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*Permanent address.

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Left-Right Asymmetry in the Scattering of Electrons by Magnetic Impurities, and a Hall Effect

A. Fert and O. Jaoul

Laboratoire de Physique des Solides, Université de Paris-Sud, Orsay, France*

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Left-right asymmetry is expected in the scattering of electrons by magnetic impurities in metals; we present a simple calculation of the asymmetry in a virtual-bound-state model. When a magnetic field lines up the impurity moments, this left-right asymmetry should generate an extraordinary Hall effect proportional to the impurity concentration. This effect appears to occur in many magnetic alloys (e.g., Ni-, Cu-, and Au-based alloys).

It has been known[1] for a long time that the scattering of fast (few MeV) spin-polarized electrons by nuclei exhibits a left-right asymmetry which is induced by spin-orbit coupling. When the scattering potential depends on the spin only through the spin-orbit term, the asymmetry becomes inverted for electrons of opposite spin; and so, for unpolarized electrons, the effect of the electrons with opposite spin balances the asymmetry. On the other hand, this balance cannot occur and an asymmetry remains when the scattering potential —even without the spin-orbit term—is different for each spin direction. This is the case for the potential of magnetic impurities in a metal. We shall show that resonant scattering on magnetic-impurity levels may exhibit an observable asymmetry when the spin-orbit coupling is not much smaller than the width of the impurity virtual bound state. This left-right asymmetry should generate a Hall effect: Smit,[2] Luttinger,[3] and Kondorskii, Cheremushkina, and Kurbaniyazov[4] have already predicted this contribution—proportional to the impurity concentration—to the extraordinary Hall effect of ferromagnetics.

First, we will give a simple calculation of the asymmetry in a virtual-bound-state model of the scattering magnetic impurity. We consider an impurity having only a spin moment,[5] like Mn or Fe in Au. We assume also that the impurity is placed in a magnetic field strong enough to prevent scattering through spin-flip of the impurity moment ($\mu H \gg kT$) or Kondo scattering ($\mu H \gg kT_K$) so a Hartree-Fock approximation can be used to describe the impurity scattering; in the Friedel-Anderson model[6,7] we have then to consider spin-up and spin-down virtual bound states (vbs) in the conduction band near the Fermi level (see Fig. 1; we assume for simplicity that we deal only with d vbs).

In the usual Friedel-Anderson picture, the spin-orbit coupling is neglected (and the crystal field also) and the scattering of a free conduction electron with spin σ and energy E is mainly determined by the only phase shift of the $l=2$ par-

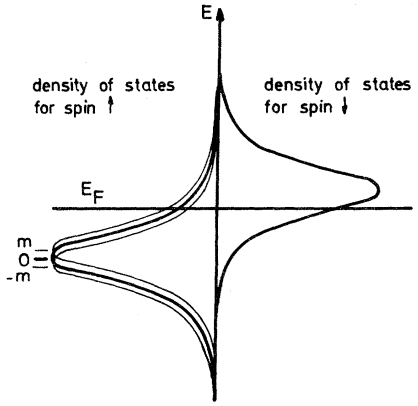

FIG. 1. Density-of-states distribution for a magnetic transition impurity with splitting of the vbs by the spin-orbit coupling.

tial wave; this phase shift $\eta_{2\sigma}$ is given by the classical expression

$$\mathrm{ctn}(\eta_{2\sigma}) = (E_{d\sigma} - E)\Delta^{-1}, \quad (1)$$

where E_d is the energy of the center of the vbs with spin σ and Δ is its half-width. It should be noted that, in this model, all the phase shifts $\eta_{2\sigma}{}^m$ are the same for all the $l=2$ partial waves, whatever is the component of the orbital moment in the spin direction.

On the other hand, if we introduce the spin-orbit coupling $V_{s.o.} = \lambda \vec{L}\cdot\vec{S} = \lambda[L_z S_z + \frac{1}{2}(L_+S_- + L_-S_+)]$, the first term $\lambda L_z S_z$ will split the impurity d levels and also the corresponding virtual bound states (Fig. 1), so the phase shifts $\eta_{2\sigma}{}^m$ become dependent on m, giving rise to a left-right asymmetry of the scattering. In reality, the effect of the spin-orbit coupling is a bit more complicated. At first, the term $\frac{1}{2}\lambda(L_+S_- + L_-S_+)$ mixes somewhat the spin-up and spin-down character of the vbs, but this mixing is weak as the spin-orbit energies are generally much smaller than the difference D between the spin-up and spin-down energies (for $3d$ electrons λ is about 0.02 eV, while typical values for D are 10 times larger). In this paper, we will neglect this mixing which does not modify the results significantly. Another factor to be considered is the enhancement of the atomic spin-orbit coefficient resulting from the lowering of the correlation energy by the splitting of the vbs; Yafet[8] has shown that, to calculate the shifts of the vbs of spin σ correctly, the atomic spin-orbit coefficient λ_{at} must be replaced by

$$\lambda_\sigma = \lambda_{at}[1 - (U - J)\rho_\sigma(E_F)]^{-1},$$

where U and J are the usual correlation energies[7] and $\rho_\sigma(E_F)$ the density of states at the Fermi level for spin σ.

Now, for each spin direction, the energies $E_{d\sigma}{}^m$ of the centers of the five vbs are $E_{d\sigma}{}^m = E_{d\sigma}{}^0 \pm \frac{1}{2}\lambda_\sigma m$ (+ or − according to the spin). Supposing $\lambda_\sigma \ll \Delta$ ($\Delta \simeq 10\lambda$ for first-transition-series impurities), we deduce from (1)

$$\eta_{2\sigma}{}^m = \eta_{2\sigma}{}^0 \mp (\lambda_\sigma m/2\Delta)\sin^2\eta_{2\sigma}{}^0. \quad (2)$$

Considering an impurity with its magnetic moment parallel to O_z axis and an incident plane wave e^{ikx}, the introduction of the phase shifts (2) in the expansion of the plane wave in O_z-axis spherical harmonics gives for the scattered amplitude, to first order in λ/Δ,

$$f_\sigma(\theta,\varphi) = \frac{\sqrt{5\pi}}{2ik}\{[\exp(2i\eta_2{}^0) - 1][(\sqrt{\tfrac{3}{2}})(Y_{2,2} + Y_{2,-2}) - Y_{2,0}] \pm 2i(\sqrt{\tfrac{3}{2}})(\lambda/\Delta)\sin^2\eta_2{}^0\exp(2i\eta_2{}^0)(Y_{2,-2} - Y_{2,2})\}$$
$$+ \text{terms with } l \neq 2. \quad (3)$$

Now the y component of the scattered current is

$$I_{\perp\sigma} = \int |f(\theta,\varphi)|^2 \sin\theta \sin\varphi \, d\Omega \sim \int |f(\theta,\varphi)|^2 [Y_{1,1}(\theta,\varphi) + Y_{1,-1}(\theta,\varphi)]\, d\Omega,$$

and the only terms in $|f(\theta,\varphi)|^2$ contributing to $I_{\perp\sigma}$ are the products of the second term in (3) and of terms with odd l. Assuming that the only non-negligible phase shift, apart from η_2, is η_1 (spin independent and small), we have retained only the product with the term $l=1$ and have calculated in this way[9] the ratio φ_σ (asymmetry factor) of the induced y component $I_{\perp\sigma}$ of the current to the change ΔI_σ of its x component ($\Delta I_\sigma \sim$ resistivity cross section $\sim \sin^2\eta_{2\sigma}{}^6$). At last one obtains

$$\varphi_\sigma = \pm(3\lambda_\sigma/5\Delta)\sin\eta_1 \sin(2\eta_{2\sigma}{}^0 - \eta_1). \quad (4)$$

It should be noticed that for magnetic impurities E_F is generally between $Ed_\uparrow$ and $Ed_\downarrow$ as in Fig. 1, so that $\eta_{2\uparrow} > \pi/2$, $\eta_{2\downarrow} < \pi/2$, and $\varphi_\uparrow$ and $\varphi_\downarrow$ have the same sign, both spin directions giving a positive[10] contribution to the Hall effect (if $\eta_1 > 0$).

The order of magnitude of the asymmetry factors can be obtained easily from (4): For an impurity belonging to the first transition series λ/Δ is about 10^{-1}, $\sin\eta_1$ may be about 10^{-1}, $\sin(2\eta_{2\uparrow} - \eta_1)$ and $\sin(2\eta_{2\downarrow} - \eta_1)$ may be close to 1, and so the asymmetry factors are expected to be around

10^{-2} or 10^{-3}. This leads to a sizable induced Hall effect at low temperatures. The introduction of crystal field splitting affects only weakly these results if the crystal field does not lift completely the impurity orbital degeneracy.

We will emphasize that, in the above model for noble-metal–based alloys, the conduction electrons are affected by the spin-orbit coupling only at the impurity sites and not in the host metal on account of their d character at the impurity and s character elsewhere; however, the effect of the spin-orbit coupling in the host metal could become important for large s-d hybridization of the conduction band. The model is not suitable for transition-metal–based alloys; however, asymmetries having the same order of magnitude and inducing positive or negative Hall effects are to be expected for these alloys also.

It is a straightforward calculation now to get the contribution of skew scattering to the Hall effect when all the moments are lined up; one obtains for the induced Hall angle φ_H (if scattering is only due to the magnetic impurities)

$$\varphi_H = (I_\uparrow/I)\varphi_\uparrow + (I_\downarrow/I)\varphi_\downarrow, \tag{5}$$

where $\varphi_\uparrow$ and $\varphi_\downarrow$ are weighted by the proportions of the spin-up and spin-down currents (it is known[11] that these proportions can be very different in ferromagnetic or polarized paramagnetic alloys). So for each type of impurity, there is a characteristic induced Hall angle that means a characteristic ratio between the induced Hall resistivity and the residual resistivity (this is a general result for the Hall effect induced by skew scattering[2,3]).

The induced Hall voltage is of course zero when the impurity moments are completely disordered, appears when a magnetic field lines up the moments, and reaches the value calculated above when the magnetization is saturated. For ferromagnetic alloys, we are only interested in the saturation value which is a contribution to the extraordinary Hall voltage. For paramagnetic alloys, the exact field dependence is difficult to predict, first because there is at low field additional spin-flip or Kondo scattering and also because $I_\uparrow/I_\downarrow$ does not remain constant. A simple field dependence can be only obtained in a crude model which ignores the additional low-field scattering and the variation of $I_\uparrow/I_\downarrow$ and supposes the impurity spin is $\frac{1}{2}$; in this model the induced Hall voltage is proportional to the excess of spin-up impurities and therefore varies as the saturation value multiplied by the polarization of the impurities. The field dependence will not be generally so simple but always will exhibit an initial linear dependence (with a slope proportional to the initial susceptibility) and a saturation for $\mu H \gtrsim kT$.

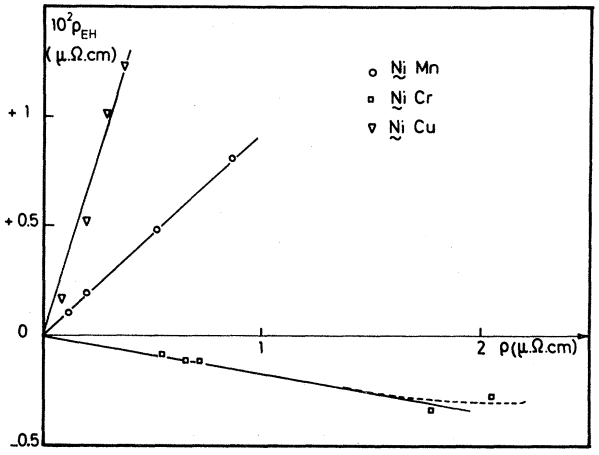

FIG. 2. Residual extraordinary Hall resistivity as a function of the residual resistivity for *Ni* Cr, *Ni* Mn, and *Ni* Cu alloys (experimental data). For the most concentrated *Ni* Cr alloys, it seems that the usual term ρ_{eH} proportional to ρ^2 begins to appear; and we have verified that it becomes dominant for higher Cr concentrations. The data for *Ni*Cu are from Juguenin and Rivier, Ref. 12.

The first experimental data we present are extraordinary Hall effect data on nickel-based dilute alloys. We recall that, at high enough temperatures or for an alloy of high enough impurity concentration, in other words for a large enough resistivity, the extraordinary Hall resistivity ρ_{eH} of transition ferromagnetic metals is nearly proportional to the square of the resistivity ρ.[12] Some theories have been proposed to explain this behavior.[3] On the other hand, in the case of our measurements—that is at low temperature, for small concentrations, and for resistivities lower than 2 $\mu\Omega$ cm—the above contribution proportional to ρ^2 becomes very small, is actually masked in our experimental results by a contribution proportional to the residual resistivity (for a type of impurity), and is very dependent on the type of impurity. Figure 2 shows this linear dependence between ρ_{eH} and ρ at 4.2°K for *Ni*Cr, *Ni*Mn, and *Ni*Cu alloys, the slope being positive for *Ni*Mn and *Ni*Cr; we have obtained a similar linear dependence also for other impurities, with slopes either positive (Fe, Co, Os) or negative (Ir, Re), and varying in absolute value between 2×10^{-2} and 10^{-3}.

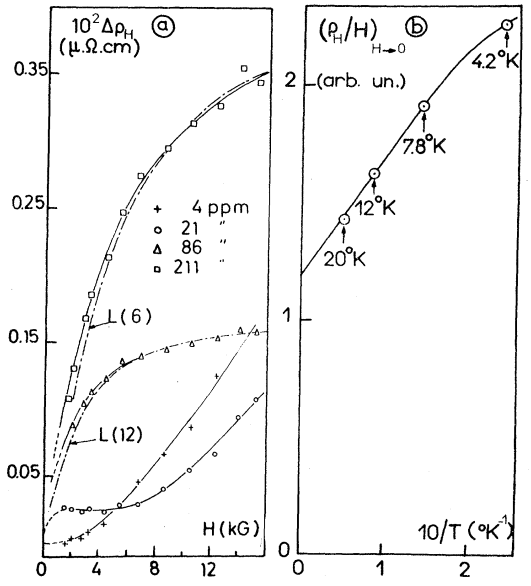

FIG. 3. Hall resistivity of *Au*Fe alloys. (a) Field dependence of the Hall resistivity $\Delta\rho_H$ induced by Fe impurities at 4.2°K, after Hurd and Alderson, Ref. 13. $\Delta\rho_H$ is the difference between the Hall resistivity ρ_H of the alloy and the low-field Hall resistivity of very dilute *Au*Fe alloys (few ppm). The term $\Delta\rho_H$ proportional to the concentration is seen clearly for the most concentrated alloys (86 and 211 ppm) while, for the lower concentrations, there is a hindering upturn of $\Delta\rho_H$ due to the change of the ordinary Hall resistivity when $\omega_c\tau \simeq 1$. (b) $(\rho_H/H)_{H\to 0}$ is plotted as a function of T^{-1} for a 200-ppm *Au*Fe alloy (after Friederich and Monod, Ref. 15).

So each impurity is characterized by a constant ρ_{eH}/ρ ratio, just the behavior expected for the Hall effect induced by skew scattering. A more precise analysis of the experimental data will be presented elsewhere.

For experimental data on dilute paramagnetic alloys, we will refer to Hurd and Alderson[13] and to Monod and Friederich.[14] Figure 3(a) shows for the most concentrated *Au*Fe alloys a Hall effect induced by the impurity (at 4.2°K) nearly proportional to the concentration and tending to saturate at high field. Similar contributions have been observed for *Au*Mn, *Cu*Cr,[15] *Ag*Mn, and *Cu*Mn,[13,15] but they are between 3 and 23 weaker than in *Au*Fe for an equal impurity concentration.

Hurd and Alderson[13] assigned this contribution to the Hall effect to the presence of ferromagnetic impurity clusters in which the conduction electrons would undergo an extraordinary Hall effect; the curves of Fig. 3(a) would then correspond approximately to magnetization curves of clusters containing six or twelve Fe atoms [curves $L(6)$ and $L(12)$]. We believe that it is difficult to explain by clusters the order of magnitude of the observed effects (at magnetic saturation, the induced Hall angle is about 10^{-2} or 10^{-3} and is comparable to the extraordinary Hall angle in bulk ferromagnetic alloys at low temperature). We suggest that the Hall resistivity induced by impurities is due to skew scattering. This mechanism gives a linear dependence on the concentration, the right order of magnitude ($\varphi_H \simeq 10^{-2}$ or 10^{-3}) and sign, and a field dependence nearly similar to that of Fig. 3(a). Also the initial slope of the field dependence, according to our model, is proportional to the initial susceptibility, that is, to T^{-1} for $T \gg T_K$ as is the case [Fig. 3(b)] for a 200-ppm *Au*Fe alloy, after Friederich and Monod[15]; the deviation from a linear dependence below 5°K may be due to the approach to the Kondo temperature ($T_K \simeq 0.4$°K).

Other magnetic alloys show also an impurity-induced Hall voltage proportional to the concentration and the polarization of the impurities (e.g., *PdH*Co alloys[16]). It would be interesting to have data on *La*Ce or *Y*Ce systems for which the well-known resonance of the conduction electrons on the $J = \frac{5}{2}$ Ce level should induce a substantial Hall effect.

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*Associé au Centre National de la Recherche Scientifique.

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Raman-Active Resonance Modes, Overtones, and Anharmonicity in NaCl:Cu^{+}†

B. N. Ganguly, R. D. Kirby,* M. V. Klein, and G. P. Montgomery, Jr.‡
Department of Physics and Materials Research Laboratory, University of Illinois, Urbana, Illinois 61801
(Received 27 December 1971)

The existence of an impurity-activated E_g resonance mode in NaCl:Cu^+ has been suggested by several previous experiments. Raman data presented here reveal this resonance directly and also reveal the three components of the first overtone of the 23.5-cm^{-1} infrared resonance mode. The frequencies of the E_g resonance and the E_g component of the overtone are shifted as a result of a strong anharmonic coupling. Their line shapes and strengths are considerably altered by an interference between the Raman amplitudes. A reasonable fit to the data has been obtained using a simple theory.

Substitutional impurities often introduce resonance modes into the lattice vibration spectrum of a crystal.[1] Most experimental studies have been on infrared-active resonance modes. Raman-active modes have been predicted, but only in KI:Ag^+ have they been found at very low frequency.[2]

The present work involves NaCl:Cu^+, which has been known for some time to have an infrared-active (T_{1u}) resonance mode at 23.5 cm^{-1}.[3] Its far-infrared properties have been studied under applied electric fields[4] and uniaxial stress,[5] and the isotope splitting has been resolved.[6] It has a pronounced temperature dependence.[3,7,8] The measured shift in peak position, increase in linewidth, and decrease in absorption strength with temperature could be explained by assuming the existence of an E_g resonance mode at about 31 cm^{-1}, and coupling it anharmonically to the 23.5-cm^{-1} mode.[8] Additional indirect evidence for even-parity resonances in NaCl:Cu^+ comes from thermal-conductivity measurements. The observed conductivity depression cannot be explained by the presence of the 23.5-cm^{-1} resonance alone.[9] It has been suggested that the data could be explained if an E_g resonance were present at a somewhat higher frequency.[10]

We now present direct evidence for such an E_g resonance mode. It is not seen in its "bare" harmonic form; it is strongly affected by an anharmonic interaction with a nearby E_g component of the first overtone of the T_{1u} mode. Raman data for all three first overtone modes will be presented to support this picture.

Figure 1 shows part of the Raman spectrum of NaCl:Cu^+ taken with the 4880-Å argon-laser line and a scattering geometry that yields all three Raman-active symmetries for the O_h point group of the substitutional Cu^+ impurity. There are peaks at 40 and 48 cm^{-1} that are sensitive to temperature in a way reminiscent of the infrared mode.[3,8] The 40-cm^{-1} peak was originally interpreted as an ordinary E_g resonance mode.[11] We have made calculations using lattice Green's functions derived from realistic NaCl shell models that give an E_g resonance at about the correct frequency and width using force-constant

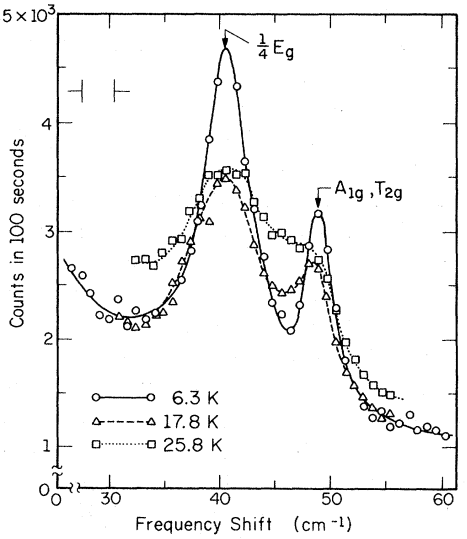

FIG. 1. Combined Raman spectrum of NaCl:Cu^+ at moderate resolution showing strong temperature dependence. Copper concentration: $3\times10^{18}/cm^3$.