Electron Scattering by the Electronic Quadrupole Moment of Rare-Earth Impurities

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Measurements of the magnetoresistance of gold with rare-earth impurities show that the resistivity of a rare-earth impurity is different according to whether its magnetic moment is directed parallel or perpendicular to the current. The longitudinal resistivity is larger for Tb, Dy, and Ho and smaller for Er, Tm, and Yb; the anisotropy vanishes for Gd. This indicates that the resistivity anisotropy is due to the interaction of the conduction electrons with the electric quadrupolar moment of the f electrons.

A magnetic rare-earth (RE) ion generally possesses an electric quadrupolar moment (except when the orbital angular momentum of the f electrons vanishes, that is, for a gadolinium ion). Kondo[1] studied the interaction between conduction electrons and the electric quadrupole of $4f$ electrons and, limiting the expansion of the wave functions of the conduction electrons to s and p waves, derived an interaction term of the form

$$V_Q = -(D/k_F{}^2)\sum_{\vec{k}'}[(\vec{J}\cdot\vec{k})(\vec{J}\cdot\vec{k}') - \tfrac{1}{3}J(J+1)\vec{k}\cdot\vec{k}']a_{k'}{}^\dagger a_k,\tag{1}$$

where $\vec{J}$ is the angular momentum of the RE ion and $a_k{}^\dagger$ (a_k) the creation (annihilation) operator of the conduction electron with wave number $\vec{k}$.

Let us consider now the problem of electron scattering by RE impurities in solution in a metal. We assume that the scattering potential is the sum of a potential[2] $V\delta(r)$, of an exchange interaction, and of the interaction V_Q with the quadrupole:

$$V_{\text{scat}} = \sum_{\vec{k}\vec{k}'}\left\{V + J_{\text{ex}}\vec{s}\cdot\vec{J} - \frac{D}{k_F{}^2}\left[(J\cdot k)(J\cdot k') - \frac{J(J+1)}{3}\vec{k}\cdot\vec{k}'\right]\right\}a_{k'}{}^\dagger a_k.\tag{2}$$

The problem of the scattering by the two first terms is well understood; in a magnetic field the exchange term induces a negative magnetoresistance[3] which is isotropic, that is independent of the relative direction of the current and of the magnetization. In contrast one sees easily that the interaction with the quadrupole (third term) scatters currents parallel or perpendicular to $\vec{J}$ differently. The resistivity for a current in the direction of the unit vector $\vec{u}$ is

$$\rho_{\vec{u}} = \left(\frac{\hbar}{8\pi^3 ne}\right)^2 \int d^3k\, d^3k'\left(-\frac{\partial f^0}{\partial\epsilon_k}\right)(\vec{k}\cdot\vec{u})[(\vec{k}-\vec{k}')\cdot\vec{u}]\,W_{kk'}$$

with

$$W_{kk'} = \frac{2\pi}{\hbar}|\langle k|V_{\text{scat}}|k'\rangle|^2\delta(\epsilon_i - \epsilon_f)$$

in the first Born approximation. A straightforward calculation provides the resistivity terms $\rho_\parallel{}^Q$ induced by the quadrupole for a current parallel or perpendicular to the direction of the field z. In the case of a potential V much larger than J_{ex} or D, one retains in $|\langle k|V_{\text{scat}}|k'\rangle|^2$ only the cross term VD and obtains, for $\rho_\parallel{}^Q$, $\rho_\perp{}^Q$, and the resulting anisotropy of the impurity resistivity,

$$\rho_\parallel{}^Q/\rho_0 = -2\rho_\perp{}^Q/\rho_0 = \frac{2D}{3V}\left(\langle J_z{}^2\rangle - \frac{J(J+1)}{3}\right),\tag{3}$$

$$\frac{\rho_\parallel(H) - \rho_\perp(H)}{\rho_0} = \frac{D}{V}\left(\langle J_z{}^2\rangle - \frac{J(J+1)}{3}\right),\tag{4}$$

where ρ_0 is the resistivity at zero field and $\langle J_z{}^2\rangle$ the mean value of $J_z{}^2$. At low field ($gJ\mu_B H \ll k_B T$) and without crystal field or interactions, (4) becomes

$$\frac{\rho_\parallel(H) - \rho_\perp(H)}{\rho_0} = (J - \tfrac{1}{2})(2J^2 + 5J + 3)\frac{D}{45V}\left(\frac{gJ\mu_B H}{k_B T}\right)^2.$$

At low temperature, however, the anisotropy should be generally greatly dependent on the crystal electric field (CEF) structure. In particular the anisotropy should vanish within a doublet ground state, leaving only a term due to a mixing of the CEF states by the field. We shall present in a further paper[4] a more detailed calculation of the magnetoresistance induced by RE impurities in gold or silver.

Such a resistivity anisotropy of dilute magnetic

impurities has been observed[5] for anomalous Ce impurities in La but unfortunately in this case only a small part of the magnetoresistance was anisotropic. In contrast, the resistivity anisotropy is observed very clearly in new measurements on AuRE alloys that we report in this Letter.

We have studied the magnetoresistance of several $Au_{1-x}RE_x$ alloys (RE: Gd, Tb, Dy, Ho, Er, Tm, Yb; $5 \times 10^{-3} < x < 2 \times 10^{-2}$). The measurements were performed in a superconductive coil (up to 40 kG) by an ac technique (synchronous detection providing a sensitivity of 10^{-9} V).

Figure 1(a) shows the magnetoresistance of a AuHo alloy for a field parallel or perpendicular to the current. It appears first that there is a *clear magnetoresistance linked with the polarization of the impurities* (and so vanishing at high temperature) and secondly that the longitudinal magnetoresistance is positive and the transverse negative, the curves showing *an effect of resistivity anisotropy much stronger than the isotropic negative magnetoresistance* [$\Delta \rho = \rho_\parallel - \rho_\perp$ is much stronger than $\delta \rho = \rho_0 - \frac{1}{3}(\rho_\parallel + 2\rho_\perp)$].

A similar behavior is observed for the other alloys except AuGd: *the longitudinal magnetoresistance is positive and the transverse is negative for AuTb, AuDy, AuHo, while the longitudinal magnetoresistance is negative and the transverse is positive for AuEr, AuTm, AuYb.* It turns out that the resistivity anisotropy of the RE impurities changes sign at the middle of the heavy RE series. This indicates clearly that the anisotropy is due to the interaction with the quadrupolar moment of the f electron since, from Table I (see column c_1) of the Kondo paper,[1] one expects a different sign of D for Tb, Dy, Ho, and for Er, Tm, Yb. We shall present in a further paper[4] a detailed analysis of the field and temperature dependence of the anisotropy and, in particular, we shall discuss the effects of the CEF structure. It turns out that the energy of the quadrupolar coupling amounts to about a few hundredths of an eV.

The magnetoresistance of AuGd is quite different. Figure 1(b) shows that $\rho_\parallel(H)$ and $\rho_\perp(H)$ coincide very nearly. One observes only the usual isotropic negative magnetoresistance of a dilute magnetic alloy. This is obviously related to the cancelation of the quadrupole moment for the S state.

We have also studied the magnetoresistance of some AgRE alloys and observed a resistivity anisotropy similar to that of the AuRE alloys. The transverse magnetoresistance of AgRE alloys
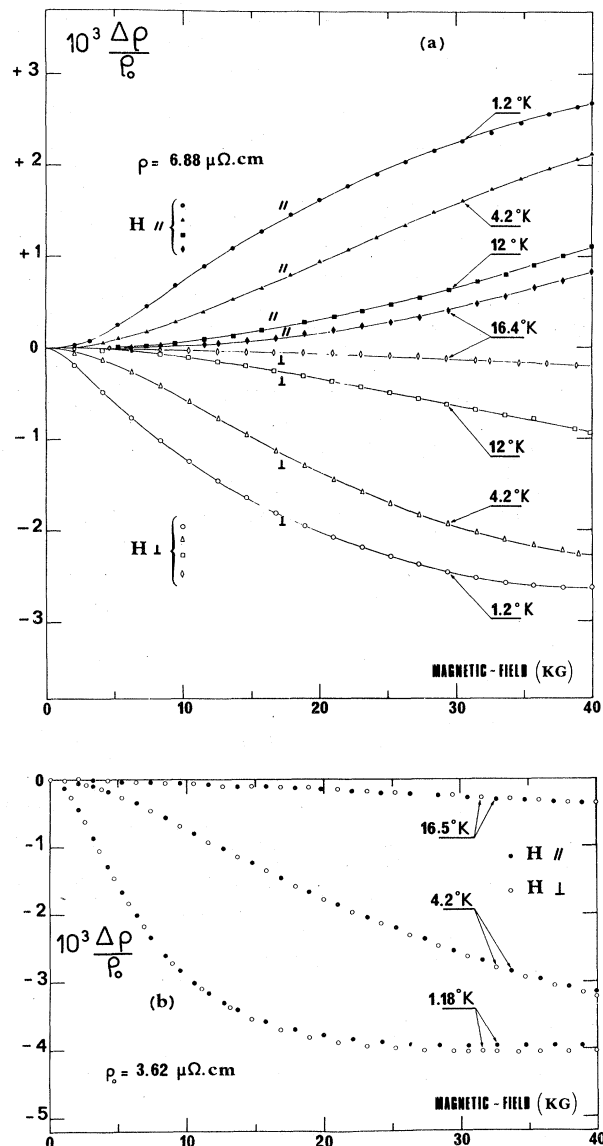

FIG. 1. The fractional longitudinal and transverse magnetoresistance of (a) a 1 at.% AuHo alloy and (b) of a 0.5 at.% AuGd alloy at several temperatures. The different behavior of the magnetoresistance for a non-S state (Ho) and an S state (Gd) is obvious: For AuHo the main effect appears to result from the anisotropy of the impurity resistivity ($\Delta \rho_\parallel > 0$ and $\Delta \rho_\perp < 0$), while for AuGd one observes only an isotropic negative magnetoresistance. Note also that for both of the alloys the normal magnetoresistance (independent of the temperature) is small in comparison to the magnetoresistance linked with the impurity magnetization.

had been studied already by de Vries and Bijvoet[6] and interpreted as a magnetoresistance due to the exchange interaction. It appears now that —except for Gd—the main effect results from

the resistivity anisotropy and this explains that the transverse magnetoresistance was found negative for Tb, Dy, and Ho and positive for Er.

We have reported in this Letter the observation of the resistivity anisotropy of dilute magnetic impurities (to our knowledge this is the first clear observation of such an effect). This effect is interesting because it should give information on the coupling of conduction electrons with the quadrupolar moment of RE impurities and also because it should be very sensitive to the CEF structure. Similar experiments for transition impurities would also be of interest, as they could provide evidence of small orbital contributions to the magnetic moment.

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[2]For RE impurities in a noble metal it is more correct to take instead of $V\delta(r)$ a potential $P_2(\cos\theta_{kk'})V_2$ which expresses a d-resonant scattering ($5d$ nonmagnetic virtual bound state). This changes the expression (4) for the anisotropy slightly.

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Deuterium Lattice Location in Cr and W†

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Direct determination of the lattice location of implanted deuterium in single-crystal chromium has been made for the first time. Ion-channeling measurements of the angular distributions along the ⟨100⟩ axial and {100} planar directions indicate that implanted D occupies the octahedral position in bcc Cr. This contrasts to the expected tetrahedral interstitial position recently observed under the same conditions for bcc W. These results further clarify the apparent anomaly in the thermodynamic data for hydrogen solubility in Cr.

Fundamental structural information for hydrogen in transition metals is particularly important because of the great theoretical and technological interest. The low solubility of hydrogen in chromium and tungsten (group VI B) has prevented previous measurements of the lattice location of hydrogen by the usual technique of neutron diffraction. Recently ion channeling has been applied to studies of the lattice location of hydrogen in single-crystal metals.[1,2] The first lattice-location data for deuterium in W have been obtained by combining ion implantation with ion channeling and nuclear-reaction analysis.[2] These results showed that the implanted deuterium resides in the tetrahedral interstitial site, which is the expected site in bcc metals. The absence of any lattice-location data for hydrogen in Cr and the apparent inconsistency in the thermodynamic results for hydrogen solubility in Cr relative to other bcc and close-packed metals[3] suggested that the hydrogen lattice location in bcc Cr could be other than the expected tetrahedral site.

This Letter presents the first lattice-location data for hydrogen in Cr and shows that implanted D occupies the octahedral interstitial site and not the tetrahedral site previously found for implanted D in W. The results provide a direct comparison of the lattice location of D in Cr and W by the same technique and indicate anomalous high-temperature hydrogen-solubility behavior of Cr relative to the other bcc metals.[3]

The ⟨100⟩-oriented single crystals of 99.995% pure Cr and 99.999% pure W were obtained from Metals Research and from Materials Research, respectively. The D was introduced by ion implantation into the ⟨100⟩ faces of Cr and W samples along a nonchanneling direction 7° from the ⟨100⟩ axis. The 15- and 30-keV D^+ ion implantations were made, respectively, into the Cr and W samples by accelerating the molecular species D_3^+ at a factor of 3 higher energy. Implants were performed at 296 K to fluences of 3×10^{15} D atoms/