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Field-Dependent Thermopower of Dilute Magnetic Alloys*

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The thermopower of dilute magnetic alloys in an external magnetic field is calculated using the perturbation series for the *s-d* exchange Hamiltonian. We explicitly include terms proportional to the spin polarization of the impurities. In low fields and in the absence of interactions between the impurities, we expect the thermopower to vary as the square of the impurity magnetization. In high fields we find a $1/H$ behavior which should persist even with interactions between the impurities. Comparison is made with the only available data, on *Au*Fe alloys, and the encouraging agreement suggests that new experiments on the field-dependent thermopower would be most interesting.

I. INTRODUCTION

This paper extends the author's[1–3] perturbative studies of the magnetic-field dependence of the transport properties of dilute magnetic alloys exhibiting Kondo[4] behavior to the giant thermopower S typical of these systems. This is a somewhat more difficult calculation than the previous ones since, as Kondo[5] has shown, the zero-field contributions to S come from the part of the lifetimes which is odd in the electron energy (measured with respect to the Fermi energy ϵ_F). These are first encountered in the fourth-order terms in the perturbation series for the lifetimes. We have, therefore, extended our calculation of the lifetimes to this order and obtained the field-dependent thermopower. This calculation is described in Sec. II.

In Sec. III our results are compared with some recent experimental data on *Au*Fe.[6,7] The analysis of the data in low fields ($g\mu_B H/kT \lesssim 1$) is complicated by the presence of internal fields due to interaction effects between the impurities[7] in all samples studied except the most dilute one (0.5 ppm of Fe). But in external fields high enough to make the internal fields negligible (this requires $g\mu_B H/kT > 2$, at least), the behavior of the data of Ref. 6 is consistent with the field dependence we predict in that regime, $S(H) \propto 1/H$. However, the temperature dependence of the relative thermopower $[S(H)/S(0)]$ in this high-field regime can be understood only if we take into account internal-field contributions to the zero-field thermopower $S(0)$. At any rate, the $\alpha^2 e^{-\alpha}$ behavior ($\alpha = g\mu_B H/kT$) given by Kondo's internal-field theory[5] and used in previous analyses of the same data[6,7] is definitely ruled out.

We conclude by suggesting several further experiments which would help to clarify the high-field behavior of the relative thermopower.

II. CALCULATION OF THE THERMOPOWER

To obtain the correct result for the zero-field giant thermopower, we must include the imaginary parts of the second Born approximation for the scattering amplitudes in the calculation of the lifetimes.[5] The only subtle, but significant, point in doing so is that one must take care to obtain the correct signs of the imaginary parts of the energy denominators for those parts of the scattering amplitudes which are due to hole scattering; these terms must be treated as antiparticle scattering terms,[8] which gives the imaginary parts in the energy denominators the opposite sign from those appearing in the electron-scattering terms of the scattering amplitude. For the *s-d* exchange scattering Hamiltonian

$$H' = Vn - 2J\vec{S}\cdot\vec{s} \ , \tag{1}$$

where n and $\vec{s}$ are the conduction-electron density and conduction-electron spin density at the impurity site, respectively, and $\vec{S}$ is the impurity spin, the lifetimes are given by

$$\frac{1}{\tau_\sigma}(\epsilon_{k\sigma}) = \frac{mk_f}{2\pi k^3}\, cN\Big[V^2 - 2\sigma VJ\langle S_z\rangle + J^2\langle S_z^2\rangle - 4J^2(\sigma V\langle S_z\rangle - J\langle S_z^2\rangle)g^{-\sigma}(\epsilon_{k\sigma} + \sigma g\mu_B H)$$

$$+\frac{S(S+1)-\langle S_z^2\rangle-\sigma\langle S_z\rangle}{[1-f_{k\sigma}(1-e^{-\sigma\alpha})]}\{J^2+2J^3[g^{-\sigma}(\epsilon_{k\sigma}+\sigma g\mu_B H)+g^{\sigma}(\epsilon_{k\sigma})]\}+\pi^2\rho^2V^2$$
$$\times\left(V^2+4\sigma VJ\langle S_z\rangle+2J^2[S(S+1)+2\langle S_z^2\rangle]-2\sigma J^2S(S+1)(1-2f_{k-\sigma})\langle S_z\rangle+4J^2\frac{S(S+1)-\langle S_z^2\rangle-\sigma\langle S_z\rangle}{1-f_{k\sigma}(1-x^{-\sigma\alpha})}\right)$$
$$+4\pi^2\rho^2J^3V\left(\sigma\langle S_z\rangle S(S+1)+\langle S_z^2\rangle(1-2f_{k-\sigma})+(1-f_{k+}-f_{k-})\frac{S(S+1)-\langle S_z^2\rangle-\sigma\langle S_z\rangle}{1-f_{k\sigma}(1-e^{-\sigma\alpha})}\right)$$
$$+(\pi\rho J)^2J^2\left(S^2(S+1)^2-2\sigma S(S+1)(1-2f_{k-\sigma})\langle S_z\rangle+\frac{S(S+1)-\langle S_z^2\rangle-\sigma\langle S_z\rangle}{1-f_{k\sigma}(1-e^{-\sigma\alpha})}\right)\Bigg], \tag{2}$$

where c is the impurity concentration; N the number of atoms; $\langle S_z\rangle(\langle S_z^2\rangle)$ the thermal average of the impurity spin (spin squared); $f_{k\sigma}$ the Fermi distribution function for conduction electrons of momentum k and spin σ; and ρ is the conduction-electron density of states at $\epsilon_{k\sigma}$. The functions $g^\sigma(\epsilon)$ are given by

$$g^\sigma(\epsilon)=\frac{3z}{2\epsilon_f}\left[1+\frac{1}{2}\ln\frac{kT}{2\epsilon_F}+\tfrac{1}{2}I^\sigma\!\left(\frac{\epsilon}{kT}\right)\right], \tag{3}$$

$$I^\sigma(x)=\int d\epsilon'\left(-\frac{\partial f}{\partial\epsilon'}\right)\ln\left|\frac{\epsilon'}{2kT}-x\right|. \tag{4}$$

The thermopower is obtained from the lifetimes by using the standard results of transport theory. We have

$$S=-\frac{1}{eT}\sum_\sigma\int\tau_\sigma(\epsilon)\frac{\partial f}{\partial\epsilon}\,\epsilon\,d\epsilon\Big/\sum_\sigma\int\tau_\sigma(\epsilon)\frac{\partial f}{\partial\epsilon}\,d\epsilon, \tag{5}$$

where all energies are measured from ϵ_F. The last two terms of the $\pi^2\rho^2J^3V$ part of Eq. (2) give the lowest-order contribution to the zero-field thermopower. Our procedure for obtaining the field-dependent thermopower is to write $1/\tau_\sigma$, as given by Eq. (2), as a series in J/V, $V/\epsilon_F\simeq\rho V$, and $J/\epsilon_F\simeq\rho J$. The terms proportional to $Jg^\sigma(\epsilon)$ are also of order J/ϵ_F. We then expand τ in a power series, treating J/V and V/ϵ_F as small quantities of the same order of magnitude, and therefore treating J/ϵ_F as a second-order quantity. This expansion procedure is identical with that described in our previous work,[1-3] the only change being that the terms giving the zero-field thermopower are of fifth order counting powers this way, and hence, the expansion for the field-dependent thermopower is considerably more complicated arithmetically. These complications are the reason why this study is restricted to the case $|J|\ll V$, which seems to be a reasonable approximation for most dilute alloy systems.

The final result for the relative thermopower $S(H)/S(0)$ is

$$\frac{S(H)}{S(0)}=\left[\frac{1}{2S(S+1)\sinh^2(\frac{1}{2}\alpha)}\left(\alpha\langle S_z\rangle+\frac{\alpha^2}{2}\langle S_z^2\rangle-3\alpha^2\langle S_z\rangle^2\right)-\frac{1}{(2\pi\rho V)^2}\frac{\alpha^2\langle S_z\rangle^2}{S(S+1)\sinh^2(\frac{1}{2}\alpha)}-\frac{\langle S_z\rangle}{\pi^2\rho JS(S+1)}I(\alpha)\right]\frac{\rho(H)}{\rho(0)}, \tag{6}$$

$$I(\alpha)=\int_0^\infty du\,\ln\left|\frac{u-\alpha}{u+\alpha}\right|\frac{u}{4\sinh^2(\frac{1}{2}u)}\left(1-\frac{u}{2}\coth\frac{u}{2}\right), \tag{7}$$

$$I(\alpha)\sim\alpha/2,\quad \alpha\ll1. \tag{8a}$$

$$I(\alpha)\sim\pi^2/3\alpha,\quad \alpha\gg1. \tag{8b}$$

and $\rho(H)$ is the field-dependent resistivity.[1] The first two terms in Eq. (6) give the zero-field thermopower; the last two terms, which are of lower order in J/V and/or V/ϵ_F contribute to the field-dependent thermopower only. It is these two terms which are the significant contribution of allowing for nonzero spin polarization of the impurities.

In the limits of small and large fields we have

$$\frac{S(H)}{S(0)}=\left[1-\alpha^2\left(\frac{S(S+1)}{9(\pi\rho V)^2}+\frac{1}{6\pi^2\rho J}+\frac{5}{36}+\frac{2}{3}S(S+1)\right)\right]\frac{\rho(H)}{\rho(0)},\quad \alpha\ll1, \tag{9a}$$

$$\frac{S(H)}{S(0)}=\frac{-\langle S_z\rangle}{3\rho JS(S+1)\alpha}\frac{\rho(H)}{\rho(0)},\quad \alpha\gg1. \tag{9b}$$

For small fields[1] $\rho(H)/\rho(0)=1-a\alpha^2$, with a of order $(J/V)^2$; for large fields the experimental and theoretical evidence[1,3] is that

$$\rho(H)/\rho(0) \sim b + c \ln H.$$

The analysis of the additional small behavior in the relative thermopower due to the explicit α^2 term in Eq. (9a) is complicated since it depends on the values of V, J (which is negative for antiferromagnetic coupling in the s-d exchange Hamiltonian), and the spin S. However, for typical values of these three parameters[1,9] ($V \simeq 2$ to 4 eV, $|J| \simeq 0.3$–1 eV, and $S = \frac{3}{2}$, 1, $\frac{5}{2}$), in noble-metal hosts ($\epsilon_F \simeq 5$–7 eV), the coefficient of $-\alpha^2$ is positive and essentially given by the terms proportional to $S(S+1)$. This means that in Eq. (6) the major contribution to the low-field behavior of $S(H)/S(0)$ is given by the terms proportional to $\langle S_z \rangle^2$. Therefore, in low fields (in the sense $g\mu_B H/kT < 1$) and in the absence of interactions,

$$\Delta S/S(0) = [S(H) - S(0)]/S(0) \propto -M^2 , \tag{10}$$

M being the impurity magnetization. The same proportionality to M^2 was true of the low-field behavior of the negative magnetoresistivity[1] and the Hall coefficient[2] in dilute magnetic alloys. As has already been pointed out, this is because the spin-polarization factors $\langle S_z \rangle$ and $\langle S_z \rangle^2$ vary much more rapidly in a small applied field than the scattering amplitudes of the Kondo series. This analysis is somewhat more complicated in the case of the thermopower, because the presence of the field induces asymmetries in the scattering amplitudes which give field-dependent contributions which are of lower order, in the sense of our expansion procedure, than those which give the zero-field thermopower. However, a numerical calculation using approximate values for J and V[1,9] shows that these formally lower-order terms are actually smaller in magnitude than those coming from the field dependence of the terms which give the zero-field thermopower.[10]

On the other hand, the magnetization is saturated, or almost saturated, in the high-field regime and the field dependence of the scattering amplitudes is dominant. We can ignore the thermal smearing of the Fermi surface for high fields; then the lifetimes go roughly as $\ln|\epsilon + H|$. The lifetime, evaluated at $\epsilon = 0$, appears in the resistivity and Hall coefficient, which then vary as $\ln H$,[1-3] while the derivative of the lifetime with respect to the energy, also evaluated at $\epsilon = 0$, appears in the thermopower, giving the $1/H$ behavior which is found here.

III. COMPARISON WITH EXPERIMENTS

The only field-dependent thermopower measurements on dilute magnetic alloys have been made on *Au*Fe alloys.[6,7] Berman *et al.*[6] give results for a 300-ppm sample over a wide range of field values (up to 75 kG), while Huntley and Walker[7] use smaller fields (up to roughly 40 kG), but study more dilute alloys: 230-ppm, 15-ppm, and 0.5-ppm iron impurities. In all but the 0.5-ppm sample the relative thermopower, as a function of the applied field H at fixed temperature, increases with H for small fields (up to $g\mu_B H/kT \simeq 2$) and then decreases for higher fields. If we take the magnetoresistivity estimates for J and V for *Cu*Mn,[1] *Cu*Fe,[1] and *Au*Fe,[9] our small-field approximation, Eq. (9a), predicts that for these three alloys, in the very dilute case, the relative thermopower should *decrease* monotonically as a function of the applied field:

$$\frac{\Delta S}{S(0)} \simeq \frac{\rho(H) - \rho(0)}{\rho(0)} - \frac{M^2}{S(S+1)} \times \frac{\alpha^2}{4\sinh^2(\alpha/2)} \left(\frac{3}{2} + \frac{1}{(2\pi\rho V)^2} \right),$$

where $[\rho(H) - \rho(0)]/\rho(0)$ has already been shown[1] to be proportional to $-M^2$ in that region. Huntley and Walker[7] have interpreted the experimental increase in the relative thermopower in terms of internal fields due to interactions between the impurities using Kondo's[5] result for $S(H)/S(0)$ in which only internal fields were included. This approach seems to satisfactorily account for the low-field maximum in the $S(H)/S(0)$ curves. Further corroboration of this interpretation of the maximum as due to interaction effects is found in the relative thermopower of the 0.5-ppm sample[7]: There, interaction effects are negligible and $S(H)/S(0)$ decreases monotonically with increasing field, even at the lowest fields, in qualitative agreement with Eq. (9a). A quantitative comparison between our results and the data on this sample could not be made as too few experimental points are available.

While meaningful comparisons with the low-field data cannot be made, for large applied fields one might expect that effects due to the internal fields would be relatively less important and that comparisons could be made with our asymptopic form, Eq. (9b). The experiment of Berman *et al.*[6] is carried to a large enough field to allow a comparison to be made. We have, somewhat arbitrarily, included all experimental points lying below $S(H)/S(0) = 1$ in this comparison, feeling that all points where the field-dependent thermopower was greater than the zero-field thermopower definitely exhibited interaction effects. These points, taken at three temperatures (2.19 °K, 1.19 °K, and 0.43 °K), are plotted against $1/H$ in Fig. 1. Since only two points are available at 2.19 °K, we may ignore that curve; the data at the lower temperatures do appear to lie on straight lines which confirm the $1/H$ behavior predicted by Eq. (9b). The temperature de-

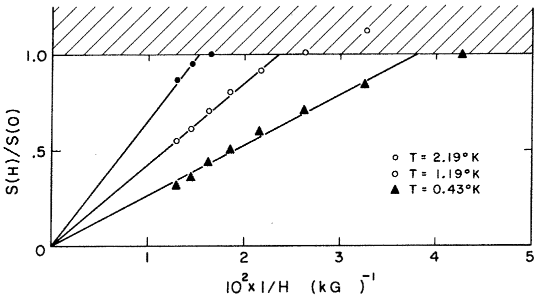

FIG. 1. Experimental values of $S(H)/S(0)$ from Ref. 6 for a 300-ppm alloy of *Au*Fe at three temperatures, plotted against $1/H$. In the shaded region, interaction effects play an important role, and the experimental points deviate from the $1/H$ law valid for extreme dilution.

pendence is less satisfactorily fit; for large $g\mu_B H/kT$, $\langle S_z \rangle$ is saturated if the magnetization follows a Brillouin law, which is assumed in our calculation. Then Eq. (9b) gives the relative thermopower proportional to T for fixed H. This does not seem to be the case experimentally, though only two temperatures can be considered, and hence, only rough estimates could be made of the actual temperature dependence at a fixed high field. From the experimental data it appears that the actual asymptopic form is

$$S(H)/S(0) \propto (T + 0.8\ ^\circ\mathrm{K})/H. \qquad (11)$$

We suspect that this deviation from being proportional to T is due to internal field effects in $S(0)$. We note that Kondo,[5] following Guénault,[11] proposed for $S(H=0)$ the formula

$$S \propto T/(T + T_0). \qquad (12)$$

Equation (12) gives a satisfactory fit to experiments made in zero applied field[12] and takes into account interactions between the impurities through T_0, which is identified with the average internal field due to the other impurities acting on each impurity. In the case of *Au*Fe, interpolation of several values of T_0 deduced by Guénault[11,5] from the experiments[12] leads to $T_0 \approx 0.75$ °K for a 300-ppm *Au*Fe alloy. Assuming $S(H=0)$ given by Eq. (12) and $S(H) \propto T/H$ for $g\mu_B H/kT \gg 1$, we would have

$$S(H)/S(0) \propto (T + T_0)/H, \qquad (13)$$

which, with the value of T_0 deduced from the zero-field thermopower, agrees with our results for the asymptopic form of the relative thermopower in the 300-ppm sample, Eq. (11).

We think that several further experiments on the relative thermopower would be most useful in clarifying the situation with respect to these various interaction effects. First, for the 300-ppm *Au*Fe alloy it would be useful to have measurements of the relative thermopower between 50 and 75 kG for several temperatures between, say, 0.43 and 2.19 °K in order to determine T_0 more accurately. Second, it would be useful to have relative thermopower data on *Au*Fe between 0 and 75 kG and at several temperatures for very small Fe concentrations, e.g., 0.5–50 ppm, to allow a comparison between experiments and our low-field result, Eq. (10). This would also allow a determination of whether T_0 is indeed due to internal fields. If this is so, T_0 should be approximately zero for the very dilute alloys and $S(H)/S(0) \propto T/H$ should be observed at large fields. Furthermore, measurements between 50 and 75 kG would be very useful in the different *Au*Fe alloys in order to see if $\langle S_z \rangle$ is indeed saturated in these fields[13]; if it was not saturated, one could plot the relative thermopower divided by the experimental value of $\langle S_z \rangle$ to remove field and temperature dependence due to the magnetization. Finally, we believe that the measurements of the field dependence of the thermopower should be extended to alloys such as *Cu*Mn, *Cu*Cr, *Cu*Fe, and *Au*Mn for which many other field-dependent properties related to the Kondo effect are known.

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[10] The fact that a formally higher-order term is larger numerically is a consequence of the slow convergence of the logarithmic series for the scattering amplitudes, which has been noted before (Ref. 1). As we have mentioned in that reference, this implies that perturbative calculations such as this one can reproduce the qualitative features of the experimental behavior, e.g., low-field dependence on M^2, but estimates of J and V from explicit use of these perturbative formulas are valid only for the relative orders of magnitude.

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Polarization Fluctuations and the Optical-Absorption Edge in $BaTiO_3$[†]

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Results of optical absorption and electroabsorption (EA) measurements in the vicinity of the interband absorption edge are reported for top-seeded solution-grown crystals of $BaTiO_3$. In common with other perovskite oxides, the absorption edge in $BaTiO_3$ is found to display Urbach-rule behavior. The exponential absorption tail can be described between 20 and 450 °C by an effective temperature $T^* = T + T_0$, where $T_0 = 140$ °K, i.e., $\alpha \propto e^{\hbar\omega/kT^*}$. Although no uniquely defined band gap can be extracted from an exponential edge, we propose, on the basis of indirect arguments, that the room-temperature band gaps are 3.38 and 3.27 eV, respectively, for light polarized parallel and perpendicular to the ferroelectric c axis. At high temperatures in the cubic phase, the band gap decreases at the rate -4.5×10^{-4} eV/°C. EA measurements in the tetragonal phase show that an applied electric field along the c axis shifts the entire Urbach edge rigidly upward in energy by an amount $\Delta\mathcal{E}$, which is proportional to the square of the total polarization P, spontaneous plus field-induced, i.e., $\Delta\mathcal{E} = \beta P^2$. The effect can be described by a temperature-independent band-edge polarization potential β having the value $\beta_{11} = 1.16$ eV m^4/C^2. The smaller β_{12} coefficient could not be measured, because of photoconductivity and carrier-trapping effects. An anomalous increase in the band gap with decreasing temperature within 150 °C of the Curie point is attributed to coupling between polarization fluctuations and the band edge. A simple thermodynamic model is shown to describe the temperature dependence of this fluctuation contribution with reasonable accuracy. The results suggest that the correlation volume V_c is at most a weak function of temperature and that V_c does not display critical behavior. This conclusion is consistent with several recent experiments in displacive ferroelectrics. The magnitude of the observed mean square polarization fluctuation contribution to the band-edge position (≈ 15 meV at $T = T_C$) can be understood using the simple fluctuation theory with the value $V_c \approx 4.5 \times 10^4$ Å^3 deduced previously from photoelastic constant measurements. It is also suggested that a mean square polarization fluctuation contribution to the band-edge position is present in the tetragonal phase below approximately 100 °C owing to the proximity of the tetragonal-orthorhombic transition. A fluctuation contribution of about 40 meV is indicated at room temperature.

I. INTRODUCTION

Several studies of the optical-absorption edge in $BaTiO_3$ have been reported. Casella and Keller[1] and Gähwiller[2] find a broad absorption tail extending to nearly 2.5 eV, while Cox *et al.*[3] have attempted to fit similar absorption data to well-known formulas. Gähwiller[2] has also reported results of electroabsorption (EA) experiments in the vicinity of the band edge and related the field-induced band-edge shifts to crystal polarization. Recently, DiDomenico and Wemple[4] have shown that these ab-