s-BAND POLARIZATION EFFECTS IN Rh:Co ALLOYS

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Exchange polarization of s conduction bands is a well-known effect in metallic systems containing local moments such as Cu:Mn[1] or the ferromagnetic Heusler alloys.[2] In principle, these phenomena are also present in transition metals and alloys having purely band paramagnetism, although experimental evidence for this is largely absent. Here we present such evidence for the dilute Rh:Co alloy system in the form of measured NMR shifts at the first three shells of Rh^{103} nuclei which neighbor a Co impurity site. Because of their large size, the observed shifts can only be satisfactorily explained if they are primarily attributed to polarization of the Rh 5s conduction band with its large associated Fermi contact hyperfine field.[3] This polarization is in turn generated by the field-induced moment corresponding to the strongly enhanced d-spin susceptibility which characterizes the Rh:Co impurity state[4]: $\Delta\chi(\mathrm{Co}) = 2.4\times10^{-3}$ emu/mole of Co solute, as compared with $\chi(\mathrm{Rh}) \cong 1\times10^{-4}$ emu/mole. The radial dependence of the inferred s-band polarization is in reasonable accord with the Ruderman-Kittel-Kasuya-Yosida (RKKY) model theory.[5-7] These results have important consequences for the study of hyperfine fields in transition metal systems, and particularly to impurity neighbor shifts, where s-band effects have for the most part been neglected.[8]

The Rh^{103} impurity-neighbor shift data have been obtained with the technique of spin-echo double resonance[9] (SEDOR), in which the observed Co^{59} spin-echo amplitude is caused to decrease by striking the nuclear resonance of a given set of Rh^{103} neighbors with a pulsed rf magnetic field. The Rh^{103} rf pulse is applied between the Co^{59} rf pulses of the echo sequence. In addition to the shifts, the SEDOR experiments provide data on the magnetic coupling strength between the Co^{59} and neighboring Rh^{103} nuclear moments; they consequently permit a measurement of the associated indirect nuclear-spin coupling.[5] Since this coupling arises mainly through an effective exchange polarization of the s band,[10] this investigation offers a unique opportunity to compare the radial dependence of s-band polarization from two sources—s-d exchange and s-electron–nuclear-spin exchange (Fermi contact interaction)—for the same system.

The experiments were carried out on carefully prepared alloys[11] containing 0.25, 0.44, and 0.79 at.% cobalt. SEDOR spectra for these alloys were taken by monitoring the Co^{59} spin-echo amplitude $S(\omega)$ on a chart recorder while sweeping the frequency ω of the Rh^{103} rf pulse. We take the quantity $-\ln[S(\omega)/S_0]$ as a measure of the double-resonance effect, where S_0 is the echo amplitude when ω is far from resonance. A typical spectrum of $-\ln[S(\omega)/S_0]$ vs ω is shown in Fig. 1. The three double-resonance lines observed are attributed to the first three Rh neighbor shells as indicated. The identification of these lines is based on a straightforward calculation of the SEDOR effect, which yields for the spectral area contribution from the nth shell of Rh^{103} neighbors

$$A_n = \int_{-\infty}^{\infty}\{-\ln[S(\omega)/S_0]\}_n d\omega = CZ_n(0.8+J_n'^2)/r_n^6, \tag{1}$$

where Z_n and r_n are the number of atoms in and the radial distance to the nth shell, respectively. J_n' is the ratio of the nuclear indirect-

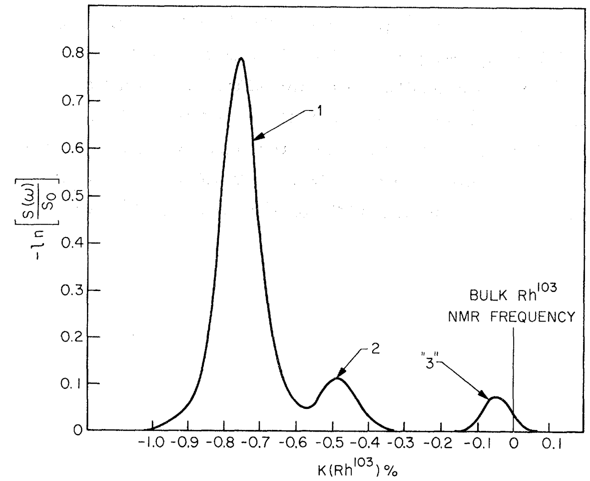

FIG. 1. SEDOR spectrum of Rh^{103} in $\mathrm{Co}_{0.0025}\mathrm{Rh}_{0.9975}$, with $H_1 = 5.6$ G, $\tau = 1.25$ msec, and $t_w = 510$ μsec (see text). The bulk Rh^{103} NMR frequency was found for this specimen by direct observation: $f_0 = 2157.2$ kHz. The frequency scale is in percent shift from this value.

exchange[5] coupling constant to the corresponding dipolar coupling coefficient $\gamma_{\text{Co}}\gamma_{\text{Rh}}\hbar^2/r_n^3$. The constant C is the same for all neighbors and is given by $\frac{1}{3}[\tau^2 I(I+1)\gamma_{\text{Rh}}^3\gamma_{\text{Co}}^2\hbar^2 H_1 I(\theta_0)]$, where $I=I(\text{Rh}^{103})=\frac{1}{2}$, γ_{Rh} and γ_{Co} are nuclear gyromagnetic ratios, H_1 is the rf pulse amplitude in gauss, τ is the time from the first Co^{59} pulse to the Rh^{103} pulse, and $I(\theta_0)$ is a function of the pulse angle $\theta_0=\gamma_{\text{Rh}}H_1 t_w$ (t_w = pulse width) which peaks at $\theta_0=2.4$ rad. This peak value $[I(\theta_0=2.4)=4.62]$ was maintained throughout the investigation. Ignoring the variation of J_n' for the moment, one finds the ratio $A_1{:}A_2{:}A_3$ to be 1.000:0.067:0.074 for fcc Rh metal. The total contribution of all other neighbors is estimated to be 6% of A_1 with no individual shell contribution being more than 1.6%. Clearly, then, the largest peak in Fig. 1 is the first-neighbor line. The other two follow since the shift must diminish rapidly with distance. The "third neighbor" line is seen to overlap the bulk Rh^{103} frequency and is therefore likely to contain contributions from more distant neighbors as well.

The first three Rh^{103} neighbor shells are seen to undergo shifts $K_1=-0.75\%$, $K_2=-0.49\%$, and $K_3=-0.05\%$, respectively, relative to the bulk Rh^{103} NMR line. These shifts include contributions from both d- and s-band polarization effects near the impurity site, with the s-band part predominant. To demonstrate the latter point, we express the NMR shift of Rh^{103} nuclei in the nth neighbor shell of a Co impurity as $K_n=\alpha_s\Delta\chi_n^s+\alpha_d\Delta\chi_n^d$. $\Delta\chi_n^s$ and $\Delta\chi_n^d$ are effective changes in the s- and d-band molar susceptibility, respectively, for the nth neighbors, and α_s(estimated) = 590 (emu/mole)$^{-1}$ and α_d(measured) = -28.9 (emu/mole)$^{-1}$ are the corresponding shift coefficients for pure Rh metal.[3] From the calculations of Inoue and Moriya[12] we estimate the upper limit of total induced d-spin susceptibility $\sum_n Z_n\Delta\chi_n^d$ to be ~50% of that at the impurity site, i.e., $\sim 0.8\times10^{-3}$ emu/mole of Co. That this amount of polarization is inadequate to explain the observed shifts may be seen by assuming it to reside entirely on the first neighbors, whereupon the corresponding shift $\alpha_d\Delta\chi_1^d$ would be only -0.2% or about one quarter of K_1. Viewed another way, the amount of induced d-spin susceptibility necessary to account for K_{1-3} (if the $\Delta\chi_n^s$ were zero) is nearly twice the total measured increase $\Delta\chi(\text{Co})$. Since $\sum_n Z_n\Delta\chi_n^d$ must be considerably smaller than $\Delta\chi(\text{Co})$, it is concluded that the bulk of the shifts are of s-band origin. We obtain estimates $\Delta\chi_1^s=-13\times10^{-6}$, $\Delta\chi_2^s=-8\times10^{-6}$, and $\Delta\chi_3^s=-0.8\times10^{-6}$, all in emu/mole, by setting $\Delta\chi_n^d=0$. The resulting total s-band polarization $\sum_n Z_n\Delta\chi_n^s$ is an order of magnitude smaller than $\Delta\chi(\text{Co})$.

Neglecting the smaller d-spin contributions to the shifts K_n, we compare them with the approximate RKKY theory of s-band polarization. With the crude assumption of constant $J_{sd}(q)$, the spin density [Ref. 7, Eq. (3.12)] is expected to vary as the function $f_{\text{RKKY}}(x)=x^{-4}(x\cos x-\sin x)$ with $x=2k_{\text{F}}r$. The shifts and f_{RKKY} are plotted in Fig. 2(a), both multiplied by factors $\propto r^3$ to eliminate the abrupt radial falloff and to simplify comparison with the nuclear-spin exchange data to follow. The shifts are scaled to coincide with $x^3 f_{\text{RKKY}}(x)$ at the second-neighbor position. The value of k_{F} is taken from recent de Haas–van Alphen measurements[13] for pure Rh, which show the s-like sheet of the Fermi surface to be near-

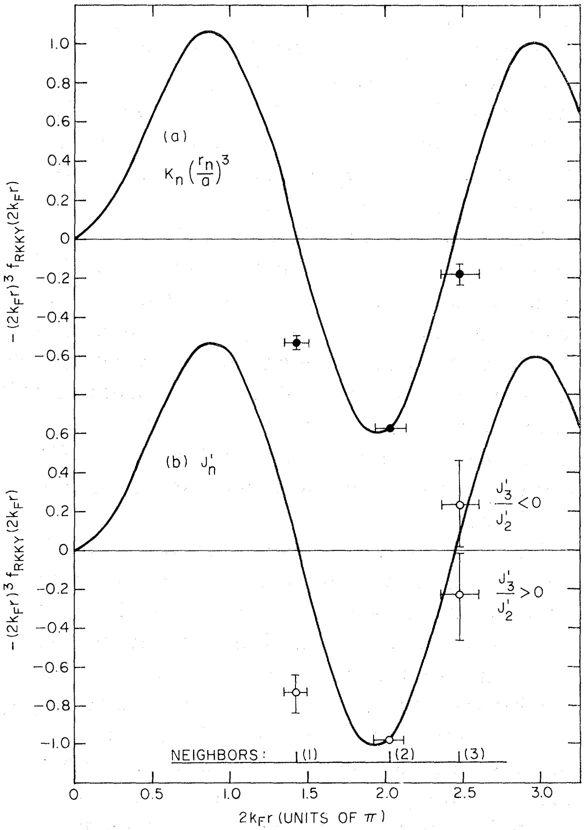

FIG. 2. Comparison of (a) shift $[K_n(r_n/a)^3]$ and (b) ratio (J_n') of R-K nuclear-spin coupling to classical dipolar coupling coefficient with the function $-(2k_{\text{F}}r)^3 f_{\text{RKKY}}(2k_{\text{F}}r)$.

ly spherical with $k_Fa = 3.17 \pm 5\%$ (a = lattice constant). The agreement with theoretical range dependence is seen to be rather good, considering the approximations involved, and helps to further corroborate the s-band origin of the shifts. The serious deviation of K_1 from the RKKY curve is not unexpected, since the detailed variation of $J_{sd}(q)$ with q would be most crucial to spin-density behavior at small r.

By substituting the induced moment $\Delta\chi(\mathrm{Co})_{\mathrm{atomic}} \times H_0$ for the expectation value $g\mu_B\langle S_z\rangle$ in Yosida's expression[7] for s-band polarization, we find that the observed second-neighbor shift corresponds to an effective exchange coupling $J_{sd} \sim 2.5$ eV. This is much too large to be accounted for with direct s-d exchange[1] and suggests that a modified form of the s-d mixing exchange mechanism[14,15] may be operating here. The latter mechanism has been used, for example, by Caroli and Blandin[2] to calculate s-band polarization effects in the ferromagnetic Heusler alloy $\mathrm{Cu_2MnAl}$. From their results we find a ratio of nearest-neighbor polarization to d-spin moment[16] $\langle S_z\rangle_{\mathrm{Cu}}{}^s/\langle S_z\rangle_{\mathrm{Mn}}{}^d = -5.8 \times 10^{-3}$, which, interestingly, is very close to the analogous ratio $\Delta\chi_1{}^s/\Delta\chi(\mathrm{Co}) = -5.1 \times 10^{-3}$ for the Rh:Co system. The s-d mixing effect gives the same asymptotic oscillatory radial dependence[2] as f_{RKKY} and is consistent with the comparison in Fig. 2(a).

We also note that s-band polarization appears to make the dominant contribution to the Co^{59} NMR linewidth in the alloys studied. This linewidth was found to be purely magnetic and proportional to cobalt concentration. A reasonable agreement was found between the observed width ($\langle\Delta H\rangle/H_0 \sim 5\times10^{-3}$/percent of Co) and an estimate of the type developed by Behringer[1] for Cu:Mn, based in the present case on the observed Rh^{103} shifts.

We now turn to the Ruderman-Kittel (R-K) coupling data yielded by the SEDOR spectral area measurement via Eq. (1). Consistent results were obtained with the three alloys mentioned above under a variety of experimental conditions. From the ratio $A_1(\text{measured})/A_1(J_1' = 0) = 2.5 \pm 0.25$, where $A_1(J_1' = 0)$ is the calculated area in the absence of indirect nuclear-spin coupling, we find $|J_1'| = 1.1 \pm 0.1$. The observed ratio $A_2/A_1 = 0.12 \pm 0.02$ then leads to $|J_2'| = 1.65 \pm 0.2$. These values are in reasonable accord with an estimate $J_n' \sim 1$ obtained from the measured exchange coupling in Ag metal[17] by estimating the s-band and hyperfine-field parameters in the R-K theory.[5] To find J_3' we note that "A_3" includes contributions from all the more distant neighbors with the possible exception of A_4. We may correct for these contributions using Eq. (1). With "A_3"/$A_1 = 0.065 \pm 0.005$ we estimate $0.030 \le A_3(\text{corr})/A_1 \le 0.048$, yielding $0 \le |J_3'| \le 0.7$. The limiting values correspond, respectively, to cases of large and of essentially negligible contributions to $\sum_{n=5}^{\infty} A_n$ from the J_n'.

According to their definition above, the J_n' are expected to vary as $(2k_Fr)^3 f_{\mathrm{RKKY}}(2k_Fr)$. The three values obtained are plotted with this function in Fig. 2(b), scaled to fit at the second-neighbor position. Again, the major deviation from theory is seen to occur for the nearest neighbors, where nodal behavior is expected. We suggest that the large value found for "J_1'" may arise from short-range pseudodipolar coupling terms[18] [not explicity included in Eq. (1)] which decrease more rapidly than f_{RKKY}. This interpretation is consistent with the findings of Narath, Fromhold, and Jones[19] for pure Rh metal, where additional broadening of the Rh^{103} NMR line suggested that for nearest neighbors pseudodipolar coupling is predominant.

J_2' undoubtedly reflects a large isotropic exchange contribution, whereas J_3' may again be dominated by pseudodipolar terms because of the associated node in f_{RKKY}. Thus we find at least a gross consistency between J_2' and J_3' and the corresponding shifts.

Finally, we turn our attention to another aspect of our NMR investigation of these alloys, namely the anomalously fast spin-lattice relaxation rate[14] associated with the Co^{59}: $T_1T = 39.5$ msec °K. This effect is apparently due to exchange-enhanced d-spin hyperfine field fluctuations in accord with the one-band model calculation of Lederer and Mills.[20] The measured T_1 corresponds to an enhancement by ~250 of the d-spin rate contribution,[4] whereas the one-band model[20] predicts a corresponding enhancement by a factor $\epsilon^2 \sim 600$, where $\epsilon \sim \Delta\chi(\mathrm{Co})/\chi(\mathrm{Rh})$ is the static-susceptibility enhancement factor.

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STUDY OF THE JOSEPHSON PLASMA RESONANCE*

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We report direct observation of the plasma resonance in Josephson tunnel junctions. The properties of the plasma mode are found to agree quantitatively with theoretical predictions.

The electrodynamics of Josephson tunnel junctions has been the subject of numerous theoretical and experimental studies in recent years. One of the salient predictions of the theory, first noted by Josephson,[1] is the existence of a plasma-like mode of oscillation in such junctions. Although the experimental basis for our understanding of electrodynamic phenomena in junctions is rather extensive, this plasma mode has heretofore escaped direct experimental observation. We report here the first observation and study of the Josephson plasma resonance.

Before describing the experimental results, we would like to indicate how the plasma oscillation arises and to exhibit its dependence on various experimental parameters. We consider a tunnel junction consisting of two plane films of superconductor separated by an insulating barrier. Josephson has shown[2,3] that in the absence of externally applied magnetic and radio-frequency fields, the phenomenological equations describing the Josephson effects can be combined with Maxwell's equations to yield a nonlinear equation for the relative pair phase φ:

$$\nabla^2\varphi-\bar{c}^{-2}(\partial^2\varphi/\partial t^2)=\lambda_J^{-2}\sin\varphi, \tag{1}$$

where (in Gaussian units) $\bar{c}=c(l/\epsilon d)^{1/2}$ and $\lambda_J=(\hbar c^2/8\pi j_1 e d)^{1/2}$. Here l is the barrier thickness, d is the sum of the barrier thickness and the penetration depths in the superconductors, j_1 is the Josephson current-density amplitude, and ϵ is the dielectric constant of the barrier material. In the case where φ undergoes small oscillations $\delta\varphi$ about φ_0, Eq. (1) can be linearized by setting $\sin\varphi=\sin\varphi_0+\delta\varphi\cos\varphi_0$. This yields the usual Meissner-effect equation plus the wave equation

$$\nabla^2\delta\varphi+\frac{1}{\bar{c}^2}\frac{\partial^2\delta\varphi}{\partial t^2}=\frac{\cos\varphi_0}{\lambda_J^{\,2}}\delta\varphi. \tag{2}$$