low temperatures, the quantum motion of a local spin is introduced to take into account the Kondo effect.[4] In our systems with highly concentrated or stoichiometric magnetic ions, however, the spins are coupled among themselves through the exchange interaction. Thus, there exists collective motion of spins even in the paramagnetic phases. Therefore, one must take into account the inelastic scattering of electrons due to the spins.

In Sec. II, we propose a model Hamiltonian suitable for our compounds. In Sec. III, the effect of local spins in the paramagnetic phases of both ferromagnets and antiferromagnets on T_c is studied. The weak-coupling-limit condition for spins is investigated. In this limit, the effective BCS coupling constant is expressed as a function of the staggered spin susceptibilities. Our theoretical study shows that the superconducting electrons are different from electrons which contribute to the exchange interaction between local spins. The rare-earth ions in the compounds RMo_6X_8 can easily be substituted by nonmagnetic ions such as La and Sn. In Sec. IV, we calculate the dependence of T_c on the concentration of magnetic ions in ferromagnets and antiferromagnets, extending the effective-Hamiltonian method of spin

statistics proposed by Oguchi *et al.*[16,17] The experimental results on T_c for $La_{1-x}Gd_xMo_6Se_8$,[18] and $Sn_{1.2(1-x)}Eu_xMo_{6.35}S_8$,[12,13] are analyzed, and the dependence of T_c on the concentration of the magnetic ions in $ErRh_4B_4$ and $Ho_{1.2}Mo_6S_8$ is predicted.

In a magnetic field, local spins are polarized, and the up- and down-spin bands of the conduction electrons are split. Furthermore, the orbital motion of electrons (the Meissner term) is modified by the spin polarization. These effects are easily included in the usual formulation for type-II superconductors.[19,20] It is also important to consider the spin fluctuations in a magnetic field.[21,22] The magnetic field suppresses the spin fluctuations so that the effective electron-electron interaction, which has been reduced by the spin fluctuations from the BCS interaction, increases. In Sec. V, H_{c2} is determined as the resultant of the interplay of the following terms: the field-dependent term of the effective BCS interaction, the Meissner term, and the spin splitting of the bands. In Sec. VI, the numerical results of various H_{c2} versus temperature T curves are shown, limited to ultrahigh-field superconductors. The theoretical results contained in the H_{c2}-vs-T curves qualitatively explain the experimental results observed by Fischer *et al.*[12,13] in $Sn_{1.2(1-x)}Eu_xMo_{6.35}S_8$. A quantitative comparison as well as results for H_{c2} in low- or moderate-field superconductors will be given in a separate paper.

II. MODEL

The ternary rare-earth molybdenum chalcogenides (X=S or Se) have a rhombohedral crystal structure of a distorted CsCl type with a Mo_6X_8 cluster on the corner and a rare-earth ion on the center.[23] It has been experimentally concluded that the superconducting electrons of the sulfides are the 4*d* electrons of Mo atoms.[6,12,13] Although such a conclusion has not been obtained in the selenides, the similarity between the sulfides and the selenides suggests that the same conclusion holds for the selenides. The local 4*f* spins of the rare-earth ions are coupled through the exchange interaction. Since the local spins form a primitive lattice, it is possible for them to order magnetically with a single wave number $\vec{Q}$.[24] The exchange interaction between the local spins originates from the superexchange mechanism[25] and from the indirect interaction through the conduction electrons (the Ruderman-Kittel-Kasuya-Yosida interaction). It is considered that the indirect interaction occurs through the 5*d* and 6*s* electron bands of the rare-earth ions which have large wave-function overlap integrals with the 4*f* electrons. The superconducting 4*d* electrons of Mo atoms also interact with the local spins through the exchange interaction I. Since the overlap integral of the wave function of the 4*d* electrons of a Mo atom with the 4*f* spin of a rare-earth ion is very small, it is expected that the interaction I is extremely weak compared with that between the 5*d* and 6*s* electrons and the 4*f* spins of a rare-earth ion. Therefore, the contribution of the superconducting electrons to the indirect interaction between local spins may be neglected. Actually, we will show in Sec. III that a superconducting state should not exist in the compounds at any temperature if the magnetic ordering were caused by the indirect interaction only through the superconducting electrons.

The ternary rare-earth rhodium borides RRh_4B_4 have a tetragonal crystal structure, and the rare-earth ions form a body-centered-tetragonal lattice.[26] For these compounds we have no precise information about the electronic state as found in the sulfides.[27] However, these compounds may also be described from the same view point as RMo_6X_8, because of the similarity of properties between RRh_4B_4 (Ref. 8) and RMo_6X_8 (Ref. 28).

In the rest of this section the model Hamiltonian for these systems is constructed. $k_B=\hbar=c=1$ is used. Neglecting the anisotropy of the crystal, we write the Hamiltonian as

$$\mathcal{H}=\mathcal{H}_0+\mathcal{H}_{ep}+\mathcal{H}_{cf}+\mathcal{H}_{ff}. \tag{2.1}$$

The Hamiltonian for the superconducting electrons is written

$$\mathcal{H}_0=\sum_\sigma \int d^3x\, \psi_\sigma^\dagger(\vec{x})\left(-\frac{1}{2m}[\vec{\nabla}_x-ie\vec{A}(\vec{x})]^2-\mu\right)\psi_\sigma(\vec{x})$$
$$+\mu_B\int d^3x\, H(\vec{x})[\psi_\uparrow^\dagger(\vec{x})\psi_\uparrow(\vec{x})-\psi_\downarrow^\dagger(\vec{x})\psi_\downarrow(\vec{x})], \tag{2.2}$$

where m is the electron effective mass, $\vec{A}$ is the vector potential, μ is the chemical potential, μ_B is the Bohr magneton, $H(\vec{x})$ is the magnetic field whose direction is parallel to the z direction, and $\psi_\sigma(\vec{x})$ is the electron field with spin σ. The electron-electron Coulomb interaction will not explicitly be considered. The Hamiltonian $\mathcal{H}_{ep}$ is the electron-phonon interaction given by

$$\mathcal{H}_{ep}=\sum_\sigma\int d^3x\int d^3x'\, C(\vec{x}-\vec{x}')\psi_\sigma^\dagger(\vec{x})\psi_\sigma(\vec{x})\phi(\vec{x}'), \tag{2.3}$$

where $C(\vec{x}-\vec{x}')$ is the electron-phonon interaction potential and $\phi(\vec{x})$ is the phonon field. The free-phonon Hamiltonian is not written explicitly. In the next sections, the weak-coupling limit will be taken. However, in order to clarify the effect of local spins on superconductivity it is useful to start our study from the more general viewpoint. The Hamiltonian $\mathcal{H}_{cf}$ is that of the local spin and electron interaction, and $\mathcal{H}_{ff}$ is for the local spins:

$$\mathcal{H}_{cf} = -I\sum_i \int d^3x\ \delta(\vec{R}_i - \vec{x})\{S_i^z[\psi_\uparrow^\dagger(\vec{x})\psi_\uparrow(\vec{x}) - \psi_\downarrow^\dagger(\vec{x})\psi_\downarrow(\vec{x})] + S_i^+\psi_\downarrow^\dagger(\vec{x})\psi_\uparrow(\vec{x}) + S_i^-\psi_\uparrow^\dagger(\vec{x})\psi_\downarrow(\vec{x})\}, \quad (2.4)$$

$$\mathcal{H}_{ff} = -\sum_{i,j} J_{ij}\vec{S}_i\cdot\vec{S}_j + g_J\mu_B H\sum_i \mathcal{J}_i^z, \quad (2.5)$$

Here, the exchange interaction constant I may have either sign. $\vec{S}_i$ and $\vec{\mathcal{J}}_i$ are the spin and total angular momenta of the rare-earth ion at the site $\vec{R}_i$, respectively, and are related to each other by $\vec{S}_i = (g_J - 1)\vec{\mathcal{J}}_i$, g_J being the Landé g factor. J_{ij} is the exchange interaction constant. We note that in our compounds RMo_6X_8 and RRh_4B_4, J_{ij} is not a function of I. The rare-earth ions except Gd^{3+} and Eu^{2+} have large magnetic-anisotropy energies because they have orbital angular momenta. However, we will not write them explicitly.

The compounds which we are concerned with belong between dirty superconductors. Therefore, spin-flip scattering of the conduction electrons due to the spin-orbit interaction as well as non-spin-flip scattering are crucial to describe the superconductivity. These scattering effects will be taken into account later.

III. SUPERCONDUCTING TRANSITION TEMPERATURES

In this section, the superconducting transition temperature T_c is studied. Several authors[29-32] have extended the Abrikosov and Gorkov theory[15] to include the effect of spatial correlation between impurity spins. In their theories, impurity spins are assumed to exert static potentials on electrons. In our system with highly concentrated or stoichiometric magnetic ions, however, the spins behave just like a Bose system because they are strongly correlated through the exchange interaction. As a result, the electrons are inelastically scattered by the spins and exchange their energies and momenta with the spins.[31,33,34] Several authors[35-39] have also proposed indirect coupling between conduction electrons owing to virtual excitation of the spins in magnetically ordered states. However, in the paramagnetic phases which we are interested in, the motion of local spins is of damping form because of the thermal effect.[33,34] Therefore, we extend the previous theories in the following way.

To set up the generalized Gorkov equations when local spins are included, we first introduce the following Green's functions:

$$\begin{aligned}
&G_{\sigma,\sigma}(\vec{x}\tau,\vec{x}'\tau') = -\langle T_\tau[\psi_\sigma(\vec{x},\tau)\psi_\sigma^\dagger(\vec{x}',\tau')]\rangle,\\
&F_{\sigma,-\sigma}(\vec{x}\tau,\vec{x}'\tau') = -\langle T_\tau[\psi_\sigma^\dagger(\vec{x},\tau)\psi_{-\sigma}^\dagger(\vec{x}',\tau')]\rangle,\\
&F_{-\sigma,\sigma}^\dagger(\vec{x}\tau,\vec{x}'\tau') = -\langle T_\tau[\psi_{-\sigma}(\vec{x},\tau)\psi_\sigma(\vec{x}',\tau')]\rangle,\\
&D(\vec{x}\tau,\vec{x}'\tau') = -\langle T_\tau[\phi(\vec{x},\tau)\phi(\vec{x}',\tau')]\rangle,\\
&\chi^{zz}(\vec{R}_i\tau,\vec{R}_j\tau') = \langle T_\tau[S_i^z(\tau)S_j^z(\tau')]\rangle,\\
&\chi^{-+}(\vec{R}_i\tau,\vec{R}_j\tau') = \langle T_\tau[S_i^-(\tau)S_j^+(\tau')]\rangle,
\end{aligned} \quad (3.1)$$

where the spin Green's functions are defined by using the fluctuating parts of the spins; $S_i^z - \langle S_z\rangle$ with $\langle S_z\rangle$ being the polarization of a local spin due to a magnetic field.[21,22] Here, τ is the imaginary time, T_τ is the time-ordering operator, and $\langle A\rangle$ denotes the thermal average of A taken in the exact state; $\langle A\rangle = \mathrm{Tr}Ae^{-\beta\mathcal{K}}/\mathrm{Tr}e^{-\beta\mathcal{K}}$ and $\beta = 1/T$. The spin Green's functions have opposite signs from the others so that they are related to the spin susceptibilities. Using Hamiltonian (2.1), the differential Green's-function equations are obtained as

$$\left(-\frac{\partial}{\partial\tau} + \frac{1}{2m}[\vec{\nabla}_x - ie\vec{A}(\vec{x})]^2 + \mu_\uparrow\right)G_{\uparrow\uparrow}(\vec{x}\tau,\vec{x}'\tau') = \delta(\tau-\tau')\delta(\vec{x}-\vec{x}') - \int d^3x_1\, C(\vec{x}-\vec{x}_1)\langle T_\tau[\phi(\vec{x}_1,\tau)\psi_\uparrow(\vec{x},\tau)\psi_\uparrow^\dagger(\vec{x}',\tau')]\rangle + I\sum_i \delta(\vec{R}_i-\vec{x})\{\langle T_\tau[S_i^z(\tau)\psi_\uparrow(\vec{x},\tau)\psi_\uparrow^\dagger(\vec{x}',\tau')]\rangle + \langle T_\tau[S_i^-(\tau)\psi_\downarrow(\vec{x},\tau)\psi_\uparrow^\dagger(\vec{x}',\tau')]\rangle\}, \quad (3.2)$$

$$\left(-\frac{\partial}{\partial\tau} - \frac{1}{2m}[\vec{\nabla}_x + ie\vec{A}(\vec{x})]^2 - \mu_\downarrow\right)F_{\downarrow\uparrow}(\vec{x}\tau,\vec{x}'\tau') = \int d^3x_1\, C(\vec{x}-\vec{x}_1)\langle T_\tau[\phi(\vec{x}_1,\tau)\psi_\downarrow^\dagger(\vec{x},\tau)\psi_\uparrow^\dagger(\vec{x}',\tau')]\rangle + I\sum_i \delta(\vec{R}_i-\vec{x})\{\langle T_\tau[S_i^z(\tau)\psi_\downarrow^\dagger(\vec{x},\tau)\psi_\uparrow^\dagger(\vec{x}',\tau')]\rangle - \langle T_\tau[S_i^-(\tau)\psi_\uparrow^\dagger(\vec{x},\tau)\psi_\downarrow^\dagger(\vec{x}',\tau')]\rangle\}, \quad (3.3)$$

where

$$\mu_\sigma = \mu - \sigma h, \quad \sigma = + \text{ or } -, \quad h = -\mu_B B + Ic\langle S_z\rangle, \quad (3.4)$$

c being the magnetic-ion concentration and $\vec{B}$ the magnetic induction. The electron-phonon (multiparticle) Green's function in Eq. (3.2) is calculated as

$$\langle T_\tau[\phi(\vec{x}_1,\tau)\psi_s(\vec{x},\tau)\psi_s^\dagger(\vec{x}',\tau')]\rangle = -\int_0^\beta d\tau_1 \int d^3x_2 \int d^3x_3\, C(\vec{x}_2-\vec{x}_3)D(\vec{x}_1,\vec{x}_2:\tau-\tau_1)F_{s,s}^\dagger(\vec{x},\vec{x}_3:\tau-\tau_1)$$
$$\times F_{s,s}(\vec{x}_3,\vec{x}':\tau_1-\tau')+\cdots, \tag{3.5}$$

where the dots denote the term which contributes to the normal self-energy. The Green's functions on the right-hand side of Eq. (3.5) are determined self-consistently. On the other hand, the spin-electron Green's functions in Eq. (3.2) are calculated up to first order of the electron-spin interaction as

$$\langle T_\tau[S_i^z(\tau)\psi_s(\vec{x},\tau)\psi_s^\dagger(\vec{x}',\tau')\rangle = I\sum_j \int d^3x_1 \int_0^\beta d\tau_1\, \delta(\vec{R}_j-\vec{x}_1)\chi^{zz}(\vec{R}_i,\vec{R}_j:\tau-\tau_1)F_{s,s}^\dagger(\vec{x},\vec{x}_1:\tau-\tau_1)F_{s,s}(\vec{x}_1,\vec{x}':\tau_1-\tau')+\cdots, \tag{3.6}$$

$$\langle T_\tau[S_i^-(\tau)\psi_s(\vec{x},\tau)\psi_s^\dagger(\vec{x}',\tau')]\rangle = I\sum_j \int d^3x_1 \int_0^\beta d\tau_1\, \delta(\vec{R}_j-\vec{x}_1)\chi^{-+}(\vec{R}_i,\vec{R}_j:\tau-\tau_1)F_{\bar{s},s}^\dagger(\vec{x}_1,\vec{x}:\tau_1-\tau)F_{s,s}(\vec{x}_1,\vec{x}':\tau_1-\tau')+\cdots. \tag{3.7}$$

Here, the dots in Eqs. (3.6) and (3.7) denote the terms which contribute to the normal self-energy. When the order parameter is defined as

$$\Delta(\vec{x},\vec{x}_1:\epsilon_n) = -T\sum_l \Big(\int d^3x_2 \int d^3x_3\, C(\vec{x}-\vec{x}_3)C(\vec{x}_1-\vec{x}_2)D(\vec{x}_3,\vec{x}_2:\epsilon_n-\epsilon_l)$$
$$+I^2\sum_{i,j}\delta(\vec{R}_i-\vec{x})\delta(\vec{R}_j-\vec{x}_1)\left[\chi^{zz}(\vec{R}_i,\vec{R}_j:\epsilon_n-\epsilon_l)+\chi^{-+}(\vec{R}_i,\vec{R}_j:\epsilon_n+\epsilon_l)\right]\Big)F_{\uparrow,\downarrow}^\dagger(\vec{x},\vec{x}_1:\epsilon_l), \tag{3.8}$$

Eqs. (3.2) and (3.3) are rewritten

$$\left(i\epsilon_n+\frac{1}{2m}[\vec{\nabla}_x-ie\vec{A}(\vec{x})]^2+\mu_\uparrow-\Sigma_\uparrow(\vec{x},\vec{x}':\epsilon_n)\right)G_{\uparrow,\uparrow}(\vec{x},\vec{x}':\epsilon_n)+\int d^3x_1\,\Delta(\vec{x},\vec{x}_1:\epsilon_n)F_{\downarrow,\uparrow}(\vec{x}_1,\vec{x}':\epsilon_n)=\delta(\vec{x}-\vec{x}'), \tag{3.9}$$

$$\int d^3x_1\,\Delta^*(\vec{x},\vec{x}_1:\epsilon_n)G_{\uparrow,\uparrow}(\vec{x}_1,\vec{x}':\epsilon_n)+\left(i\epsilon_n-\frac{1}{2m}[\vec{\nabla}_x+ie\vec{A}(\vec{x})]^2-\mu_\downarrow+\Sigma_\downarrow(\vec{x},\vec{x}':-\epsilon_n)\right)F_{\downarrow,\uparrow}(\vec{x},\vec{x}':\epsilon_n)=0, \tag{3.10}$$

where $\Sigma_\sigma(\vec{x},\vec{x}':\epsilon_n)$ is the integral operator for the normal self-energy with spin σ, and ϵ_n and ϵ_l are the imaginary frequencies defined as $\epsilon_n=2\pi T(n+\frac{1}{2})$ and $\epsilon_l=2\pi T(l+\frac{1}{2})$ with n and l integers. Here, the relation $F_{\uparrow,\downarrow}^\dagger(\vec{x}_1,\vec{x}:\epsilon_n)=F_{\downarrow,\uparrow}^\dagger(\vec{x},\vec{x}_1:\epsilon_n)$ was used. Contrary to the usual Gorkov equations,[19,20] the order parameter is nonlocal in space. This nonlocality originates from the fact that the spin fluctuations as well as the phonons are of long range in space. The parameter $\Delta(\vec{x},\vec{x}':\epsilon_n)$ corresponds to the wave function of a Cooper pair, and $\vec{x}$ and $\vec{x}'$ are the coordinates of the electrons constructing a Cooper pair. As seen in Eq. (3.8), the spin fluctuations inside a Cooper pair act on electrons as an effective interaction.

In this section we neglect for simplicity the terms involving the vector potential. Then, the electronic Green's functions recover the translational symmetry. By using the Fourier coefficients of the functions, we find

$$\Delta(\vec{k},\epsilon_n)=T\sum_l\sum_q\left[|C(\vec{q})|^2D(\vec{q},\epsilon_n-\epsilon_l)+I^2\chi^{zz}(\vec{q},\epsilon_n-\epsilon_l)+I^2\chi^{-+}(\vec{q},\epsilon_n\epsilon_l)\right]$$
$$\times\frac{-\Delta(\vec{k}-\vec{q},\epsilon_l)}{-[|i\epsilon_l+\xi_{k-q\uparrow}(\epsilon_l)][i\epsilon_l-\xi_{k-q\downarrow}(-\epsilon_l)]+|\Delta(\vec{k}-\vec{q},\epsilon_l)|^2}, \tag{3.11}$$

where $C(\vec{q})$ is the Fourier transform of the electron-phonon interaction. In deriving Eq. (3.11) we used

$$\vec{S}_i=N_0^{-1}\sum_q\vec{S}_q\exp(i\vec{q}\cdot\vec{R}_i). \tag{3.12}$$

In Eq. (3.11), $\xi_{k\sigma}(\epsilon_n)$ is the normal electron energy including the self-energy $\Sigma_\sigma(\vec{k},\epsilon_n)$ with momentum $\vec{k}$ and spin σ. The energy is measured from the Fermi energy. Equation (3.11) is essentially the same as that for the paramagnon system[40-42] if the electron-spin interaction I and the spin Green's functions are replaced by the short-ranged electron-electron interaction U_0 and the paramagnon

propagators,[33,34] respectively.

Equation (3.11) depends on the phonon and spin Green's functions so that it belongs to the strong-coupling system.[43] In the following, we consider the weak-coupling condition. The phonon Green's function is written[43]

$$D(\vec{q},\epsilon_\nu) = -2\omega_q/(\epsilon_\nu^2+\omega_q^2), \tag{3.13}$$

where ω_q is the phonon energy and $\epsilon_\nu = 2\pi T\nu$, ν being integer. The parameter $\Delta(\vec{k},\epsilon_n)$ with $|\epsilon_n| \ll \omega_D$, is finite below T_c, ω_D being the phonon Debye energy. In the weak-coupling limit ($T_c \ll \omega_D$), replacing the phonon energy ω_q by ω_D and taking $(\epsilon_n-\epsilon_l)^2$ to be zero because $|\epsilon_n-\epsilon_l| \ll \omega_D$, the phonon-mediated electron-electron interaction in Eq. (3.11) is substituted with the BCS interaction $g_{\rm BCS}$ as

$$-|C(\vec{q})|^2 D(\vec{q},\epsilon_n-\epsilon_l) \approx |C(\vec{q})|^2(2/\omega_D) \equiv g_{\rm BCS}.$$

The spin Green's functions in the paramagnetic state are of damping-type and are written[33]

$$\chi^{zz}(\vec{q},\epsilon_\nu) = \tfrac{1}{2}\chi^{-+}(\vec{q},\epsilon_\nu) = \frac{\chi(\vec{q})\Gamma(\vec{q})}{\Gamma(\vec{q})+|\epsilon_\nu|}, \tag{3.14}$$

where the anisotropy of the spin fluctuations was neglected, for simplicity. Here, $\chi(\vec{q})$ is the static spin susceptibility which is defined to be the staggered susceptibility measured in units of $(g_J-1)^2 \times (g_J\mu_B)^2$, and $\Gamma(\vec{q})$ is the damping constant. Referring to the case of the phonon-mediated interaction, the weak-coupling treatment for the spin-mediated electron-electron interaction requires that $T_c \ll \Gamma(\vec{q})$ with certain $\vec{q}$ values. The damping constant $\Gamma(\vec{q})$ is conventionally expressed as[21,22]

$$\Gamma(\vec{q}) = \beta B_0/\chi(\vec{q}), \tag{3.15}$$

where B_0 is a constant dependent on the magnetic materials but independent of temperature. Although we have no information on $\Gamma(\vec{q})$ in the compounds which we are concerned with, we assume that the condition $T_c \ll \Gamma(\vec{q})$ holds. Since our study is restricted to the weak-coupling limit for both the electron-phonon and the electron-spin interactions, we may also neglect the normal self-energy due to both phonon and spin fluctuations.

In the weak-coupling limit without magnetic field, Eq. (3.11) is written

$$\Delta(\vec{k}) = T\sum_l{}' \sum_q [g_{\rm BCS} - I^2\chi^{zz}(\vec{q}) - I^2\chi^{-+}(\vec{q})] \times \frac{\Delta(\vec{k}-\vec{q})}{\epsilon_l^2+\xi_{k-q}^2+|\Delta(\vec{k}-\vec{q})|^2}. \tag{3.16}$$

As seen in Eq. (3.16) the spin fluctuations suppress the BCS interaction because the sign of the terms is opposite to that of the BCS term. We assume that the BCS interaction is usually stronger than the interaction due to the spin fluctuations. Therefore, the summation in Eq. (3.16) is taken over $|\epsilon_l| < \omega_D$ and the prime on the summation in Eq. (3.16) indicates this restriction. The electrons which contribute to superconductivity are restricted to those near the Fermi surface. Since both the incident electron and the electron scattered by the spin fluctuation should be near the Fermi surface, the equation to determine T_c is given from Eq. (3.16) by

$$\Delta(\vec{k}) = g_{\rm eff}N(0)\int d\xi_p\, T_c \sum_l{}' \frac{\Delta(\vec{p})}{\epsilon_l^2+\xi_p^2}, \tag{3.17}$$

$$g_{\rm eff} = g_{\rm BCS} - \frac{I^2}{2}\int_{-1}^{1} d(\cos\theta)\left[\chi^{zz}\left(2k_F\hat{q}\sin\frac{\theta}{2}\right) + \chi^{-+}\left(2k_F\hat{q}\sin\frac{\theta}{2}\right)\right], \tag{3.18}$$

where θ is the scattering angle, $\hat{q}$ is the unit vector in the direction $\vec{k}-\vec{p}$, and $N(0)$ is the density of states at the Fermi level in the normal state.

A. Ferromagnets

When we define the Fourier transform of the exchange interaction given in Eq. (2.5) as

$$J_q = \sum_{(i-j)} J_{ij}\exp[i\vec{q}\cdot(\vec{R}_i-\vec{R}_j)], \tag{3.19}$$

the staggered susceptibility in mean-field theory,[21,22] is written

$$\chi(\vec{q}) = \chi^{zz}(\vec{q}) = \tfrac{1}{2}\chi^{-+}(\vec{q}) = C_0/(T-T_q), \tag{3.20}$$

with

$$T_q = 2C_0J_q, \tag{3.21}$$

$$C_0 = \tfrac{1}{3}cS(S+1), \tag{3.22}$$

c being the magnetic-ion concentration. In ferromagnets with magnetic-phase-transition temperature T_M equal to T_0, the spin fluctuations with small momenta are dominant so that $\chi(\vec{q})$ may be written

$$\chi(\vec{q}) = C_0/(T-T_M+Dq^2), \tag{3.23}$$

$$D = -\frac{1}{2}\left(\frac{\partial^2 T_q}{\partial q^2}\right)_{q=0}, \tag{3.24}$$

Inserting Eq. (3.23) into Eq. (3.18), we obtain

$$T_c = 1.14\omega_D \exp\left\{-1\Big/\left[g_{\mathrm{BCS}}N(0) - \frac{3C_0 I^2 N(0)}{4k_F^2 D} \times \ln\left(\frac{T_c - T_M + 4k_F^2 D}{T_c - T_M}\right)\right]\right\}. \quad (3.25)$$

Since the value of k_F may be of the order of the inverse of the lattice constant, Eq. (3.25) is approximated by

$$T_c = 1.14\omega_D \exp\left\{-1\Big/\left[g_{\mathrm{BCS}}N(0) - \frac{3I^2 N(0)}{2J_0} \times \ln\left(\frac{T_c}{T_c - T_M}\right)\right]\right\}. \quad (3.26)$$

The numerical calculation shows that T_c determined from Eq. (3.25) is well approximated by that from Eq. (3.26). As seen in Eq. (3.26), T_c decreases with increasing T_M and I when $T_c > T_M$. The relation between T_c and T_M obtained from Eq. (3.26) is plotted in Fig. 1 for four values of $3I^2/2J_0 g_{\mathrm{BCS}}$ the parameter T_{c0} is the superconducting transition temperature of the system without local spin and is given by

$$T_{c0} = 1.14\omega_D \exp[-1/g_{\mathrm{BCS}}N(0)]. \quad (3.27)$$

As seen in Fig. 1, the superconducting region is drastically reduced by the spin fluctuations. This is because the spin fluctuations prefer the spin-triplet state of conduction electrons rather than the spin-singlet state in a Cooper pair. This fact is not restricted to ferromagnets. In Sec. III B, T_c in antiferromagnets is discussed.

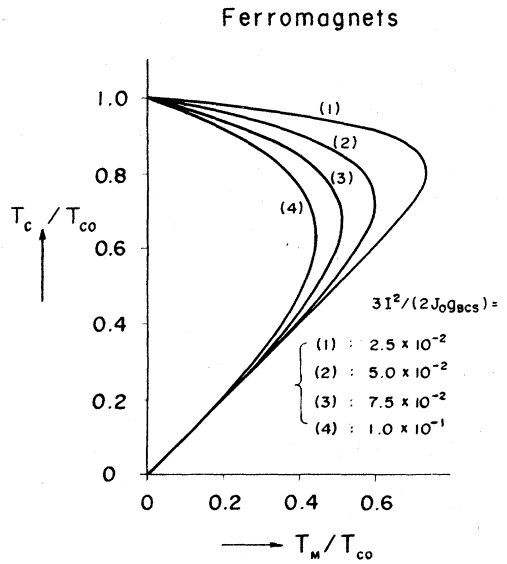

FIG. 1. Relation between the superconducting transition temperature T_c and the Curie temperature T_M in ferromagnets obtained from Eq. (3.26). The parameter T_{c0} is defined in Eq. (3.27).

B. Antiferromagnets

As seen in Eq. (3.18), the spin fluctuations which weaken the BCS coupling depend on the Fermi wave number. When we define the wave number $\vec{Q}$ which specifies the magnetic state below T_M, the spin fluctuations around $\vec{Q}$ are dominant. When Q is much smaller than $2k_F$, the spin fluctuations around $\vec{Q}$ contribute effectively in Eq. (3.18) so that the result is similar to that in ferromagnets, as discussed above. When Q is much larger than $2k_F$, the spin fluctuations around $\vec{Q}$ do not contribute to the effective interaction in Eq. (3.18) because the fluctuations around $\vec{Q}$ cannot scatter electrons on the Fermi surface. In this case, the momentum of the spin fluctuations included in Eq. (3.18) is much smaller than Q so that we may replace the staggered susceptibilities in the equation by that with $q = 0$. Then from Eq. (3.18) we have

$$T_c = 1.14\omega_D \exp\left[-1\Big/\left(g_{\mathrm{BCS}}N(0) - \frac{3C_0 I^2 N(0)}{T_c - T_0}\right)\right], \quad (3.28)$$

where $T_0 < T_M$. Although the effect of the spin fluctuation is weak compared to that in ferromagnets, we still find that the effect is crucial. When Q is not greatly different from $2k_F$, the scattering of the electrons due to the spin fluctuations becomes anisotropic. In this case, the anisotropy of the order parameter should be taken into account for solving Eq. (3.17). This problem will be treated in a separate paper. However, Eq. (3.28) holds semiquantitatively even in this case.

At this stage, it is worthwhile to mention the mechanism of the exchange interaction between local spins. Let us assume that the exchange interaction between local spins comes from the indirect interaction only via the electrons which contribute to the onset of superconductivity. Then, the interaction I, which is estimated from the relation $J_0 \approx I^2 N(0)$,[44-46] is considerably strong if the paramagnetic Curie temperature Θ is of order of 1 °K $[\Theta = \frac{2}{3}S(S+1)J_0]$. In this case, the effect of the spin fluctuations becomes extremely large. Referring to Eqs. (3.26) and (3.28) as well as to Fig. 1, we find that superconductivity does not exist at any temperature in these magnetic systems. Therefore, we conclude that in the compounds, $R\mathrm{Mo}_6X_8$ and $R\mathrm{Rh}_4\mathrm{B}_4$, the superconducting electrons are neither 5d nor 6s of the rare-earth ions which are responsible for the indirect interaction between local spins.

The dependence of the staggered susceptibilities on the concentration of local spins was calculated

within mean-field theory. However, mean-field theory does not work when the concentration decreases substantially. In Sec. IV, the mean-field theory for calculating the staggered susceptibilities is improved.

IV. MAGNETICALLY DILUTE SYSTEMS

In the compounds $R\mathrm{Mo}_6X_8$, the magnetic ions can easily be substituted by nonmagnetic ions such as La^{3+} and Sn^{2+}. The concentration of magnetic ions was introduced with mean-field theory in Sec. III. In this section, the superconducting transition temperature T_c in a magnetically dilute system is studied by improving mean-field theory.

When magnetic ions are substituted by nonmagnetic ions, the magnetic transition temperature T_M decreases, and at a certain value of the concentration of the magnetic ions T_M vanishes, although at high temperatures the magnetic susceptibility shows the Curie-Weiss law with a finite paramagnetic Curie temperature (here, we neglect the possibility of a spin-glass state). For simplicity, we assume that there exists exchange interaction J between the nearest-neighbor spins. The concentration of the magnetic ions is given by c. In the system, some of the ions are isolated from the others and do not contribute to the collective properties of spins. The isolated-ion probability is given by $(1-C)^z$, z being the number of nearest-neighbor sites. Therefore, the concentration of nonisolated ions is

$$c' = c[1-(1-c)^z]. \tag{4.1}$$

However, even if the magnetic ions are coupled with each other, the magnetic phase transition is not expected in the low-concentration system because of the statistical effect. For treating this statistical effect, the effective-Hamiltonian method developed by Oguchi *et al.*[16,17] is used. This method is extended to calculate the spin susceptibilities. The details are given in Appendix A.

First, we discuss the ferromagnetic case. Following Appendix A, the magnetic transition temperature and the staggered susceptibility with a small wave number q are expressed as

$$\frac{T_M}{J'} = \frac{2}{\ln[z'/(z'-4)]}, \tag{4.2}$$

$$\chi(\vec{q}) = \tfrac{2}{3}c'S(S+1)\beta\{2-\tfrac{1}{2}z'(1-e^{-2\beta J'}) + [(z'+1)/z][1-(2\beta J')^{-1} \times (1-e^{-2\beta J'})]q^2\}^{-1}, \tag{4.3}$$

with

$$J' = \tfrac{4}{3}S(S+1)J, \tag{4.4}$$

$$z' = 1+(z-1)c', \tag{4.5}$$

where the distance between nearest-neighbor spins is taken as unity. Here, we note that the critical concentration c_c below which T_M vanishes is given by

$$c_c[1-(1-c_c)^z] = 3/(z-1). \tag{4.6}$$

Inserting Eq. (4.3) into Eq. (3.18), we obtain

$$T_c = 1.14\omega_D \exp\left\{-1\Big/\left[g_{\mathrm{BCS}}N(0) - \frac{3I^2N(0)C_0'}{2f_2k_F^2T_c} \times \ln\left(\frac{f_1+4k_F^2f_2}{f_1}\right)\right]\right\}, \tag{4.7}$$

where

$$C_0' = \tfrac{1}{3}c'S(S+1),$$
$$f_1 = 2-z'[1-\exp(-\beta_cJ')\cosh(\beta_cJ')], \tag{4.8}$$
$$f_2 = \frac{z'+1}{z}\left(1-\exp(-\beta_cJ')\frac{\sinh(\beta_cJ')}{\beta_cJ'}\right),$$

with $\beta_c = 1/T_c$. In Fig. 2(a), the numerical results for T_c as a function of c are given by the solid lines for various values of $I^2N(0)/T_{c0}$. The dotted line shows T_M given by Oguchi *et al.*[17] For calculating T_c, we took $z=6$, $g_{\mathrm{BCS}}N(0)=0.3$, $4k_F^2=1$, $S=\frac{7}{2}$, and $J'/T_{c0}=0.5$. The ratio T_c/T_{c0} is not sensitive to the values of $g_{\mathrm{BCS}}N(0)$ and $4k_F^2$ (hereafter, the values of these parameters are fixed at 0.3 and 1, respectively). Even when the ferromagnetic transition does not exist because of the low concentration, the superconducting state disappears at very low temperatures. This is because the susceptibility increases with decreasing temperature at very low temperatures as $\chi(0)\propto 1/T$. Since we neglected the effect of the isolated spins which act on electrons as pair breakers, as studied by Abrikosov and Gorkov,[15] our results have only qualitative meaning at very low concentrations. In Fig. 2(b), both T_c and T_M are given for various values of J'/T_{c0}, with $I^2N(0)/T_{c0}$ taken as 3.2×10^{-4}. The other parameters are the same as those in Fig. 2(a).

Ishikawa and Fischer[10] have observed that the compound $\mathrm{Ho}_{1.2}\mathrm{Mo}_6\mathrm{S}_8$ is a superconductor in the temperature range between 1.2 and 0.64 °K. The susceptibility measurements above 1.5 °K give a positive paramagnetic Curie temperature Θ of 0.54 °K.[10] We calculated the superconducting transition temperature T_c in this compound as a function of the magnetic-ion (Ho^{3+}) concentration. In this calculation, we used $z=6$, $S=\frac{3}{2}$, $T_{c0}=1.56$ °K, and $J'=0.18$ °K, which was estimated from Θ. In Fig. 3(a), the solid lines show T_c for various values of $I^2N(0)$. The dotted line shows

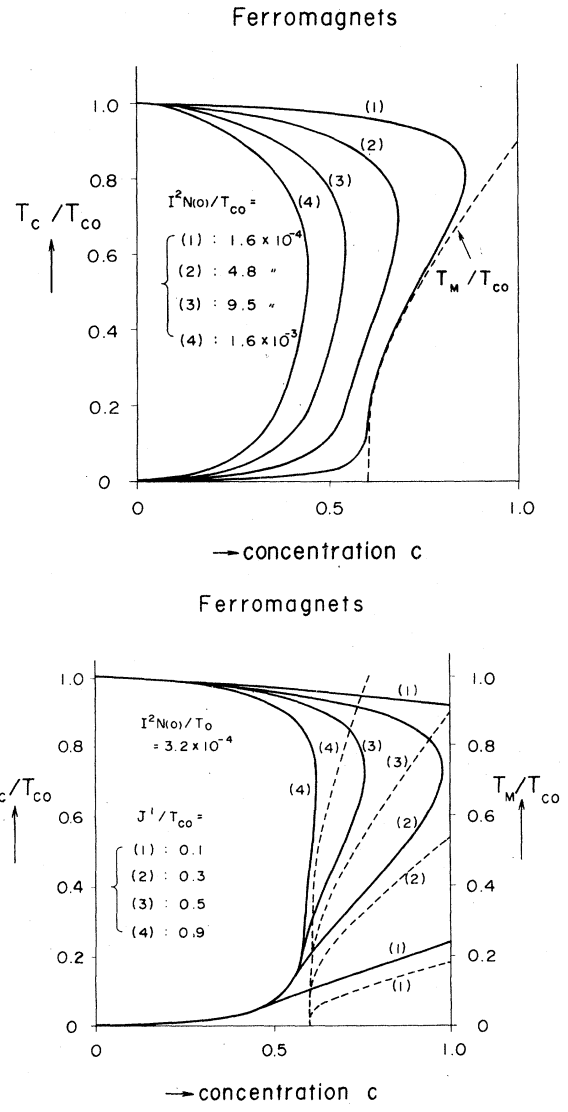

FIG. 2. (a) Dependence of T_c on the concentration of magnetic ions c in a simple cubic ferromagnet. The solid lines show T_c/T_{c0} for various values of $I^2N(0)/T_{c0}$ and the dotted line shows T_M/T_{c0}. The parameters are taken as $S=\frac{7}{2}$, $J'/T_{c0}=0.5$, $g_{BCS}N(0)=0.3$, and $4k_F^2=1$. (b) Relation between T_c and T_M for various values of J'/T_{c0} as a function of the concentration c in a simple cubic ferromagnet. The value of $I^2N(0)/T_{c0}$ is taken as 3.2×10^{-4}. The other parameters are the same as those in (a).

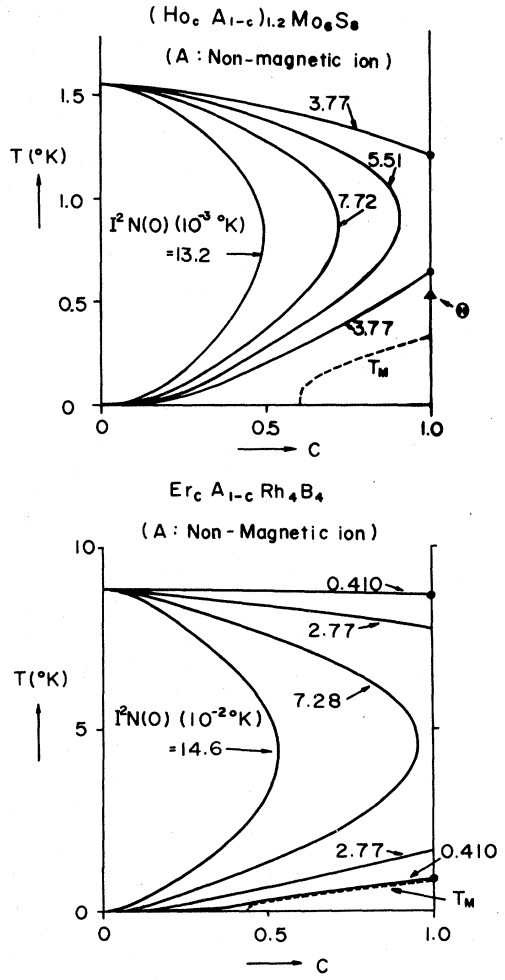

FIG. 3. (a) Theoretical results for T_c and T_M when the magnetic ions are substituted by nonmagnetic ions in the compound $Ho_{1.2}Mo_6S_8$. The abscissa gives the concentration of magnetic ions. The black circles show the experimental values of T_c observed by Ishikawa and Fischer (Ref. 10) in $Ho_{1.2}Mo_6S_8$. The triangle is the experimental value of Θ (Ref. 10). (b) Theoretical results for T_c and T_M when the magnetic ions are substituted by nonmagnetic ions in the compound $ErRh_4B_4$. The abscissa gives the concentration of magnetic ions. The solid circles show the experimental values of T_c observed by Fertig *et al.* (Ref. 8) and Moncton *et al.* (Ref. 9) in $ErRh_4B_4$.

T_M. The black circles and the triangle, respectively, represent the experimental values of T_c and Θ observed by Ishikawa and Fischer.[10] When we tentatively use the value $N(0)=0.5$ eV^{-1},[12] we find $|I|=0.81$ meV.

In $ErRh_4B_4$ the superconducting transition occurs at 8.7 °K and the superconducting to ferromagnetic phase transition at 0.9 °K.[8,9] Assuming the magnetic lattice of a body-centered-cubic crystal ($z=8$) and $S=1$ as the spin value of an Er^{3+} ion, T_c is calculated and the results are given in Fig. 3(b) by solid lines for various values of $I^2N(0)$. In the figure, the dotted line which shows T_M is almost overlapping with the solid line corresponding to $I^2N(0)=4.1\times10^{-3}$ °K. The closed circles are the experimental values of T_c observed by Fertig *et al.*[8] and Moncton *et al.*[9] The other parameters appearing in Eq. (4.7) were taken as $T_{c0}=8.83$ °K, and $J'=0.295$ °K. When we use the value $N(0)$

$=0.5\ \mathrm{eV}^{-1}$, we find $|I|=0.84$ meV. It is highly desired to observe the concentration dependence of T_c and T_M in the two compounds mentioned above.

In antiferromagnets with nearest-neighbor exchange interaction, the wave numbers $\vec{Q}$ are on the Brillouin-zone boundary. Therefore, the staggered susceptibilities in Eq. (3.18) may be replaced by the uniform susceptibility $\chi(0)$, which is obtained by changing the sign of J' as

$$\chi(0)=\tfrac{2}{3}c'S(S+1)\beta/[2-\tfrac{1}{2}z'(1-e^{2\beta|J'|})]. \qquad (4.9)$$

Then, T_c is calculated as

$$T_c=1.14\omega_D\exp\left[-1\Big/\left(g_{\mathrm{BCS}}N(0)-\frac{2c'S(S+1)I^2N(0)\beta_c}{2-\frac{1}{2}z'(1-e^{2\beta_c|J'|})}\right)\right]. \qquad (4.10)$$

McCallum *et al.*[18] have observed the specific heat and the susceptibility in $La_{1-c}Gd_cMo_6Se_8$ for various values of c. This compound has a negative paramagnetic Curie temperature Θ at any value of c. In Fig. 4(a), the theoretical T_c results for various values of $I^2N(0)$ are shown along with T_M and $|\Theta|$. The experimental values observed by McCallum *et al.*[18] are also plotted in the figure. The parameters z, S, and T_{c0} were taken as 6, $\frac{7}{2}$, and 9.0 °K, respectively. The exchange interaction J' was taken as -0.45 °K, for which value the theoretical Θ at $c=1$ agrees with the experimental one. The Néel temperature T_M at $c=1$ calculated by using the value of J' is 0.8 °K, which is in agreement with the experimental value observed by McCallum *et al.*[18] The theoretical curve with $I^2N(0)=0.018$ °K reproduces the experimental T_c results quite well. This value of $I^2N(0)$ gives $|I|=1.8$ meV if $N(0)=0.5\ \mathrm{eV}^{-1}$ is used.

In the compound $Sn_{1.2(1-c)}Eu_cMo_{6.35}S_8$ studied by Fischer *et al.*,[6,12] a Eu ion is in the divalent state Eu^{2+} and has the same ionic radius as a Sn^{2+} ion. Therefore, substitution of Eu ions by Sn ions changes neither the lattice constant nor the electron-atom ratio. In Fig. 4(b), the theoretical values of T_c as a function of the Eu concentration c for various values of the parameter $I^2N(0)$ are given, as well as the experimental values observed by Fischer *et al.*[6,13] Here, we assumed the Néel temperature of the stoichiometric Eu compound to be 1 °K ($J'=-0.64$ °K). The other parameters used for the calculation are $z=6$, $S=\frac{7}{2}$, and $T_{c0}=13.0$ °K. The theoretical curve with $I^2N(0)=0.035$ °K agrees with experiment for $c>0.4$. From this result, we find $|I|=2.5$ meV for $N(0)=0.5\ \mathrm{eV}.^{-1}$ The theoretical values deviate from the experimental ones for $c<0.4$. This discrepancy may come from the facts that the atomic mass of a Eu ion is very different from that of a

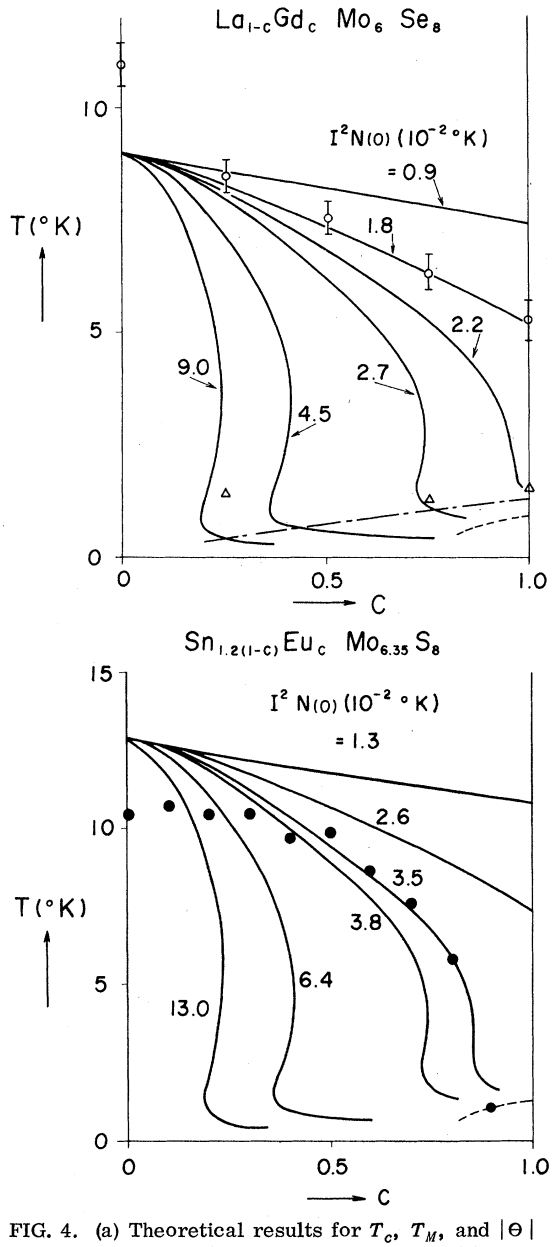

FIG. 4. (a) Theoretical results for T_c, T_M, and $|\Theta|$ are shown by the solid, dotted, and dot-dashed lines, respectively, as a function of c in $La_{1-c}Gd_cMo_6Se_8$. The parameters z, S, J', and T_{c0} were taken as 6, $\frac{7}{2}$, -0.45 °K, and 9.0 °K, respectively. The open circles and the triangles show the experimental results for T_c and $|\Theta|$, respectively, observed by McCallum *et al.* (Ref. 18). The solid line with $I^2N(0)=1.8\times10^{-2}$ °K agrees with the experiment except at $c=0$. (b) Theoretical results for T_c and T_M are shown by the solid and dotted lines, respectively, as a function of c in $Sn_{1.2(1-c)}Eu_cMo_{6.35}S_8$. The parameters z, S, J', and T_{c0} were taken as 6, $\frac{7}{2}$, -0.64 °K, and 12.5 °K, respectively. The solid circles are the experimental results for T_c observed by Fischer *et al.* (Refs. 6 and 13). The solid line with $I^2N(0)=3.5\times10^{-2}$ °K agrees with experiment when $c>0.4$.

Sn ion and our theory has only qualitative meaning when the concentration of the magnetic ions is quite low, as mentioned above. As seen in Figs. 4(a) and 4(b), T_c is almost independent of the concentration at very low temperatures. This is because the susceptibility $\chi(0)$ becomes almost zero at these temperatures. In this paper we concentrate ourselves on the paramagnetic phases. The antiferromagnetic states will be studied in a separate paper.

V. UPPER CRITICAL FIELD

In a magnetic field, the superconducting transition temperature decreases because of the Meissner effect and the spin splitting of the conduction bands. In our compounds with many magnetic ions, the local spins are polarized by the magnetic field. The vector potential acting on the orbital motion of conduction electrons is related to the magnetic induction $\vec{B}$ rather than the magnetic field $\vec{H}$,

$$\vec{B} = \mathrm{curl}\,\vec{A}, \tag{5.1}$$

where

$$\vec{B} = \vec{H} + 4\pi\vec{M}. \tag{5.2}$$

Here, $\vec{M}$ is the magnetization and is given by

$$M = -g_J(g_J-1)^{-1}\mu_B\langle S_z\rangle cN_0, \tag{5.3}$$

where N_0 is the number of local spins in a unit volume, and $\langle S_z\rangle$ is the local spin polarization induced by the field and has a negative value. In the compounds studied the value of $4\pi M$ reaches up to a few kG. The polarization of the local spins in the magnetic field causes the spin splitting of the conduction bands, as discussed in Sec. III. Since the electron-spin interaction I, which may have either sign, is of the order of 1 meV in the compounds studied, as obtained in Sec. IV, the usual Pauli paramagnetic effect may drastically be modified by the polarization of the local spins.[2,47] As studied in the preceding sections, the spin fluctuations suppress the effective BCS interaction. Since the fluctuations decrease in the field,[21,22] the effective BCS interaction increases with increasing magnetic field. In this section we formulate the upper critical field of dirty superconductors taking into account these effects of the local spins.

As discussed in Sec. III, the order parameter is nonlocal in space because the spin fluctuations are of long range. The spin fluctuations inside a Cooper pair produce an effective interaction between the electrons. The size of a Cooper pair in space is of the order of the coherence length $\xi_0 \sim v_F/T_c$, v_F being the Fermi velocity.[48] On the other hand, the force range of the spin-spin interaction is of the order of the nearest-neighbor distance between spins. Therefore, the spin correlation length is also of the order of the distance unless the temperature is extremely close to the magnetic transition temperature.[49] Because of the smallness of the spin correlation length compared with the size of a Cooper pair, we may replace the nonlocal order parameter by the local one after summing up the spin fluctuations inside a Cooper pair. We are restricted to the case of the isotropic g_{eff} given in Eq. (3.18). Then, Eq. (3.8) is reduced in the weak-coupling limit, for both electron-phonon and electron-spin interactions, to be

$$\Delta(\vec{x}) = g_{eff}(H)T\sum{}' F^{\dagger}_{\uparrow,\downarrow}(\vec{x},\vec{x}:\epsilon_l), \tag{5.4}$$

where the effective coupling defined in Eq. (3.18) was rewritten $g_{eff}(H)$ because it is a function of the field. Once the order parameter is expressed as the local one, it is straightforward to obtain the integral equations

$$G_{\uparrow,\uparrow}(\vec{x},\vec{x}':\epsilon_n) = G^n_{\uparrow,\uparrow}(\vec{x},\vec{x}':\epsilon_n) - \int d^3x_1\,\Delta(\vec{x}_1)G^n_{\uparrow,\uparrow}(\vec{x},\vec{x}_1:\epsilon_n)\,F_{\downarrow,\uparrow}(\vec{x}_1,\vec{x}':\epsilon_n), \tag{5.5}$$

$$F_{\downarrow,\uparrow}(\vec{x},\vec{x}':\epsilon_n) = \int d^3x_1\,G^n_{\downarrow,\downarrow}(\vec{x}_1,\vec{x}:-\epsilon_n)\Delta^*(\vec{x}_1)\,G_{\uparrow,\uparrow}(\vec{x}_1,\vec{x}':\epsilon_n), \tag{5.6}$$

where $G^n_{\sigma,\sigma}(\vec{x},\vec{x}':\epsilon_n)$ is the Green's function in the normal state.

Since the range of $G^n_{\sigma\sigma}(\vec{x},\vec{x}':\epsilon_n)$ in space is short compared with the radius of an electron cyclotron orbit in a magnetic field, we may introduce the semiclassical phase-integration approximation

$$G^n_{\sigma\sigma}(\vec{x}_1,\vec{x}:\epsilon_n) = G^{n0}_{\sigma\sigma}(\vec{x}_1-\vec{x}:\epsilon_n)\exp\left(ie\int_x^{x_1} d\vec{s}\cdot\vec{A}(\vec{s})\right), \tag{5.7}$$

where $G^{n0}_{\sigma\sigma}(\vec{x}_1-\vec{x}:\epsilon_n)$ is the Green's function without the term involving the vector potential. Using Eqs. (5.4), (5.5), and (5.6) and retaining a term linear in $\Delta(\vec{x})$, we have

$$\begin{aligned}\Delta(\vec{x}) &= g_{eff}(H)T\sum_n{}' \int d^3x_1 K_{\downarrow,\uparrow}(\vec{x}_1-\vec{x}:\epsilon_n) \times \exp\left(2ie\int_x^{x_1} d\vec{s}\cdot\vec{A}(\vec{s})\right)\Delta(\vec{x}_1)\\ &= g_{eff}(H)T\sum_n{}' \int d^3x_1 K_{\downarrow,\uparrow}(\vec{x}_1-\vec{x}:\epsilon_n) \times \exp[-i(\vec{x}-\vec{x}_1)\cdot\vec{\Pi}^{\dagger}]\Delta(\vec{x}),\end{aligned} \tag{5.8}$$

with

$$\vec{\Pi}^{\dagger} = i\vec{\nabla}_x - 2e\vec{A}(\vec{x}) , \tag{5.9}$$

$$K_{-\sigma,\sigma}(\vec{x}_1 - \vec{x}:\epsilon_n) = G^{n0}_{-\sigma,-\sigma}(\vec{x}_1 - \vec{x}: -\epsilon_n)\, G^{n0}_{\sigma,\sigma}(\vec{x}_1 - \vec{x}:\epsilon_n) . \tag{5.10}$$

When we introduce the Fourier coefficient $K_{-\sigma,\sigma}(\vec{q}:\epsilon_n)$ as[50]

$$K_{-\sigma,\sigma}(\vec{r}:\epsilon_n) = \int \frac{d^3q}{(2\pi)^3} K_{-\sigma,\sigma}(\vec{q}:\epsilon_n) e^{i\vec{q}\cdot\vec{r}} , \tag{5.11}$$

Eq. (5.8) becomes

$$\left(1 - g_{eff}(H) T \sum_n {}' K_{-\sigma,\sigma}(\vec{q} = \vec{\Pi}^{\dagger}:\epsilon_n)\right)\Delta(\vec{x}) = 0. \tag{5.12}$$

A. Dirty limit

Although we have not introduced the effect of impurities explicitly, it is obvious how the effect enters in the equations in the standard way.[51] Let us first calculate H_{c2} in the dirty limit taking into account the non-spin-flip scattering of electrons. Following Appendix B and neglecting the term of the order of $(h/\epsilon_F)^2$, we have

$$K_{-\sigma,\sigma}(q:\epsilon_n) = \pi N(0)\left(|\epsilon_n| + i\sigma h \epsilon_n/|\epsilon_n| + \tfrac{1}{6}\tau_0 q^2 v_F^2\right)^{-1} \tag{5.13}$$

where τ_0 is the relaxation time and is expressed, by using the non-spin-flip impurity potential u and the number density n, as

$$\tau_0^{-1} = 2\pi N(0) n |u|^2. \tag{5.14}$$

Introducing Eq. (5.13) into Eq. (5.12) and taking[50]

$$\Delta(x) = \exp(-eBx^2),$$

we find the equation for determining $H_{c2}(T)$,

$$\ln\frac{T}{T_{c0}(H)} - \mathrm{Re}\left[\psi(\tfrac{1}{2}) - \psi\left(\frac{1}{2} + \frac{i\sigma h}{2\pi T} + \frac{e\tau_0 v_F^2 B}{6\pi T}\right)\right] = 0, \tag{5.15}$$

with

$$T_{c0}(H) = 1.14\omega_D \exp[-1/g_{eff}(H)N(0)], \tag{5.16}$$

$\psi(z)$ being the digamma function.

The spin-orbit interaction of conduction electrons reduces the effect of the spin splitting of the band on the superconducting transition temperature.[19,20] This interaction is quite important in our system because the splitting becomes extremely large. The spin-orbit interaction potential is expressed as

$$i u_{SO} k_F^{-2} (\vec{k} \times \vec{k}') \cdot \vec{\sigma} , \tag{5.17}$$

where $\vec{k}$ and $\vec{k}'$ are the momenta of the incoming and outgoing electrons, respectively, and $\vec{\sigma}$ is the Pauli spin matrix. Leaving the detailed calculation to Appendix B, we find the equation for determining $H_{c2}(T)$:

$$\ln\frac{T}{T_{c0}(H)} + \frac{1}{2}\left[\left(1 + \frac{b_s}{(b_s^2 - I_s^2)^{1/2}}\right)\psi(\tfrac{1}{2} + \rho_-) + \left(1 - \frac{b_s}{(b_s^2 - I_s^2)^{1/2}}\right)\psi(\tfrac{1}{2} + \rho_+)\right] - \psi(\tfrac{1}{2}) = 0, \tag{5.18}$$

$$b_s = (3\tau_{SO})^{-1},$$

$$I_s = \sigma h, \tag{5.19}$$

$$\rho_{\pm} = (1/2\pi T)[a_s \pm (b_s^2 - I_s^2)^{1/2}],$$

with

$$a_s = b_s + \tfrac{1}{3} e\tau_0 v_F^2 B ,$$
$$\tau_{SO}^{-1} = \tfrac{4}{3}\pi N(0) n_s |u_{SO}|^2 , \tag{5.20}$$

where n_s is the number density of the scatterers. Here, we assumed $\tau_0 \ll \tau_{SO}$. In the limit of weak spin-orbit interaction, Eq. (5.18) is reduced to Eq. (5.15). On the other hand, in the limit of strong spin-oribt interaction, Eq. (5.18) is reduced to

$$\ln\frac{T}{T_{c0}(H)} + \psi\left(\frac{1}{2} + \frac{e\tau_0 v_F^2 B}{6\pi T}\right) - \psi(\tfrac{1}{2}) = 0. \tag{5.21}$$

B. Effective coupling constant

Equation (5.18) is different from that for the usual superconductors[52] because $T_{c0}(H)$, h, and $\vec{B}$ are functions of the magnetic field. The functional forms of h and $\vec{B}$ are given in Eqs. (3.4) and (5.2), respectively. In this subsection, we consider $T_{c0}(H)$ and $g_{eff}(H)$. The effective coupling constant $g_{eff}(H)$ is a function of the staggered susceptibilities in a magnetic field. The susceptibilities were calculated by using the mean-field theory of Ref. 21. According to Ref. 21 we have

$$\chi^{zz}(q) = cS^2 B_S'(\beta S a)/[T - 2cJ_q S^2 B_S'(\beta S a)], \tag{5.22}$$

$$\chi^{-+}(q) = 2cSB_S(\beta S a)/[a - 2cJ_q S B_S(\beta S a)], \tag{5.23}$$

$$a = -g'\mu_B H + 2cJ_0\langle S_z\rangle ,$$
$$g' = g_J/(g_J - 1) , \tag{5.24}$$

where $B_S(z)$ is the Brillouin function, $B_S'(z) = (d/dz)B_S(z)$, and J_q is given in Eq. (3.19). For simplicity, the concentration of spins c was introduced within mean-field theory instead of using

the effective-Hamiltonian method given in Sec. IV. When the magnitude of $|\langle S_z\rangle|$ is less than 0.3S at the temperature and field we are concerned with, we may expand the Brillouin function and retain terms up to third order and have

$$\chi^{zz}(q)=C_0(1-b)/[T-T_q(1-b)], \tag{5.25}$$

$$\chi^{\perp\perp}(q)=2C_0(1-\tfrac{1}{3}b)/[T-T_q(1-\tfrac{1}{3}b)], \tag{5.26}$$

$$b=\tfrac{1}{10}\beta^2[S^2+(S+1)^2]a^2, \tag{5.27}$$

where T_q and C_0 are defined in Eqs. (3.21) and (3.22), respectively. From Eqs. (5.25) and (5.26), it is easy to see that the staggered susceptibilities decrease with increasing magnetic field.

In ferromagnets, the susceptibilities around $q=0$ contribute to $g_{\rm eff}(H)$ dominantly so that we approximate J_q as

$$2J_q=2J_0-D_0q^2. \tag{5.28}$$

Using Eqs. (3.18), (5.22), (5.23), and (5.28), we have

$$g_{\rm eff}(H)=g_{\rm BCS}-\frac{I^2}{4k_F^2D_0}\times\left[\ln\left(\frac{T-c(2J_0-4k_F^2D_0)S^2B_S'(\beta Sa)}{T-2cJ_0S^2B_S'(\beta Sa)}\right)+2\ln\left(\frac{a-c(2J_0-4k_F^2D_0)SB_S(\beta Sa)}{a-2cJ_0SB_S(\beta Sa)}\right)\right]. \tag{5.29}$$

When we approximate $4k_F^2D_0$ to be $2J_0$ because k_F is of the order of the inverse of the lattice constant and because the results are not sensitive to the value of $4k_F^2D_0$, Eq. (5.29) becomes

$$g_{\rm eff}(H)=g_{\rm BCS}-\frac{I^2}{2J_0}\left[\ln\left(\frac{T}{T-2cJ_0S^2B_S'(\beta Sa)}\right)+2\ln\left(\frac{a}{a-2cJ_0SB_S(\beta Sa)}\right)\right]. \tag{5.30}$$

In antiferromagnets, $g_{\rm eff}(H)$ depends on the wave number $\vec{Q}$ which describes the antiferromagnetic properties as discussed in Sec. III. In the case that Q is large enough, the dispersion of the staggered susceptibilities in Eq. (3.18) may be neglected. Substituting the staggered susceptibilities with the uniform ones, we have

$$g_{\rm eff}(H)=g_{\rm BCS}-I^2c\left(\frac{S^2B_S'(\beta Sa)}{T-2cJ_0S^2B_S'(\beta Sa)}+\frac{2SB_S(\beta Sa)}{a-2cJ_0SB_S(\beta Sa)}\right), \tag{5.31}$$

where $J_0<J_Q$.

VI. ULTRA-HIGH-FIELD SUPERCONDUCTORS

Since the compounds we are concerned with belong between the dirty superconductors, the spin-oribt interaction is quite strong, as shown in experiments.[12-14] Therefore, we first study $H_{c2}(T)$ in the limit of strong spin-oribt interaction ($\tau_{\rm SO}\to 0$), in which the band-splitting effect is erased [Eq. (5.21)].

Near the superconducting transition temperature T_c where $H_{c2}(T)$ is small, $H_{c2}(T)$ is expressed by expanding Eq. (5.21) up to second order in the field as

$$\frac{T_{c0}(H)-T}{T_{c0}(H)}=\frac{\pi e\tau_0v_F^2B}{12T_{c0}(H)}+15.938\left(\frac{e\tau_0v_F^2B}{6\pi T_{c0}(H)}\right)^2, \tag{6.1}$$

where we used $\psi'(\frac{1}{2})=\zeta(2)$ and $\psi''(\frac{1}{2})=-14\zeta(3)$ with $d^n\psi(z)/dz^n=\psi^{(n)}(z)$. Here, B is a function of the field and given, from Eqs. (5.2) and (5.3), by

$$B=[1+4\pi g'\mu_BN_0\chi^{zz}(0)]H. \tag{6.2}$$

We note that $T_{c0}(H)$ is also a function of the field. Using the susceptibilities in Eqs. (5.25) and (5.26), the effective coupling constant $g_{\rm eff}(H)$ is written

$$g_{\rm eff}(H)=g_{\rm BCS}-\frac{I^2}{2J_0}\left[\ln\left(\frac{T}{T-T_M(1-b)}\right)+2\ln\left(\frac{T}{T-T_M(1-\frac{1}{3}b)}\right)\right] \tag{6.3}$$

for ferromagnets, and

$$g_{\rm eff}(H)=g_{\rm BCS}-I^2\left(\frac{C_0(1-b)}{T-T_0(1-b)}+\frac{2C_0(1-\frac{1}{3}b)}{T-T_0(1-\frac{1}{3}b)}\right) \tag{6.4}$$

for antiferromagnets. It is easy to see from Eqs. (6.3), (6.4), and (5.16) that $g_{\rm eff}(H)$ and thus $T_{c0}(H)$ are functions of H^2. This is in strong contrast to the case of the usual superconductors in which $T_{c0}(H)$ in Eq. (6.1) is replaced by a constant T_{c0} independent of H. From the above relations, we find that the polarization of the local spins reduces the usual value $12/\pi e\tau_0v_F^2$ of the initial slope of H_{c2}, $[dH_{c2}(T)/dT]_{T=T_c}$, to

$$[1+4\pi g'\mu_BN_0\chi^{zz}(0)]^{-1}(12/\pi e\tau_0v_F^2).$$

When the temperature goes to zero and the Zeeman energy of the local spins is much larger than the exchange energy, Eq. (5.21) is rewritten

$$\tfrac{1}{6}e\tau_0v_F^2B=4\gamma\pi T_{c0}(H), \tag{6.5}$$

γ being the Euler constant ($\ln\gamma=0.577\ldots$). Since

the effective coupling constant is expressed as

$$g_{\mathrm{eff}}(H) = g_{\mathrm{BCS}} - 2cI^2S/g'\mu_B H, \tag{6.6}$$

for both ferromagnets and antiferromagnets, $T_{c0}(H)$ is written

$$T_{c0}(H) = T_{c0}\left(1 - \frac{2cI^2S}{g_{\mathrm{BCS}}^2 N(0) g'\mu_B H}\right), \tag{6.7}$$

where we assumed $g_{\mathrm{BCS}} \gg 2cI^2S/g'\mu_B H$. Inserting Eq. (6.7) into Eq. (6.5), we have

$$H_{c2}(0) = \frac{24\gamma\pi}{e\tau_0 v_F^2} T_{c0}\left(1 - \frac{2cI^2S}{g_{\mathrm{BCS}}^2 N(0) g'\mu_B H_{c2}(0)}\right) - 4\pi g'\mu_B N_0 cS. \tag{6.8}$$

As seen in Eq. (6.8), at low temperatures $H_{c2}(T)$ almost recovers the value it has in the system

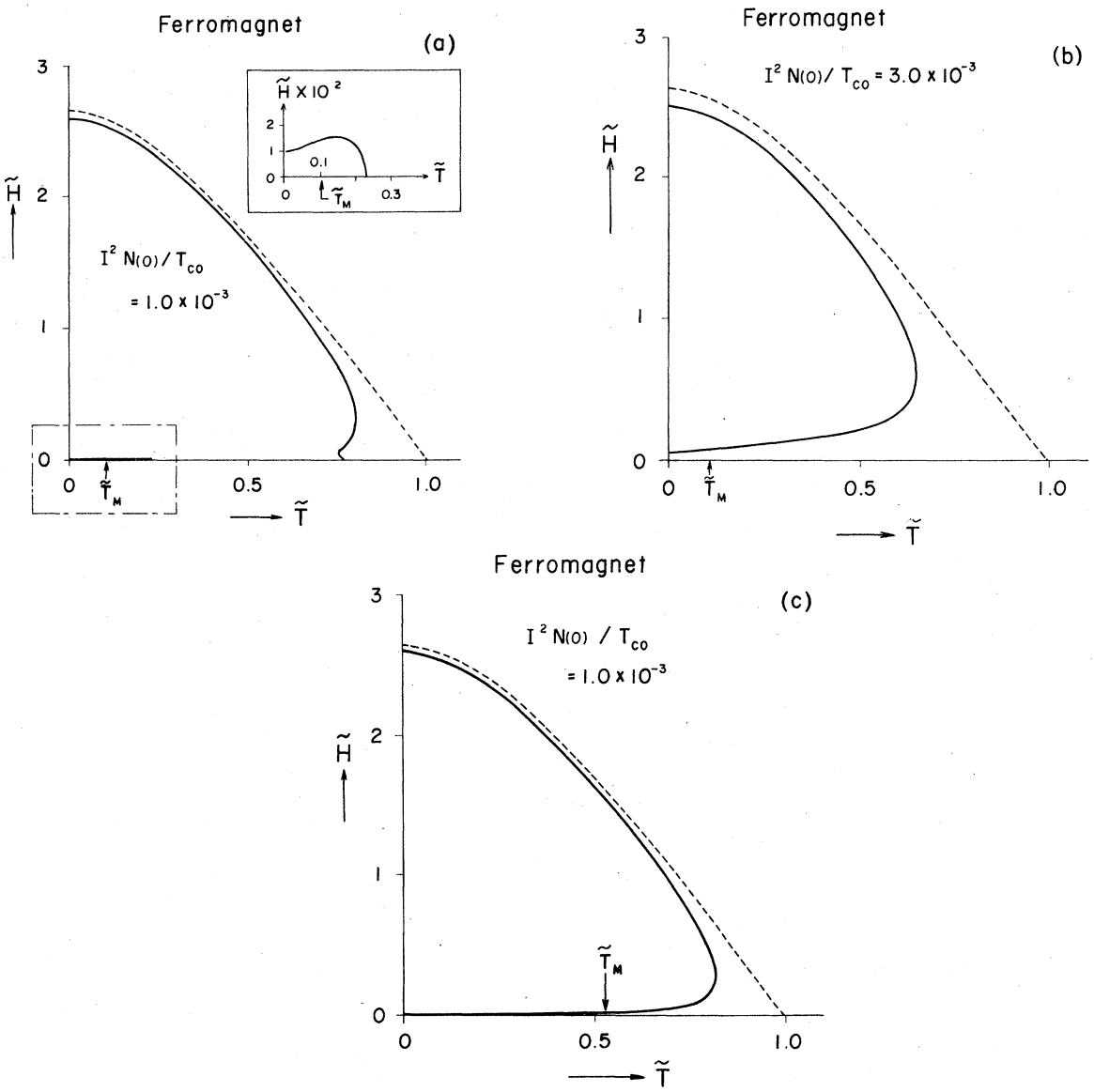

FIG. 5. (a) Theoretical results for $H_{c2}(T)$ as a function of $\tilde{T} = T/T_{c0}$ in a ferromagnet with $T_M/T_{c0} = 0.105$ and $I^2N(0)/T_{c0} = 1.0\times10^{-3}$. The ordinate gives the magnetic field $\tilde{H} = \alpha H$ with $\alpha = e\tau_0 v_F^2/T_{c0}$. In the calculation the parameters S, g', c, and α were taken as $\frac{7}{2}$, 2, 1.0, and 6.72×10^{-3} kG^{-1}, respectively. The dotted line shows $H_{c2}(T)$ in the system without local spin, as a reference. The inset is the enlarged portion of the figure which shows the lower critical temperature. (b) Theoretical results for $H_{c2}(T)$ when the value of $I^2N(0)/T_{c0}$ increases to 3.0×10^{-3} from the value 1.0×10^{-3} in (a). (c) Theoretical results for $H_{c2}(T)$ when $\tilde{T}_M$ increases to 0.525 from 0.104 in (a).

without local spin. In the following, we present the numerical results for $H_{c2}(T)$.

A. Ferromagnets

The numerical results for $H_{c2}(T)$ in ferromagnets as a function of temperature T are shown in Fig. 5, for various values of $I^2N(0)/T_{c0}$ and T_M/T_{c0}. Here, the temperature and the magnetic field H are respectively normalized by T_{c0} and α as $\tilde{T}=T/T_{c0}$ and $\tilde{H}=\alpha H$, where $\alpha=e\tau_0 v_F^2 T_{c0}^{-1}$. For the numerical calculation, S, g', c, and α are taken as 3.5, 2, 1.0, and 6.72 $\times 10^{-3}$ kG^{-1}, respectively, referring to the compound $Sn_{1.2(1-x)}Eu_xMo_{6.35}S_8$.[12,13] In this case, unity for $\tilde{H}$ corresponds to 149 kG. Changing α only causes scaling of the magnetic field in ultra-high-field superconductors. In each Fig. 5, the dotted line denotes $H_{c2}(T)$ in the system without local spin as a reference. Figure 5(a) is the result for $T_M/T_{c0}=0.105$ and $I^2N(0)/T_{c0}=1.0\times10^{-3}$. When there is no magnetic field, the superconducting state appears in the temperature range between $T/T_{c0}=0.765$ and 0.230. With increasing magnetic field, the upper critical temperature decreases according to Eq. (6.1). On the other hand, the lower critical temperature rapidly shrinks because the ferromagnetic transition temperature disappears in the field, as shown in the inset. By further increasing the magnetic field, the upper critical temperature starts to increase because the spin fluctuations are suppressed in the field. When the field becomes strong enough, the local spins are forced to align because of the field and the spin fluctuations almost disappear. Therefore, $H_{c2}(T)$ behaves as if there were no local spin. The small deviation of $H_{c2}(T)$ at low temperatures from the $H_{c2}(T)$ for the system with no local spin is due to the fact that the suppression of the fluctuation is not complete in a finite field, as seen in Eq. (6.8).

In Fig. 5(b), we show $H_{c2}(T)$ when the value of $I^2N(0)/T_{c0}$ is increased, and in Fig. 5(c), we show $H_{c2}(T)$ when the exchange interaction between local spins is strengthened. As seen in these figures, the upper critical temperature at zero field decreases with increasing $I^2N(0)$ and T_M/T_{c0}, and for these parameters the superconducting state does not exist at zero field. However, application of the magnetic field induces the superconducting state. This is due to the following reason: In no magnetic field, the electron-electron interaction due to the spin fluctuations overcompensates the BCS interaction, and $g_{eff}(H)$ becomes negative. In the magnetic field, the spin fluctuations are suppressed and $g_{eff}(H)$ returns positive. This fact suggests the possibility of the onset of superconductivity in the field.

B. Antiferromagnets

Figures 6 show the numerical results for $H_{c2}(T)$ in antiferromagnets. In Fig. 6(a), $I^2N(0)/T_{c0}$ and $\Theta/T_{c0}=T_0/T_{c0}$ are taken to be 3.0×10^{-3} and -1.04, respectively. We note that the paramagnetic Curie temperature $|\Theta|$ differs from the magnetic transi-

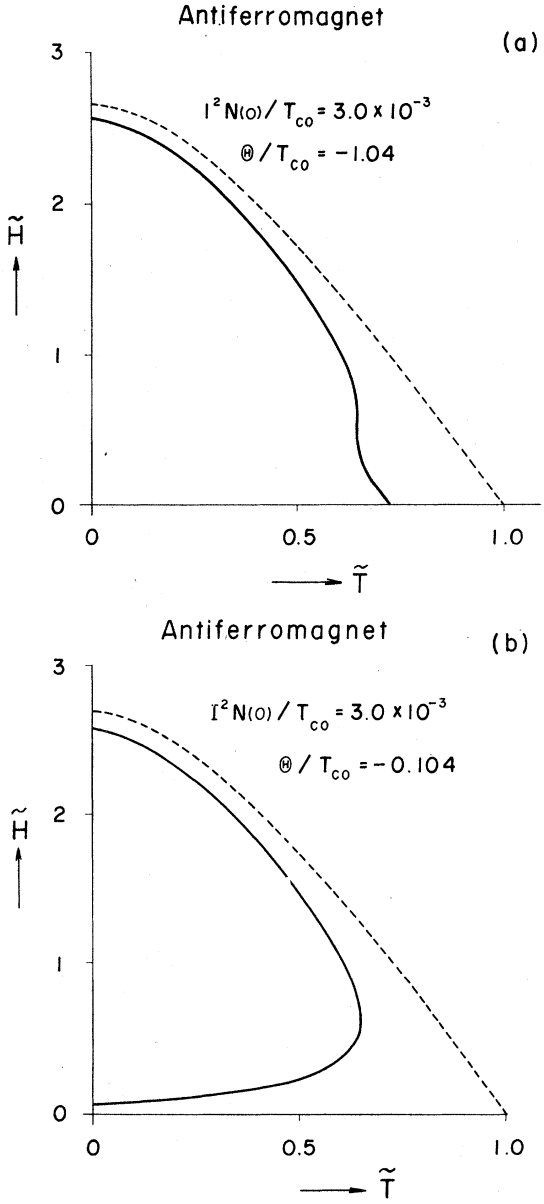

FIG. 6. (a) Theoretical results for $H_{c2}(T)$ as a function $\tilde{T}$ in an antiferromagnet with paramagnetic Curie temperature $\Theta/T_{c0}=-1.04$ and $I^2N(0)/T_{c0}=3.0\times10^{-3}$. The other parameters are the same as those used in Fig. 5(a). (b) Theoretical results for $H_{c2}(T)$ with $\Theta/T_{c0}=-0.104$ and $I^2N(0)/T_{c0}=3.0\times10^{-3}$. The other parameters are the same as those used in (a).

tion temperature T_M in antiferromagnets when they have distant-neighbor exchange interactions. When the magnetic field is larger than $(T-T_0)/g'\mu_B$, the spins are forced to align uniformly owing to the field, and above the field $H_{c2}(T)$ increases along the dotted line with decreasing temperature. The spin fluctuations decrease with increasing magnetic field. Therefore, in ultra-high-field superconductors the behavior of $H_{c2}(T)$ is similar to that in ferromagnets except for the small-field region. In Fig. 6(b), the $H_{c2}(T)$-vs-T curve with $I^2N(0)/T_{c0}=3.0\times10^{-3}$ and $\Theta/T_{c0}=-0.104$ is given. Even in antiferromagnets, the superconducting state at zero field does not exist when I is large and/or $|\Theta|$ is small. It has been observed that in the compound $Sn_{1.2(1-x)}Eu_xMo_{6.35}S_8$,[6,13] the superconducting state at zero magnetic field does not exist above $x=0.9$. From the above theoretical results, we suggest that application of the magnetic field may induce the superconducting state in the compound.

The temperature dependence of the upper critical field $H_{c2}(T)$ has been studied in the strong spin-orbit interaction limit. In the following, we briefly discuss how the spin-orbit interaction modifies $H_{c2}(T)$ when the interaction is reduced. In Fig. 7, lines (1) and (2) represent the numerical results for $\lambda_{SO}=1/3\pi T_{c0}\tau_{SO}=\infty$ and 4.24, respectively, in the system without local spin, and the lines (3) and (4) represent those for $\lambda_{SO}=\infty$ and 4.24, respectively, in antiferromagnets with $\Theta/T_{c0}=-1.26$, $I/T_{c0}=-1.0$, and $IN(0)=-3.0\times10^{-3}$. When I is negative, the Pauli paramagnetic term is reduced by the polarization of the local spins in the field.[47] Therefore, line (4) increases at low temperatures compared with line (2). Furthermore, we see that the $H_{c2}(T)$ curve becomes steeper when $\lambda_{SO}=4.24$ at intermediate temperatures. The anomalous behavior of $H_{c2}(T)$ has been observed by Fischer *et al.*[12,13] in $Sn_{1.2(1-x)}Eu_xMo_{6.35}S_8$. The quantitative comparison between theory and experiment will be given in a separate paper. If I is taken to be positive the value of H_{c2} becomes very small even when $\lambda_{SO}=4.24$. Therefore, in the compound, the interaction I must be negative.

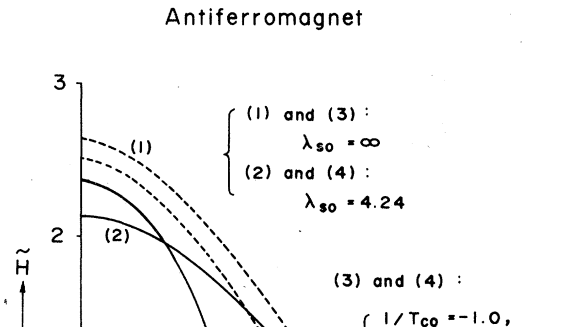

FIG. 7. Theoretical results for $H_{c2}(T)$. The lines (1) and (2) represent $H_{c2}(T)$ with $\lambda_{SO}=1/3\pi T_{c0}\tau_{SO}=\infty$ and 4.24, respectively, in the system without local spin. The lines (3) and (4) represent H_{c2} with $\lambda_{SO}=\infty$ and 4.24, respectively, in an antiferromagnet with $\Theta/T_{c0}=-1.26$, $I/T_{c0}=-1.0$, and $IN(0)=-3.0\times10^{-3}$. The other parameters are the same as those used in Fig. 6(b).

In this paper, we restricted ourselves to the superconducting state of spin-singlet BCS pairings. We also note the possibility of triplet BCS pairing in the region of low temperatures and weak magnetic fields which we assigned as the normal state in Figs. 5(b), 5(c), and 6(b), because the spin fluctuations prefer the electron spin-triplet state, as mentioned in Sec. III. This possibility will be discussed in a separate paper.

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APPENDIX A: STAGGERED SUSCEPTIBILITIES OF A MAGNETICALLY DILUTE SYSTEM

Let us consider a randomly diluted magnetic system, in which spins with $S=\frac{1}{2}$ interact among themselves through the nearest-neighbor exchange interaction J. We take a nearest-neighbor $\vec{S}_R$ and $\vec{S}_{R+\rho}$ spin pair in the system, the subscripts indicating the lattice site $\vec{R}$ and its nearest-neighbor site $\vec{R}+\vec{\rho}$, respectively. The effective Hamiltonian for the spin $\vec{S}_R$ may be written

$$\mathcal{H}_I=-z'\lambda S_R^z, \tag{A1}$$

where z' is given in Eq. (4.5), and λ is a parameter which is determined self-consistently. When a magnetic field H^z, which is measured in units of $g_J\mu_B(g_J-1)^{-1}$, is applied in the z direction, Eq. (A1) is rewritten

$$\mathcal{H}_I=-z'\lambda S_R^z-(z'\delta\lambda+H^z)S_R^z, \tag{A2}$$

where $\delta\lambda$ represents the increase of λ due to the field and is proportional to H^z. From Hamiltonian (A2), the density matrix $\rho_{\rm I}$ for the spin at $\vec{R}$ is constructed.

The effective Hamiltonian for two spins at the sites $\vec{R}$ and $\vec{R}+\vec{\rho}$ is written

$$\mathcal{H}_{\rm II} = -2J\vec{S}_R\cdot\vec{S}_{R+\rho} - \{(z'-1)\lambda + [(z'-1)\delta\lambda + H^z]\} \times (S^z_R + S^z_{R+\rho}) . \tag{A3}$$

Using Eq. (A3), we have the density matrix $\rho_{\rm II}$ for two spins. Then, we take a trace over $\vec{S}_{R+\rho}$ in $\rho_{\rm II}$, and determine the parameters λ and $\delta\lambda$ by the relation

$$\mathrm{Tr}_{R+\rho}\,\rho_{\rm II} = \rho_{\rm I} . \tag{A4}$$

The parallel susceptibility $\chi^{zz}(0)$ in paramagnetic phases ($\lambda = 0$) is obtained as

$$\chi^{zz}(0) = c'(\mathrm{Tr} S^z_R \hat{\rho}_{\rm I})/H^z = \tfrac{1}{2}c'\beta/[z'e^{-\beta J}\cosh(\beta J) - z' + 2] , \tag{A5}$$

where the effect of isolated spins was neglected.

We shall calculate the longitudinal-spin correlation function in the paramagnetic phases without magnetic field. When the spin at the origin 0 is fixed as "+," the probability that the neighboring spins are "+" increases. This effect propagates to the more distant spins through the exchange interaction. Let us consider the spin at $\vec{R}$. Because of the effect due to the spin at 0, the parameter λ of $\vec{S}_R$ in Eq. (A1) must be replaced by $\lambda + \xi(\vec{R}+\vec{\rho}')$, where $\vec{\rho}'$ is one of the vectors from $\vec{R}$ to the nearest neighbors. Therefore, the Hamiltonian for the spin at $\vec{R}$ is written

$$\mathcal{H}_{\rm I} = -[z'\lambda + \sigma(\vec{R})]S^z_R , \tag{A6}$$

where $\sigma(\vec{R})$ is the statistical average of the deviation of the interaction given as

$$\sum_{\rho'} \xi(\vec{R}+\vec{\rho}') = \sigma(\vec{R}) . \tag{A7}$$

The density matrix $\rho_{\rm I}$ for the spin $\vec{S}_R$ is calculated to first order in σ. In the same way, the effective Hamiltonian for two spins at $\vec{R}$ and $\vec{R}+\vec{\rho}$ is written

$$\mathcal{H}_{\rm II} = -2J\vec{S}_R\cdot\vec{S}_{R+\rho} - (z'-1)\lambda(S^z_R + S^z_{R+\rho}) - \sum_{\rho'\neq\rho} \xi(\vec{R}+\vec{\rho}')S^z_R - \sum_{\rho''\neq-\rho} \xi(\vec{R}+\vec{\rho}+\vec{\rho}'')S^z_{R+\rho} . \tag{A8}$$

Using Eq. (A8), the density matrix $\rho_{\rm II}$ for two spins is also constructed. Taking the trace over $\vec{S}_{R+\rho}$ in $\rho_{\rm II}$ and using the relation (A4), we find $\sigma(\vec{R})$. The longitudinal-spin correlation function $\langle S^z_0 S^z_R\rangle$ is obtained as

$$\langle S^z_0 S^z_R\rangle = \tfrac{1}{8}\beta\sigma(R) , \tag{A9}$$

which is the same as the Fourier transform of the staggered susceptibility $\chi^{zz}(q)$ times the temperature T.

In the system with $S > \frac{1}{2}$, we replace J by $J' = (4/3)S(S+1)J$ and the factor $\frac{1}{2}$ in Eq. (A5) by $\frac{2}{3}S(S+1)$. Then we find Eqs. (4.2) and (4.3) for T_M and $\chi(\vec{q})$, respectively. For the calculation of the Néel temperature in an antiferromagnet the reader is referred to the papers by Oguchi *et al.*[16,17]

APPENDIX B: DERIVATION OF THE KERNEL $K_{-\sigma,\sigma}(\vec{q}:\epsilon_n)$

The impurity potentials are introduced as follows[53]:

$$V(\vec{k},\vec{k}') = u + iu_{\rm SO}k_F^{-2}(\vec{k}\times\vec{k}')\cdot\vec{\sigma} , \tag{B1}$$

where u is the non-spin-flip scattering potential and $u_{\rm SO}$ is the spin-flip scattering potential defined in Eq. (5.17). Using the Born approximation and assuming that the Fermi surface is spherical, we have the normal-electron Green's function without the term involving the vector potential,

$$G^{n0}_{\sigma,\sigma}(\vec{k},\epsilon_n) = (i\tilde{\epsilon}_n - \xi_{k\sigma})^{-1} , \tag{B2}$$

where $\xi_{k\sigma}$ is the normal-electron energy with momentum $\vec{k}$ and spin σ, which is measured from the Fermi energy, and

$$\tilde{\epsilon}_n = \epsilon_n\eta_n , \quad \eta_n = 1 + 1/2\tau|\epsilon_n| , \tag{B3}$$

with

$$\tau^{-1} = \tau_0^{-1} + \tau_{\rm SO}^{-1} , \tag{B4}$$

where τ_0 and $\tau_{\rm SO}$ are given in Eqs. (5.14) and (5.20), respectively. For calculating the kernel $K_{-\sigma,\sigma}(\vec{q}:\epsilon_n)$ in Eq. (5.12) involving the potentials Eq. (B.1), the self-consistent equations are given in Fig. 8 and expressed as

$$K_{-\sigma,\sigma}(\vec{q}:\epsilon_n) = K^0_{-\sigma,\sigma}(\vec{q}:\epsilon_n) \times [1 + (v_0+v_1)K_{-\sigma,\sigma}(\vec{q}:\epsilon_n) + 2v_1K_{\sigma,-\sigma}(\vec{q}:\epsilon_n)] , \tag{B5}$$

$$v_0 = [2\pi N(0)\tau_0]^{-1} , \quad v_1 = [6\pi N(0)\tau_{\rm SO}]^{-1} , \tag{B6}$$

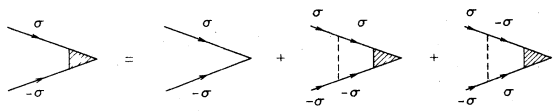

FIG. 8. Self-consistent equations for the kernel $K_{\sigma,\sigma'}(\vec{q}:\epsilon_n)$ due to the impurity potentials Eq. (B1), where σ denotes the spin state of the electron.

where $K^0_{-\sigma,\sigma}(\vec{q}:\epsilon_n)$ is defined as

$$K^0_{-\sigma,\sigma}(\vec{q}:\epsilon_n)=\int \frac{d^3k}{(2\pi)^3}\, G^{n0}_{-\sigma,-\sigma}(\vec{q}-\vec{k}:-\epsilon_n)\, G^{n0}_{\sigma,\sigma}(\vec{k}:\epsilon_n)\,. \tag{B7}$$

Solving Eq. (B5), we have

$$\begin{aligned}K_{-\sigma,\sigma}(\vec{q}:\epsilon_n)=&K^0_{-\sigma,\sigma}(\vec{q}:\epsilon_n)[1-(v_0-v_1)K^0_{\sigma,-\sigma}(\vec{q}:\epsilon_n)]\\ &\times\{[1-(v_0+v_1)K^0_{-\sigma,\sigma}(\vec{q}:\epsilon_n)]\\ &\times[1-(v_0+v_1)K^0_{\sigma,-\sigma}(\vec{q}:\epsilon_n)]\\ &-2v_1K^0_{-\sigma,\sigma}(\vec{q}:\epsilon_n)K^0_{\sigma,-\sigma}(\vec{q}:\epsilon_n)\}^{-1}\,.\end{aligned} \tag{B8}$$

It is easy to see that Eq. (B8) is reduced to Eq. (5.13) when $\tau_{SO}\to\infty$. Taking the dirty limit and assuming $\tau_0\ll\tau_{SO}$, we find

$$K_{-\sigma,\sigma}(\vec{q}:\epsilon_n)=\frac{\pi N(0)(|\epsilon_n|+iI_s\epsilon_n/|\epsilon_n|+a_s+b_s)}{(|\epsilon_n|+a_s)^2-b_s^2+I_s^2}\,, \tag{B9}$$

where b_s, I_s, and a_s are given in Eqs. (5.19) and (5.20). Inserting Eq. (B9) into Eq. (5.12), we obtain Eq. (5.18).

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