Nuclear-Magnetic-Resonance Studies of Dilute Molybdenum-Cobalt and Tungsten-Cobalt Alloys*

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A detailed nuclear-magnetic-resonance study of the dilute magnetic alloys *Mo*Co ($T_K \approx 24$ °K) and *W*Co ($T_K \approx 11$ °K) has been carried out in the temperature range 0.5–300 °K and for cobalt impurity concentrations of 0.1–1.0 at.%. Two distinct types of ^{59}Co impurity resonances were observed in every sample. The dominant resonance is characterized by a large temperature-dependent negative frequency shift and is associated with the magnetic impurity sites. Severe inhomogeneous broadening of the magnetic-site resonances indicates an inhomogeneous impurity polarization resulting from long-range oscillatory spin polarizations of the conduction electrons. A weaker, essentially unshifted resonance whose intensity increases with increasing impurity concentration is associated with relatively nonmagnetic impurity sites in regions of high local impurity concentration. At temperatures well above T_K, the magnetic-site resonance shifts exhibit the same Curie-Weiss temperature dependences (with $\theta = -T_K$) as do the respective bulk susceptibilities. The slope $dK/d\chi$ yields cobalt hyperfine fields of −23 and −3 kOe/μ_B in *Mo*Co and *W*Co, respectively. In the temperature range 0.5–4 °K, the ^{59}Co resonance shifts in *Mo*Co, and to a much lesser extent in *W*Co, become composition dependent unlike the bulk susceptibility. The low-temperature (1–4 °K) ^{59}Co spin-lattice relaxation rates in *Mo*Co are directly proportional to T and have magnitudes which correlate well with the observed resonance shifts using a Korringa-like relationship. From an analysis of the experimental Korringa products, a positive 1–2% orbital contribution to the measured resonance shifts is inferred. The molybdenum and tungsten nuclear resonances exhibit inhomogeneous broadening and enhanced spin-lattice relaxation rates. Within the experimental uncertainties, the widths and enhancement factors scale linearly with the impurity susceptibility. Our results provide no evidence for the existence below T_K of significant nonperturbative long-range spin-correlation contributions to the field-induced magnetization of isolated cobalt impurities in either *Mo*Co or *W*Co. In this regard *Mo*Co and *W*Co, despite their lower Kondo temperatures, resemble *Au*V ($T_K \approx 300$ °K).

I. INTRODUCTION

A well-known consequence of the s-d exchange interaction $-2J_{sd}\vec{S}\cdot\vec{\sigma}$ between a localized impurity spin ($\vec{S}$) and the host-metal conduction-electron spins ($\vec{\sigma}$) is the logarithmic divergence of the conduction-electron scattering amplitude below the Kondo temperature T_K.[1] Anomalies in the low-temperature magnetic, thermal, and transport properties which are associated with this divergence have been identified in many dilute alloys.[2] In fact, since the s-d model is only valid in the limit $U/\Delta \gg 1$ (where U is the effective intra-atomic Coulomb potential and Δ is the width of the impurity state due to interactions with the conduction electrons), the observation of these anomalies in a given alloy has traditionally been accepted as proof for the existence of a localized magnetic moment in the Friedel-Anderson sense.[3,4] For the case of an antiferromagnetic J_{sd}, the low-temperature ($T < T_K$) properties of such moments are usually attributed to a nondegenerate "quasibound" state in which the required spin compensation arises from long-range spin correlations in the electron gas. Unfortunately, as might be expected from the nonperturbative nature of the problem, few rigorous theoretical predictions exist for the low-temperature regime of the s-d exchange model. The interpretation of observed magnetic-impurity properties is further complicated by recent evidence which suggests that Kondo-like anomalies may persist into the nonmagnetic regime ($U/\Delta \lesssim 1$), where the s-d exchange model is clearly inappropriate.[5] In this case, the impurity is characterized by localized spin fluctuations[6–8] whose mean lifetime decreases rapidly with decreasing U/Δ. It is likely that a Hartree-Fock treatment of the intra-atomic correlation energy provides a physically meaningful first approximation in this regime. It is conceivable, therefore, that the low-temperature magnetic properties of many dilute alloys which exhibit Kondo anomalies in their transport properties may not be as strongly dominated by nonperturbative effects as has commonly been supposed. This view is sup-

ported by the results of a recent nuclear-magnetic-resonance (NMR) study of dilute *Au*V alloys.[9,10] The bulk properties of the *Au*V system had previously been interpreted successfully in terms of the spin-compensation model leading to an estimate of ~300 °K for the Kondo temperature.[11] The experimental impurity-site nuclear resonance shifts (K) and spin-lattice relaxation rates (T_1^{-1}), on the other hand, were shown[10] to be consistent with a locally exchange-enhanced Pauli-spin susceptibility treated in the usual Hartree-Fock approximation. Moreover, the impurity-induced host spin polarization was shown to have the familiar long-range oscillatory Ruderman-Kittel-Kasuya-Yosida (RKKY) form,[12–14] as predicted by perturbation treatments of spin-dependent scattering potentials. No evidence was found for the substantial negative-definite spin polarization which had been predicted[15] on the basis of the s-d model for temperatures below T_K.

Note added in proof. A recent calculation [P. R. Sievert, P. Bloomfield, and R. Hecht, Phys. Rev. (to be published)] of the field-induced polarization near an impurity site yields a negative-definite spin polarization in addition to the RKKY polarization. However, the negative-definite term has an exponential cutoff range of a few lattice spacings, and the amplitude inside this distance is at least an order of magnitude smaller than the mean amplitude of the oscillatory RKKY polarization.

In marked contrast to the situation in *Au*V, evidence has recently been reported[16] for the possible existence of significant nonperturbative spin-polarization effects in *Cu*Fe ($T_K \sim 15$ °K). For example, it was argued that at temperatures well below T_K only one-half of the field-induced impurity magnetization is localized on the iron impurity sites, the remainder being distributed over near-neighbor host sites. In other words, the local susceptibility is claimed to increase much less rapidly at low temperatures than the total susceptibility. However, results of a recent neutron diffraction study[17] on a 0.1-at.% *Cu*Fe alloy in an external magnetic field using polarized neutron techniques have cast some doubt on the existence of such anomalous polarization effects. In this connection it should also be noted that the existence of a field-induced negative-definite spin polarization for the s-d model below T_K has been questioned recently on theoretical grounds by the work of Ishii[18] based on Yosida's[19] singlet bound-state formalism. Because of the considerable uncertainties which remain in both theoretical as well as experimental treatments of the magnetic impurity problem, it is nevertheless unclear whether there exists a fundamental difference between the magnetic behavior of *Au*V and *Cu*Fe.

In order to provide additional information relevant to these perplexing questions we have carried out a detailed NMR study of dilute *Mo*Co ($T_K \approx 24$ °K) and *W*Co ($T_K \approx 11$ °K) alloys. These alloys exhibit pronounced Kondo-like properties. The magnetic susceptibilities obey Curie-Weiss laws over a wide temperature range with $\theta \approx -24$ and -11 °K (independent of composition), respectively.[20,21] The effective moments $\mu_{eff} = [g^2 S(S+1)]^{1/2}$ are approximately $2.4\mu_B$. Moreover, a well-defined resistance minimum has been observed in both *Mo*Co[21] and *W*Co[22] below 50 °K. The feasibility of observing the ^{59}Co NMR in *Mo*Co and *W*Co was demonstrated by the earlier work of Brog *et al.*,[23] whose NMR measurements, however, were restricted to the high-temperature regime ($T > T_K$). The interest in these alloys stems in large part from the fact that their Kondo temperatures are the lowest among those dilute alloys in which the impurity NMR has been observed. The potential disadvantage of a transition-metal host is minimized in the present case by the small electronic specific heats (and hence small electronic state densities at the Fermi energy) of molybdenum[24] and tungsten.[25] In this regard, these metals resemble nontransition metals such as the noble metals copper, silver, and gold.

A brief description of our experimental techniques is given in Sec. II. The results of our *Mo*Co and *W*Co studies are described in Secs. III A and III B, respectively, and discussed in Sec. IV.

II. EXPERIMENTAL TECHNIQUES

Alloys containing 0.1–1.0-at.% cobalt were fabricated by powder metallurgical techniques, as described by Booth *et al.*,[20] and were subsequently reduced to 325-mesh powders by crushing. The starting materials were the elemental metals whose purities were in excess of 99.9%. Some of the specimens used in the present study were used previously[20,21] for the magnetic susceptibility and electrical transport studies.

The NMR measurements were accomplished with either cw or pulsed spectrometers, depending on the temperature. In the range 27–300 °K, the nuclear resonances were observed with a Varian field-modulated wide-line spectrometer operating near 8 and 16 MHz. Signal-averaging techniques were employed where necessary to improve the signal-to-noise ratio. Transient NMR experiments in the range 0.5–76 °K were performed with a phase-coherent crossed-coil spectrometer in fields to 60 kOe produced by a superconducting NbZr solenoid as in our earlier studies[9,10] of the *Au*V system. Field strengths were determined by measuring the ^{109}Ag NMR frequency in metallic silver using the frequency/field ratio[26]

$$\nu^{(109)}\,(\text{metal})/H = 0.19915\ \text{kHz/Oe}. \qquad (2.1)$$

Spin echos were produced with two equal-width rf pulses. Adequate sensitivity was achieved by means of a Princeton Applied Research CW-1 boxcar integrator or a Fabri-Tek 952/1062 high-speed digitizer/analyzer. The former was most convenient for resonances with short spin-lattice relaxation times (^{59}Co) while the latter was especially useful for resonances with long relaxation times (^{95}Mo, ^{97}Mo, and ^{183}W).

Stable temperatures of 0.5–1.2, 1.2–4.0, 27, and 77 °K were provided by standard cryogenic techniques using liquid ^{3}He, ^{4}He, Ne, and N_2, respectively. Below 4 °K, temperature measurements were based on the appropriate vapor-pressure scale. Temperatures in the ^{3}He cryostat were verified by the observed signal intensities. Temperatures above 77 °K were achieved by passing cold N_2 gas over the sample which contained an imbedded copper-constantan thermocouple junction.

Resonance shifts were obtained at constant frequency by comparing the measured field strengths at maximum resonance intensity against the following reference frequency/field ratios[27,28]:

$$\text{Co:}\quad \nu^{(59)}(\text{ref})/H = 1.010\ \text{kHz/Oe}, \qquad (2.2)$$

$$\text{Mo:}\quad \nu^{(95)}(\text{ref})/H = 0.27736\ \text{kHz/Oe}, \qquad (2.3)$$

$$\nu^{(97)}(\text{ref})/H = 0.28319\ \text{kHz/Oe}, \qquad (2.4)$$

$$\text{W:}\quad \nu^{(183)}(\text{ref})/H = 0.177161\ \text{kHz/Oe}. \qquad (2.5)$$

The techniques for measuring the linewidths and spin-relaxation rates followed those described in Ref. 10.

III. EXPERIMENTAL RESULTS

A. MoCo

1. *Cobalt Resonance Shifts and Widths*

The low-temperature ^{59}Co ($I = \frac{7}{2}$) resonance profiles in *Mo*Co are illustrated in Fig. 1 for three solute concentrations. In every instance, maximum signal intensities were achieved with rf field strengths (H_1) which were smaller by a factor $I + \frac{1}{2} = 4$ than would ordinarily be expected. This indicates that the first-order quadrupole broadening in our samples is sufficiently strong that only the $+\frac{1}{2} \leftrightarrow -\frac{1}{2}$ transitions contribute to the observed signal intensities.[29] The ^{59}Co spin-echo spectra in *Mo*Co are reminiscent of the ^{51}V spectra in *Au*V.[9,10] In addition to the principal high-field resonance, a weaker resonance is observed which is nearly unshifted relative to the reference. Within the experimental uncertainty, the intensity ratio of the two resonances appears to be independent of temperature. The persistence of the low-field resonance at temperature above T_K is demonstrated in Fig. 2 which shows a second-derivative absorption-mode spectrum for the 1-at.% alloy at 77 °K. Following our interpretation of the *Au*V spectra, the high-field resonance can be assigned to cobalt impurities in relatively dilute regions of the sample. The servere inhomogeneous broadening of the resonances reflects local variations in the magnetic hyperfine field. These are caused most likely by long-range oscillatory RKKY spin-density disturbances resulting from the scattering of conduction electrons by the impurity potential. The magnitude of the broadening is comparable to that observed in *Au*V. It has been established[10] that the broadening in *Au*V is much too great to result from direct hyperfine interactions between the ^{51}V nuclear moments and the RKKY spin-density oscillations. Instead, the broadening was attributed to an inhomogeneous magnetic polarization of the impurities due to the *s-d* coupling between the local *d*-spin magnetization and the RKKY conduction-electron spin polarization.[30] This indirect mechanism leads to a linewidth which is proportional to the square of the local *d*-spin susceptibility, whereas the direct RKKY width depends only linearly on the susceptibility. Thus, whenever the local *d*-spin susceptibility is sufficiently large, the indirect process be-

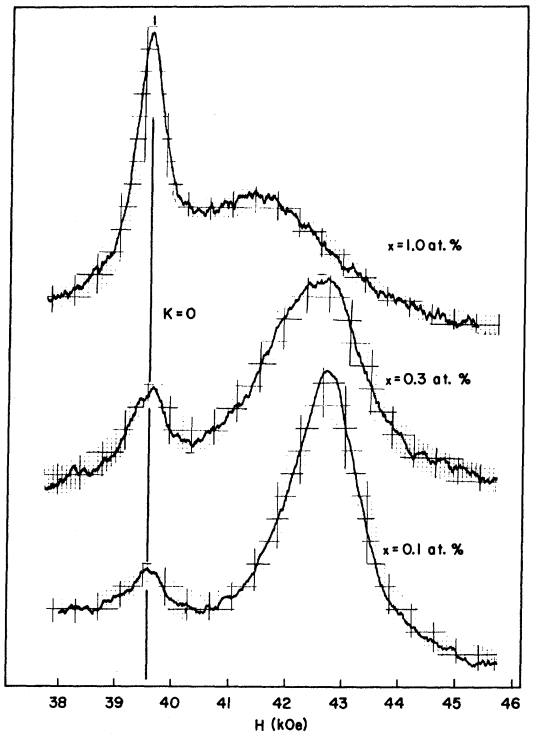

FIG. 1. Experimental ^{59}Co spin-echo spectra in $Mo_{1-x}Co_x$ at 1.2 °K. The spectra were obtained with two equal-width (7-μsec) rf pulses at 40.00 MHz.

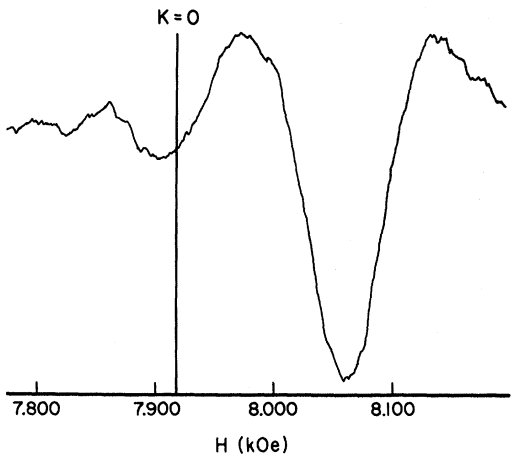

FIG. 2. Second-derivative absorption spectrum of ^{59}Co in $Mo_{0.99}Co_{0.01}$ at 77 °K and 8.000 MHz. The field modulation frequency was 40 Hz and its amplitude ~80 Oe.

comes the dominant hyperfine broadening mechanism. The low-temperature impurity susceptibility of *Mo*Co ($\chi \approx 290\times10^{-4}$ emu/g atom)[20,21] is approximately six times larger than that of *Au*V ($\chi \approx 47\times10^{-4}$ emu/g atom).[11,31] It follows that the indirect mechanism must be responsible for the ^{59}Co linewidths in *Mo*Co. Additional support for this conclusion is provided by the high-temperature linewidths (see Fig. 2) which decrease much more rapidly with increasing temperature than is the case for the resonance shifts. Because the host in *Mo*Co is a transition metal with a relatively complex Fermi surface, a comparison of the ^{59}Co linewidths with predictions based on the free-electron model developed in Ref. 10. is unfortunately not expected to yield meaningful results.

Because of their small shifts and widths, the low-field resonances in Fig. 1 can be identified with "nonmagnetic" cobalt sites in our samples. Analogous resonances in *Au*V were shown[10] to be associated with nearest- or next-nearest-neighbor vanadium pairs. It was speculated that the -ɟxəuɹent mixing of *d* orbitals centered on neighboring lattice sites broadens the virtual *d* levels sufficiently to reduce the magnitude of the local-spin susceptibility to a small value. Applying the same interpretation to the *Mo*Co data leads to the conclusion, based on the observed intensities of the "nonmagnetic" site resonances, that the cobalt impurities are not randomly distributed in our samples. In a random bcc alloy, the probability that a given site has at least one impurity as a nearest- or next-nearest neighbor is 0.014, 0.042, and 0.13 for impurity concentrations of 0.1, 0.3, and 1.0 at.%, respectively. The corresponding experimental integrated signal amplitudes, on the other hand, yield relative nonmagnetic site abundances of 0.08, 0.12, and 0.28. Although a model in which the critical interaction radius is increased greatly could in principle account for the observed signal amplitudes, the sharp distinction between the two resonances suggests that a tendency of the cobalt impurities to cluster is a more natural explanation for the anomalously high abundance of nonmagnetic cobalt impurities in our samples. Whether this clustering takes the form of an increased probability for near-neighbor pair formation in the bcc phase or the precipitation of a nonmagnetic cobalt-rich second phase[32] can, unfortunately, not be determined from the available data.

A summary of low-temperature magnetic site ^{59}Co NMR data at 40 MHz is given in Table I. The quoted shifts refer to positions of maximum spin-echo amplitude whereas the linewidths are full widths between half-amplitude points. In order to verify that the results are independent of external field strength below ~40 kOe, a few of the measurements were repeated at 15, 20, and 30 MHz. The results were found to be identical to those obtained at 40 MHz. An inspection of Table I shows that impurity-impurity interactions not only cause severe inhomogeneous broadening which increases with increasing concentration, but also lead to concentration-dependent reductions in the magnitude of the resonance shifts. These shift variations disappear at sufficiently high temperatures, as can be seen in Fig. 3. Whereas the macroscopic spin susceptibility per cobalt atom varies as $(T+24)^{-1}$ and is essentially independent of concentration to at least 1.6-at.% cobalt,[20,21] the resonance shifts become nearly independent of temperature and strongly dependent on concentration at temperatures

TABLE I. Summary of low-temperature ^{59}Co resonance shifts (K) and line-widths (W/H) at 40 MHz for the magnetic impurity site in $Mo_{1-x}Co_x$. The numbers in parentheses are estimated uncertainties in the preceding digit.

x(at.%)	T(°K)	K(%)	W/H(%)
0.1	1.2	−7.3(2)	3.0(2)
0.1	4.0	−7.1(2)	2.7(2)
0.3	1.2	−6.7(2)	4.8(3)
0.3	4.0	−6.5(3)	4.5(4)
0.5	0.5	−5.7(2)	7.1(5)
0.5	1.2	−5.7(2)	6.8(5)
0.5	4.0	−5.8(2)	
1.0	0.5	−4.7(2)	8.1(5)
1.0	1.2	−4.6(2)	7.5(5)
1.0	2.5	−4.7(2)	
1.0	4.0	−4.9(2)	6.3(5)

below ~4 °K. Thus, the resonance shifts between room temperature and ~77 °K are proportional to the total impurity susceptibility but deviate markedly from this relationship at lower temperatures. This behavior is superficially similar to that observed in *Cu*Fe.[16] In the present case, however, the effect does not appear to be an intrinsic property of dilute *Mo*Co, but rather is associated with interactions among the cobalt impurities. Because of the high probability of significant impurity clustering in our samples, it is unfortunately not possible to extrapolate our data to zero impurity concentration. In fact, the large linewidth in the 0.1-at.% cobalt alloy and its relatively slow increase with increasing cobalt concentration, together with the anomalous nonmagnetic site resonance intensities discussed earlier, suggest that the local cobalt concentration in our most dilute sample may be appreciably higher than 0.1 at.%. It is conceivable, therefore, that the cobalt resonance shifts are proportional to the impurity spin susceptibility over the entire temperature range in the infinite dilution limit. To make such an analysis quantitative would, of course, require that the experimental resonance shifts and susceptibilities be corrected for any temperature-dependent orbital contributions.

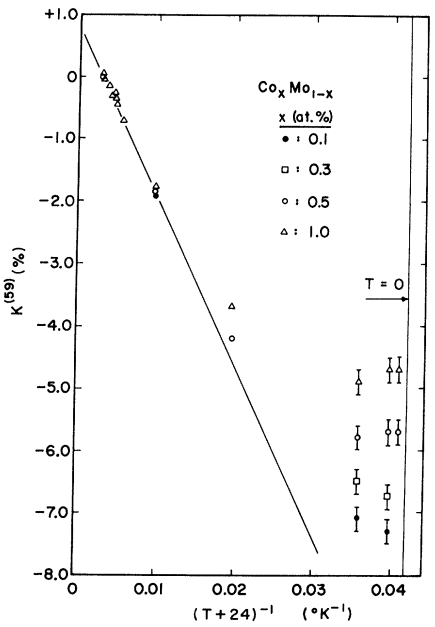

FIG. 3. Temperature dependence of ^{59}Co resonance shifts (defined by the position of peak resonance amplitude) in Co_xMo_{1-x}. The solid line represents the temperature dependence of the bulk susceptibility.

2. *Cobalt Relaxation Rates*

The ^{59}Co spin-relaxation rates in *Mo*Co are very rapid, as expected from the large magnitude of the resonance shifts. The spin-echo phase-memory decays were observed to have exponential time dependences characterized by time constants T_2 which varied with both temperature and impurity concentration, as shown in Fig. 4. The data were obtained at 40 MHz in external fields corresponding to the position of maximum intensity for the magnetic site resonance. The experimental decay rates have the form $T_2^{-1} = A + BT$. The intercept A represents an intrinsic nuclear spin-spin interaction rate which increases with increasing impurity concentration. The temperature-dependent term B can be attributed to lifetime effects resulting from spin-lattice relaxation processes. According to Walstedt,[33] the rate BT exceeds the true spin-lattice relaxation rate T_1^{-1} by a factor $(I+\frac{1}{2})^2$ in cases where the first-order electric quadrupole broadening is sufficiently strong that only the central $(+\frac{1}{2} \leftrightarrow -\frac{1}{2})$ transition is excited by the pulsed rf field. This condition is clearly satisfied in the present case and allows the spin-lattice relaxation rates to be calculated according to $T_1 T = 16B^{-1}$. We note that the experimental data are consistent with spin-lattice relaxation rates that are directly proportional to the absolute temperature in the range 1–4 °K. Direct measurements of T_1 by means of pulse saturation techniques could not be applied in the present case because of excessive quadrupole broadening, which made it impossible to achieve adequate saturation of the resonance. The accuracy of the indirect technique as applied to dilute alloys has, however, been established by previous experiments in *Au*V[10] and *Al*Mn.[34] In both cases the two techniques yielded identical results within the experimental uncertainties. Finally, we remark that the observed relaxation rates cannot be extrapolated with confidence to zero impurity concentration for reasons which were discussed above in connection with the ^{59}Co resonance shifts.

3. *Molybdenum Resonance Shifts and Widths*

The host nuclear resonance in a dilute magnetic alloy provides direct information about the long-range spin-density disturbances produced by the impurities. In view of the striking effects of impurity-impurity interactions on the cobalt resonances, the host NMR in *Mo*Co is of particular interest. As expected, the ^{95}Mo ($I=\frac{5}{2}$) and ^{97}Mo ($I=\frac{5}{2}$) resonances were found to be inhomogeneously broadened due to the combined effects of electric quadrupole and magnetic hyperfine interactions. In the case of ^{95}Mo, the first-order quadrupole broadening tended to mask the magnetic broadening. For this reason, measurements of the host linewidths were carried out on ^{97}Mo whose quadru-

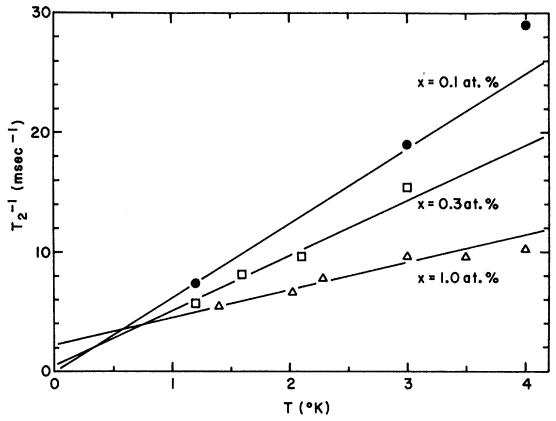

FIG. 4. Transverse relaxation rates of ^{59}Co in $Mo_{1-x}Co_x$ as a function of temperature. The data were obtained at 40.0 MHz with 3 μsec duration rf pulses. The external magnetic field strengths corresponded to the positions of peak magnetic site spin-echo amplitude. The straight lines are best fits to the experimental rates, whose uncertainties are approximately ±5–10%.

pole moment exceeds that of ^{95}Mo by a factor of 10.[28] The resulting first-order quadrupole spectrum is sufficiently broad that most of the observed intensity arises from the $+\frac{1}{2} \leftrightarrow -\frac{1}{2}$ transition. The second-order quadrupole broadening of the central transition, on the other hand, is negligible in fields above ~20 kOe allowing the magnetic broadening to be clearly identified. Figure 5 shows ^{97}Mo linewidth data for two alloy compositions as a function of resonance frequency and temperature. The zero-frequency intercepts are undoubtedly caused by residual satellite contributions to the observed line profiles. The data are consistent with a linear dependence of the magnetic linewidths on magnetic impurity concentration. The magnetic broadening must represent an inhomogeneity in the local hyperfine interaction. It is too great to be attributed to demagnetization effects since, for example, $\pi M/H$ in the 1-at.% cobalt alloy has a magnitude of only 0.01%. Because of the poorly known quadrupole line shapes, it is unfortunately not possible to achieve an unambiguous separation of the observed linewidths into electric and magnetic hyperfine contributions except when the latter is dominant. The assumption[35] that the electric quadrupole broadening is Gaussian and the magnetic broadening is Lorentzian leads to the conclusion that the latter scales linearly with the impurity susceptibility and at sufficiently low temperatures reaches a magnitude of 0.26% per at.% magnetic cobalt. The corresponding value for the ^{109}Ag linewidth in *Au*V is 0.5%.[10] In both alloys the impurity-site resonances are broadened much more severely, as expected, since the indirect mechanism discussed earlier is ineffective for the host.

In contrast to the concentration-dependent shifts of the ^{59}Co resonances, no significant systematic differences between any of the alloys and pure molybdenum metal were detected for the ^{95}Mo and ^{97}Mo resonance shifts. In the temperature range 4–76°K and concentration range 0.3–1.0-at.% cobalt the ^{95}Mo and ^{97}Mo shifts are given by +0.60(2)%, which compares with a 4 °K Knight shift of +0.610(5)% in pure molybdenum metal. The far-field effect of the cobalt impurities on the molybdenum resonance profiles is therefore a symmetric magnetic hyperfine broadening in addition to the usual electric quadrupole broadening.

4. *Molybdenum Relaxation Rates*

The inhomogeneous broadening of the host resonance in dilute magnetic alloys is usually accompanied by an appreciable enhancement of the spin-lattice relaxation rate which is approximately proportional to the differential impurity susceptibility and is therefore most easily observed at low temperatures.[36] We have measured the ^{95}Mo spin-lattice relaxation rates in the 0.3-at.% cobalt alloy. The result $T_1T = 28(3)$ sec °K is independent of temperature in the range ~1–4 °K. In this tempera-

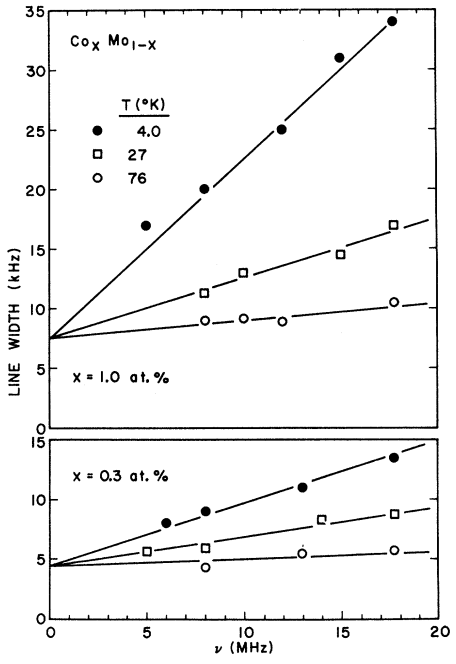

FIG. 5. Experimental linewidths (defined as the full width between half-amplitude points) in $Mo_{1-x}Co_x$ as a function of frequency. The linewidths were based on integrated echo amplitudes using 40-μsec duration rf pulses.

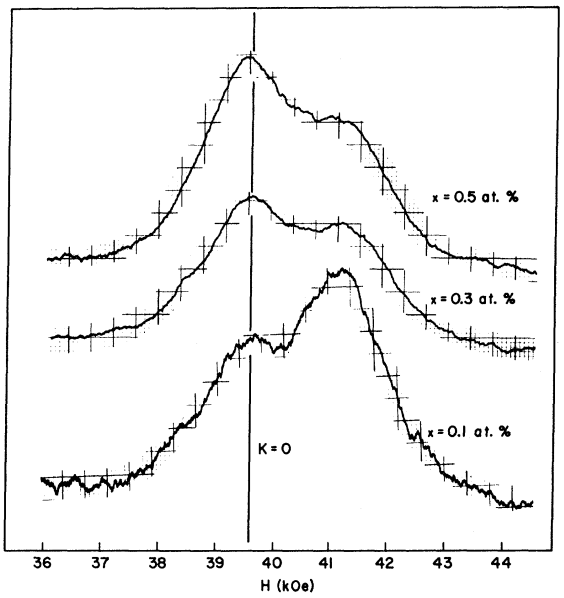

FIG. 6. Experimental ^{59}Co spin-echo spectra in $W_{1-x}Co_x$ at 1.2 °K. The spectra were obtained with two equal-width (7-μsec) rf pulses at 40.00 MHz.

ture interval the impurity susceptibility, as measured by ^{59}Co resonance shift, is also essentially constant. These relaxation times compare with $T_1T = 36(1)$ sec °K in molybdenum metal.[36]

B. WCo

1. *Cobalt Resonance Shifts and Widths*

The ^{59}Co resonance profiles in *W*Co are qualitatively very similar to those in *Mo*Co, as is demonstrated by the low-temperature spin-echo spectra in Fig. 6. As before, magnetic as well as nonmagnetic site resonances can be clearly distinguished. Both resonances are inhomogeneously broadened by magnetic hyperfine interactions, as evidenced by linewidths which are directly proportional to the resonance frequency. In the 1.0-at.% alloy, the broadening is sufficiently severe at low temperatures that the magnetic and nonmagnetic site resonances are no longer resolved. From the observed intensity ratios one may conclude that the degree of clustering is stronger in *W*Co than in *Mo*Co. This conclusion is also supported by the smaller concentration dependence of the magnetic site shifts and linewidths. A summary of the low-temperature data is given in Table II. Measurements at frequencies below 40 MHz gave essentially identical results. Despite the larger $T = 0$ susceptibility of *W*Co ($\chi \approx 800 \times 10^{-4}$ emu/g atom)[20] the shifts of the magnetic site resonance are smaller than in *Mo*Co (i.e., the cobalt hyperfine field is much smaller). The low-temperature shifts are consistent with an extrapolation of the previously reported[23] high-temperature ^{59}Co resonance shifts using a Curie-Weiss law with $\theta = -11$ °K. It should be noted that only a single resonance lacking any resolved structure was observed in the temperature range 77–300 °K. The only indication of the nonmagnetic site resonance was a slightly asymmetric broadening of the low-field side of the experimental line shape. However, the absence of any concentration dependence in the observed positions of peak resonance intensity suggests that this broadening had no effect on the measured shifts. Thus, one may conclude that the magnetic site shifts are proportional to the impurity susceptibility (unlike the situation in *Mo*Co), provided only that the -11 °K Curie-Weiss constant describes the temperature variation of the impurity susceptibility below 27 °K.[37] Because of the large ratio of the ^{59}Co linewidths to resonance shifts, the error in the determination of K/χ is unfortunately much larger than in *Mo*Co. For this reason, the absence of interaction effects in the low-temperature shifts cannot be established with certainty. It is noteworthy that the ^{59}Co shifts in *W*Co decrease substantially in magnitude between 0.5 and 4.0 °K. The experimental sensitivity is unfortunately insufficient to establish whether a Curie-Weiss law applies in this range.

2. *Cobalt Relaxation Rates*

Because of the strong overlap between the magnetic and nonmagnetic site ^{59}Co resonances in *W*Co, most measurements of the echo phase-memory times were restricted to the most dilute alloy. The decay curves, which were exponential, yielded the T_2 values shown in Fig. 7. A few experiments on more concentrated alloys verified the lack of significant concentration dependences in the relaxation rates. At first sight, the observed temperature dependence seems anomalously weak when compared to corresponding data for *Mo*Co, even when allowance is made for the difference in the

TABLE II. Summary of low-temperature ^{59}Co resonance shifts (K) and line-widths (W/H) at 40 MHz for the magnetic impurity site in $W_{1-x}Co_x$.

x (at.%)	T (°K)	K (%)	W/H (%)
0.1	1.2	−3.9(3)	4.3(3)
0.1	4.0	−2.5(5)	2.9(5)
0.3	0.5	−4.1(2)	4.3(3)
0.3	1.2	−3.7(3)	4.6(3)
0.3	4.0	−2.0(5)	3.8(5)
0.5	0.5	−3.7(3)	5.6(4)
0.5	1.2	−3.5(4)	6.0(5)
0.5	4.0	−1.9(5)	4.8(5)

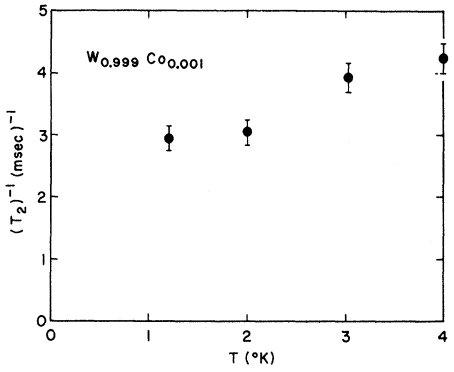

FIG. 7. Transverse relaxation rates of ^{59}Co in $W_{0.999}Co_{0.001}$ as a function of temperature. The data were obtained with 6-μsec duration rf pulses at 40.0 MHz. The external magnetic field strengths corresponded to the positions of peak magnetic site spin-echo amplitude.

low-temperature resonance shifts. Most likely, the *W*Co results reflect an increase in T_1T with increasing temperature resulting from the decreasing local susceptibility.

3. *Tungsten Resonance Shifts and Widths*

The absence of a quadrupole moment in $^{183}W(I=\frac{1}{2})$ permits the host magnetic hyperfine interactions to be studied with higher precision than in *Mo*CO. The shift and linewidth data are listed in Table III. The impurity-induced shifts of the ^{183}W resonance are seen to be nearly an order of magnitude smaller than the line broadening. The temperature dependence of these quantities in the range 1–76 °K is plotted in Fig. 8 for the 0.5-at.% cobalt alloy. The observed temperature variations are seen to be approximately linear in $(T+11)^{-1}$, except for small deviations at low temperatures which are possibly caused by the onset of magnetic saturation effects.

4. *Tungsten Relaxation Rates*

The temperature and concentration dependences of the ^{183}W spin-lattice relaxation times are summarized in Table III. The observed enhancement factors are approximately proportional to the total spin susceptibility of the impurities. The enhancement vanishes at high temperatures, whereas at low temperatures it assumes a constant value which depends on the impurity concentration.

IV. DISCUSSIONS

On the whole, our experimental data provide little, if any, support for the existence of significant nonperturbative spin-correlation effects in the field-induced magnetization of isolated impurities in a Kondo alloy. The most unusual aspect of the present *Mo*Co results is the breakdown at low temperatures of the proportionality between the mean ^{59}Co resonance shifts and the impurity susceptibilities. The strong concentration dependence of the effect indicates that the anomalous shifts are caused by impurity-impurity interactions. Because of the clustering tendency of the cobalt impurities in our samples, it is, of course, impossible to prove on the basis of the available data that the anomaly will disappear entirely for sufficiently large impurity separations. In the case of *W*Co, the experimental data have insufficient precision to demonstrate interaction effects with certainty. However, some indication that the low-temperature shifts are concentration dependent is provided by the systematic trends shown in Table II.

It is easy to demonstrate that the interaction effects observed in the ^{59}Co resonance shifts are not a simple consequence of long-range *negative-definite* spin polarizations surrounding the impurities at temperatures below T_K. We note that the ^{59}Co resonance shifts in *Mo*Co span a range of approximately 3% at the lowest temperatures, depending on the impurity concentration. The magnitude of the shift variation thus corresponds to nearly 40% of the linewidth in the 1.0-at.% cobalt alloy. On the other hand, any displacement in the corresponding ^{97}Mo shifts relative to pure molybdenum metal is less than ~10% of the ^{97}Mo linewidths. Moreover, according to Fig. 8, the ^{183}W shift in *W*Co relative to pure tungsten metal is very nearly 10 times smaller than the linewidth. Regardless of the details of the local hyperfine interaction mechanisms we may therefore conclude that any *long-range* negative-definite polarization of the conduction-electron spins, if it exists at all in these alloys, is weak compared to the mean amplitude of the oscillatory RKKY polarization, and thus cannot account for the large variations in the impurity shifts. The small variation in the ^{183}W shift in $W_{0.995}Co_{0.005}$ (Fig. 8) is entirely consistent with an

TABLE III. Summary of ^{183}W resonance shifts (K), linewidths (W/H) and spin-lattice relaxation times (T_1) in $W_{1-x}Co_x$.

x (at.%)	T (°K)	K (%)	W/H (%)	T_1T (sec °K)
0.0	1-76	+1.043(1)		39(2)
0.1	1.2	+1.071(5)	0.19(2)	36(2)
0.1	4.0	+1.079(5)	0.16(2)	38(2)
0.3	1.2	+1.12(1)	0.36(4)	25(2)
0.3	4.0	+1.12(1)	0.36(4)	25(2)
0.5	1.2	+1.12(1)	0.51(5)	16(1)
0.5	4.0	+1.12(1)	0.48(5)	16(1)
0.5	27	+1.083(5)	0.18(2)	36(3)
0.5	76	+1.059(2)	0.08(1)	40(4)

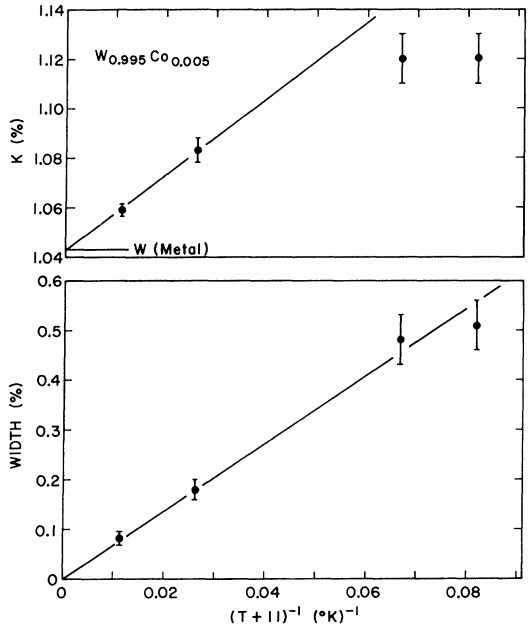

FIG. 8. Temperature dependence of ^{183}W resonance shifts and widths in $W_{0.995}Co_{0.005}$ at 9.6 MHz.

RKKY polarization, since the discreteness of the lattice generally leads to slightly different contributions from positive and negative terms in the polarization, particularly at the relatively high impurity concentrations used in our experiments. The fact that the ^{183}W shifts and widths have essentially identical temperature dependences lends support to this view. Thus, as far as possible short-range nonperturbative polarization effects below T_K are concerned, their range must lie within the "wipe-out" radius. In *Cu*Fe this radius corresponds to approximately 12 near-neighbor shells[16]; in *Mo*Co and *W*Co the wipe-out range is considerably smaller as evidenced by the low-temperature signal intensities in the most concentrated alloys.

A quantitative analysis of the observed host NMR unfortunately is not feasible because of the large number of unknown parameters. Among these is the relative weight of s- and d-spin contributions to the RKKY polarization. It should be noted that these two interactions are believed to give contributions of nearly equal magnitude but opposite sign to the Knight shifts in the elemental metals.[36] The measured Knight shifts in molybdenum and tungsten are dominated by the d-orbital hyperfine shift, whose magnitude exceeds that of the spin-dependent shifts by a factor of 5–10. In view of the relatively severe broadening of the host resonances in *Mo*Co and *W*Co, it is clear that a similar cancellation does not occur in the impurity-induced RKKY polarization. This is not surprising since a transition-element impurity is characterized by an $l = 2$ potential. In a transition-metal host the resulting d-resonance scattering should lead to an RKKY polarization having pronounced d-spin character.

Although the mechanism of the anomalous low-temperature impurity shifts in *Mo*Co remains unexplained, the data suggest two possible origins for the different temperature dependences of the resonance shifts and impurity susceptibilities:

1. The broadening of the ^{59}Co NMR might become strongly asymmetric at low temperatures, leading to a loss of high-field signal intensity. In this case the first moment of the resonance profile would not correspond to the position of maximum spin-echo amplitude.
2. Interactions among the impurities might reduce the effective impurity hyperfine field. For example, distortions in the impurity wave function could conceivably change either the magnitude of the intrinsic core-polarization hyperfine field or the strength of the local s-d polarization. Alternatively, the impurity magnetization might spread to near neighbors at low temperatures as a result of interactions.

The first explanation can probably be rejected. In the first place, the experimental resonance profiles give no evidence for significant asymmetric broadening. Second, an analysis of the observed intensities leads to the conclusion that essentially all the impurities were seen in our low-temperature experiments. The other explanation involves distinct changes in the electronic structure of the impurity. As noted earlier, any radial extension of the impurity magnetization must be limited to a small number of near-neighbor shells to be consistent with the absence of significant host resonance shifts. In this connection it is interesting to note that the high-temperature data yield unusually small impurity hyperfine fields. For *Mo*Co, the experimental value of $dK/d\chi$ yields $H_{hf} \approx -23$ kOe/μ_B; corresponding data for *W*Co give ~ -3 kOe/μ_B. These values compare with the expected ionic d-spin (core-polarization) hyperfine field for $3d$ transition elements $H_{hf}^{(d)} \approx -100$ kOe/μ_B.[38] Thus, even at temperatures above T_K, either a relatively large local s-d polarization and/or a spatially extended impurity magnetization is required to explain the impurity resonance data.

Some additional insight into the low-temperature behavior of the cobalt impurities is provided by the ^{59}Co spin-relaxation rates. As noted earlier, the spin-lattice relaxation rates may be calculated from the observed temperature dependence of T_2, at least in *Mo*Co where the ^{59}Co resonance shifts are

essentially constant below 4 °K and the temperature-independent contribution to T_2 is small. The resulting values of T_1T are listed in Table IV together with the observed shifts. It is seen that the relaxation rates are approximately proportional to K^2. This correlation suggests that the relaxation rates and shifts are determined by the same hyperfine interaction. The negative sign of the resonance shifts shows, of course, that the d-spin (core-polarization) interaction provides the dominant mechanism. The relationship $T_1T = \text{const}$ is indicative of a relaxation mechanism involving spin-flip scattering of itinerant electrons by the nuclear spins. Following the interpretation[10] of the ^{51}V relaxation rates in AuV, we assume that the amplitude of the local transverse spin fluctuations can be evaluated in the Hartree-Fock approximation. In that case the d-spin shift and relaxation rate are related by the Korringa-like[39] expression

$$K^2T_1T = \mathcal{S}\,F_d^{-1}K(\alpha)^{-1}\,, \tag{4.1}$$

where

$$\mathcal{S} \equiv (\gamma_e/\gamma_n)^2\,(\hbar/4\pi k_B)\,. \tag{4.2}$$

The inhibition factor F_d arises from the fact that spin fluctuations in orbitally degenerate states (in the absence of strong spin-orbit interactions), in effect, contribute independently to the relaxation even in the presence of intra-atomic (Hund's rule) exchange interactions.[40,41] The usual assumption that the e_g and t_{2g} d orbitals have equal weights at the Fermi level yields $F_d = \frac{1}{5}$. The factor $K(\alpha)$ corrects for differences between the exchange enhancements (due to local Coulomb interactions) of the square of the static impurity susceptibility and the imaginary part of the wave-number and frequency-dependent transverse susceptibility.[42,43] If the impurity states are well localized, $K(\alpha) = 1$, independent of the magnitude of the local exchange enhancement. On the other hand, for extended impurity potentials $K(\alpha) < 1$ and decreases rapidly with increasing exchange enhancement.[44] An example of a spatially extended impurity potential is provided by PdRh. In the dilute limit the ^{103}Rh data give $K = -15\%$ and $K(\alpha) = 0.05$.[45] The experimental $K^2T_1T/5\mathcal{S}$ ratios for MoCo are listed in Table IV. They are of order unity and essentially composition independent. This supports the conclusion derived from the ^{97}Mo resonance shifts that the impurity potential is quite localized in these alloys. The fact that $K^2T_1T/5\mathcal{S}$ is slightly *smaller* than unity can be explained, as in AuV, by assuming that the measured shifts contain a significant positive contribution (K_{VV}) arising from field-induced orbital paramagnetism of the impurities. Non-d-spin contributions to the spin-lattice relaxation rates, on the other hand, are probably small because each term in the relaxation rate depends quadratically on the respective interaction matrix element. A lower-limit estimate of K_{VV} (for the above choice of F_d) can therefore be obtained by assuming $K(\alpha) = 1$ and calculating the d-spin (core-polarization) shifts K_d (assumed to be negative) from the experimental spin-lattice relaxation rates using (4.1). The orbital shifts are then obtained by subtracting K_d from the measured shifts. The results of this analysis, which are presented in the last two columns of Table IV, may be compared with the ^{51}V shifts in dilute AuV, $K_d = -3.3\%$ and $K_{VV} = +1.8\%$. The low-temperature orbital shifts in MoCo are not substantially different from the high-temperature estimate of $+0.8\%$ which results from extrapolating the K-versus-$(T+24)^{-1}$ plot (Fig. 3) to infinite temperature. In general, it is clear that the analysis of the ^{59}Co relaxation data again leads to the conclusion that impurity-impurity interactions in MoCo cause a reduction in the magnitude of the d-spin (core polarization) resonance shift as the impurity susceptibility increases with decreasing temperature. It is puzzling that these interactions have no apparent influence on the measured impurity susceptibility. Since the analysis of the resonance data is not necessarily unique, further speculations are unwarranted.

The interpretation of the ^{59}Co relaxation rates in WCo is complicated by the fact that the resonance shifts are temperature dependent in the range 1–4 °K. The decrease in $|K|$ with increasing temperature is therefore most likely accompanied by an increase in T_1T. This would account for the small slope of the T_2^{-1}-versus-T plot shown in Fig. 7. Since the temperature-independent contribution to T_2^{-1} in $W_{0.999}Co_{0.001}$ is probably very small we may assume that $T_1 \approx 16T_2$. In order to demonstrate that the measured rates are qualitatively consistent with the model used above, we apply (4.1) to the lowest temperature (1.2 °K) relaxation rate. This gives $K_d \approx 5.9\%$ which, when compared with the experimental shift $K = -3.9\%$, yields $K_{VV} \approx +2.0\%$. This value is in reasonable agreement with the limiting high-temperature shift[23] of approximately $+1.0\%$.

Supporting evidence for the existence of apprecia-

TABLE IV. Low-temperature spin-lattice relaxation times and resonance shifts for ^{59}Co in $Mo_{1-x}Co_x$, together with the d-spin and d-orbital shifts inferred from the experimental data.

c(at.%)	T_1T (msec °K)	K(%)	$K^2T_1T/5\mathcal{S}$	K_d(%)	K_{VV}(%)
0.1	2.6(3)	−7.3(2)	0.59	−9.5(5)	+2.2(7)
0.3	3.5(4)	−6.7(2)	0.67	−8.2(5)	+1.5(7)
1.0	6.9(6)	−4.7(2)	0.65	−5.8(3)	+1.1(5)

ble ^{59}Co orbital resonance shifts in *Mo*Co and *W*Co is provided by the large temperature-independent contributions to the impurity susceptibility which have been identified in both alloys.[20] A fit of the Curie-Weiss form

$$\chi = (1-c)\chi_{\text{host}} + c\left[\chi_0 + \mu_{\text{eff}}^2/3k_B(T-\theta)\right], \qquad (4.3)$$

where c is the impurity concentration, yielded $\chi_0 = 6\times10^{-4}$ and 11×10^{-4} emu/g atom for *Mo*Co and *W*Co, respectively. If χ_0 is identified with the local orbital susceptibility χ_{VV}, and the corresponding orbital resonance shift is calculated according to

$$K_{VV} = (\mu_B N)^{-1}\chi_{VV}H_{\text{hfs}}^{(\text{orb})}, \qquad (4.4)$$

the hyperfine field required to explain an orbital shift of 1% in *Mo*Co is found to be 0.093×10^6 Oe/μ_B. This value is significantly smaller than the free-atom hyperfine field[38] of 0.599×10^6 Oe/μ_B. Thus, even if χ_0 is not entirely determined by the field-induced orbital paramagnetism of the impurities, it is probable that the cobalt orbital hyperfine field (and hence $\langle r^{-3}\rangle$) is smaller in *Mo*Co than in the free atom. This conclusion implies that the impurity d orbitals in the alloy are spatially expanded relative to the free atom. Similar behavior has also been noted in *Au*V,[10] where $\chi_0 \approx 15\times10^{-4}$ emu/g atom and $K_{VV} \approx +1.8\%$. In fact, a significant reduction in the orbital coupling constant would help to account for the apparent ineffectiveness of the orbital relaxation mechanism in dilute magnetic alloys as evidenced by the excellent correlation between the magnitudes of the measured negative resonance shifts and the spin-lattice relaxation rates.[10,34] Finally, we note that large orbital susceptibilities appear to be a general property of magnetic impurities in metals. For example, in addition to *Au*V, *Mo*Co, and *W*Co, large temperature-independent contributions to the impurity susceptibility have been identified in the magnetic alloys *Mo*Fe, *Mo*Mn, and *Rh*Mn.[46]

In summary, despite the qualitative nature of the interpretation of our *Mo*Co and *W*Co NMR data it is clear that our results give no convincing indication that nonperturbative spin-polarization effects have an important influence on the magnetization of *isolated* cobalt impurities in either *Mo*Co or *W*Co. Although the possibility of an anomalous *short-range* polarization cannot be rejected entirely, the available data indicate that such effects are not very important. In view of the strong impurity-impurity interaction effects observed in *Mo*Co, it is tempting to speculate that related effects may be responsible for some of the anomalous low-temperature properties of *Cu*Fe. At the very least, the present work suggests that great care must be exercised in attempting to derive meaningful information about the properties of *isolated* magnetic impurities from dilute alloy data. Finally, we remark that the qualitative behavior of the low-temperature nuclear resonances in *Mo*Co and *W*Co is remarkably similar to that in *Au*V despite the very different Kondo temperatures. In particular, the observed relationship between K and T_1 suggests that the independent-particle prediction

$$\left(\sum_q \chi'(q,0,0)\right)^2 \Big/ \sum_{q,q'} \omega_L^1 \chi''(q,q',\omega_L) = (2l+1)(2\pi)^{-1}\hbar\gamma_e^2 \qquad (4.5)$$

characterizes the local spin response to sufficiently weak magnetic fields even in the regime where the s-d model is presumed to be valid. Because of the lack of rigorous theoretical predictions for the low-temperature regime ($T < T_K$) of the magnetic-impurity problem, it unfortunately remains unclear whether Hartree-Fock demagnetization or many-body spin-compensation effects dominate the observed reductions in the effective impurity moments in these alloys as T/T_K approaches zero. It is hoped that further experiments on *Mo*Co and *W*Co, presently in progress, at lower cobalt concentrations and in higher magnetic fields will yield more definitive answers to some of the questions which the present study has left unanswered.

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Application of the Roth Decoupling Scheme to the Kondo Problem*

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A self-consistent treatment of the Kondo problem as described by the s-d exchange model is presented. The treatment is based on the Roth prescription for linearizing the equations of motion for the Green's functions. The result for the t matrix is the same as in the Nagaoka theory. The treatment, however, yields different results for higher-order thermal averages. Some difficulties associated with the Roth scheme are also discussed.

I. INTRODUCTION

The Kondo problem as described by the s-d exchange model has been treated by Nagaoka[1] using the method of decoupled equations of motion for Green's functions. Although the Nagaoka treatment is attractive from the viewpoint that the formalism is simple and familiar, the key approximation is a somewhat arbitrary decoupling procedure. The heuristic justification for the decoupling approximation is that it takes into account the correlation between spins of the impurity and conduction elec-