assumed to be the hydrogen of one hydroxyl group and the oxygen of one water molecule; H(5) and O(8) in the notation of Beevers and Hughes.[6] It was assumed that these atoms were shifted from positions of orthorhombic symmetry on the polarized sublattice only, and the distances they were shifted were calculated from the Na^{23} quadrupole data. Since it now seems clear that both sublattices are polarized, then it must be assumed that these atoms do not lie on positions of orthorhombic symmetry on either of the two sublattices. Thus the observed differences between the quadrupole coupling constants in the ferroelectric phase should be due to shifts of atomic positions on both sublattices. Because of the linear nature of the calculation of the displacements from the quadrupole data, the results previously obtained are still valid as long as the displacements calculated are taken as the sums of the displacements on each of the two sublattices. In view of the nearly symmetric splitting of the quadrupole coupling about the straight line in Fig. 1, it is likely that the displacements are about equal on the two sublattices, and each is about one-half of that quoted in Refs. 3 and 4.

In summary then, the data presented here agrees well with the calculations of Žekš, Shulka, and Blinc, and suggests a reinterpretation of the earlier Na^{23} quadrupole coupling data in Rochelle salt.

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Nuclear Magnetic Resonance of ^{59}Co in Dilute *Au*Co Alloys*

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Measurements of ^{59}Co NMR shifts and spin-relaxation rates in *Au*Co confirm the nonmagnetic character of isolated cobalt impurities in gold. In the temperature range 1.2–4.0 °K, a large positive resonance shift [$K = +(29.2 \pm 0.2)\%$] is observed, indicative of a dominant orbital hyperfine interaction. The absence of a strong temperature dependence of the shift below 300 °K gives evidence for a high spin-fluctuation temperature. Low-temperature measurements of the spin-echo phase-memory time T_2 yield a value $T_1T = 2.7 \pm 0.5$ msec °K for the spin-lattice relaxation time. The results of the present study illustrate the strong influence of orbital degeneracy on the magnetic properties of cobalt impurities in metals.

I. INTRODUCTION

We report here measurements of ^{59}Co nuclear-magnetic-resonance (NMR) shifts and spin-relaxation rates in *Au*Co alloys. The NMR data represent an extension of earlier hyperfine-interaction measurements in this system by Holliday and Weyhmann[1] who applied ^{60}Co nuclear-orientation (NO) techniques to extremely dilute alloys (< 5 ppm) at temperatures below ~0.02 °K and magnetic field strengths above ~20 kOe. These authors observed that the internal magnetic field at the cobalt nucleus exceeds the applied field by a factor of 1.29 ± 0.11. Since their experimental method was insensitive to the sign of the internal field, the results are consistent with either a positive shift of $+(29 \pm 11)\%$ or a negative shift of $-(229 \pm 11)\%$. The present results demonstrate that the shift is positive. We also verify that isolated Co impurities in *Au*Co, despite the large magnitude of the hyperfine-induced resonance shift, are "nonmagnetic," with a spin-fluctuation temperature above 300 °K.

II. EXPERIMENTAL METHODS AND RESULTS

Low-temperature (1.2–4.0 °K) NMR shift and relaxation experiments were carried out with a phase-coherent spin-echo spectrometer operating at 22 MHz; measurements of the resonance shift at higher temperatures were performed with a field-modulated field-swept Varian cw spectrometer, operating at 7.9 MHz, which was used in conjunction with a Fabritek-1074 time-averaging computer for signal-to-noise-ratio enhancement. Alloys containing 0.05-, 0.2-, and 1.0-at.% Co were prepared by arc melting appropriate quantities of the elemental metals.[2] No heat treatment was used following comminution of the samples.

In the temperature range 1.2–4.0 °K the ^{59}Co resonance shift (relative to the reference ratio $\nu_{\rm ref}/H = 1.005$ kHz/Oe)[3] was found to be $+(29.2 \pm 0.2)\%$ independent of temperature and alloy composition. Measurements at 120 and 300 °K gave shifts of $+(26.5 \pm 1.0)\%$. The linewidth, while temperature independent, increased from ~3% (measured between half-amplitude points) in the 0.05-at.% alloy to ~10% in the 1.0-at.% alloy. From the behavior of the spin-echo amplitudes as a function of rf driving field it was possible to attribute the observed signal intensities to $+\frac{1}{2} \leftrightarrow -\frac{1}{2}$ transitions. Hence, the first-order quadrupole broadening is sufficiently large in our samples to make the satellites unobservable. The experimental linewidths are therefore dominated by magnetic hyperfine inhomogeneities. The positive sign of the shift was established by noting the relative rf phase of the spin echo. A negative shift of −229% would have implied sign reversals in the longitudinal internal field, the transverse rf driving field, and the net precessing magnetization. The resulting reversal in the echo phase relative to a ^{59}Co reference was not observed. Moreover, the large magnitude of the negative shift should have yielded much faster nuclear-spin relaxation rates than were observed.

Because of the severe quadrupole broadening it was not possible to achieve sufficient saturation of the longitudinal nuclear magnetization to perform accurate measurements of the spin-lattice relaxation times T_1. The observed recoveries of the magnetization had exceedingly nonexponential time dependences even after long sequences of closely spaced rf pulses.[4] A lower limit for T_1T of 0.7 msec °K was established in the 0.2-at.% sample at 1.2 °K from the long-time behavior of the experimental recovery curves. Unfortunately, because of limited signal-to-noise ratios we were unable to determine the true asymptotic recovery rate. Owing to this complication, the spin-lattice relaxation times were obtained indirectly from measurements of the spin-echo phase-memory times T_2. As shown in Fig. 1, the experimental rates have the form $T_2^{-1} = A + BT$. The intercept A represents a temperature-independent contribution, presumably arising from nuclear–spin-spin interactions, which increases with increasing impurity concentration. The temperature-dependent term B is indicative of relaxation resulting from hyperfine coupling to itinerant electrons. For the case in which only the central transition (i.e., $+\frac{1}{2} \leftrightarrow -\frac{1}{2}$) is excited by the pulsed rf field, and for an assumed isotropic electronic-spin fluctuation spectrum, it is known that[5–10]

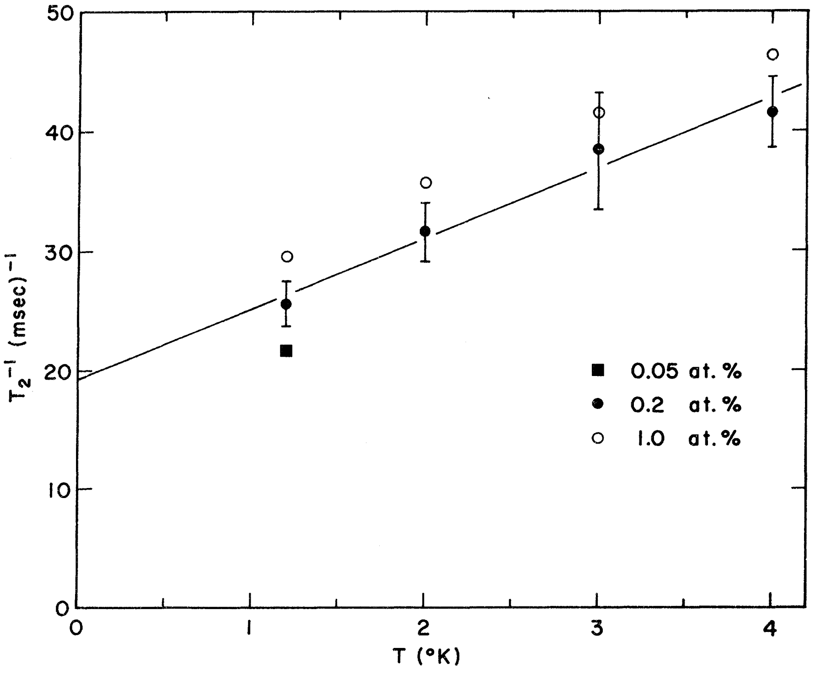

FIG. 1. Temperature dependence of the ^{59}Co spin-echo phase-memory times in *Au*Co.

$$T_1T = (I+\tfrac{1}{2})^2/B \;. \tag{2.1}$$

Our data yielded $B^{-1} = 0.17$ msec °K and, therefore, $T_1T = 2.7$ msec °K (with an estimated experimental uncertainty of $\pm 20\%$).

III. DISCUSSION

The NMR results confirm the nonmagnetic (i.e., localized-spin-fluctuation) character of isolated cobalt impurities in *Au*Co.[11] In particular, the lack of a strong temperature dependence of the resonance shift below room temperature demonstrates that the spin-fluctuation temperature is in excess of 300 °K, in general agreement with a value of ~700 °K inferred by Costa-Ribeiro *et al.* from an analysis of low-temperature electronic[12] and nuclear[11] specific-heat data. The fact that the ^{59}Co resonance shift is independent of impurity concentration, in marked contrast to the behavior of the bulk properties, demonstrates that the NMR signals are associated with relatively isolated cobalt impurities. As in the related case of *Cu*Co,[10,13] near-neighbor cobalt clusters in *Au*Co are believed to be strongly magnetic[11] with low Kondo temperatures and presumably were not observable in our NMR experiments because of excessively large shifts and short nuclear-spin relaxation times.

The positive sign of the ^{59}Co resonance shift is indicative of a dominant orbital hyperfine interaction since the *d*-spin (core-polarization) hyperfine field is characteristically negative. The *d*-orbital hyperfine field for 3*d* ions is generally much larger in magnitude than the *d*-spin hyperfine field, particularly near the end of the 3*d* period.[14] Hence, orbital effects manifest themselves much more strongly in impurity hyperfine interactions than in bulk magnetic properties.[15] In the absence of significant spin-orbit interactions, the *d*-spin and *d*-orbital interactions contribute separately to the shift and spin-lattice relaxation rate

$$K = K_{(d)} + K_{(\mathrm{orb})} \;, \tag{3.1}$$

$$T_1^{-1} = T_{1(d)}^{-1} + T_{1(\mathrm{orb})}^{-1} \;. \tag{3.2}$$

We have ignored the direct *s*-contact interaction because its contribution is expected to be relatively unimportant for most 3*d* impurities. The shifts and relaxation rates may be expressed in the usual manner in terms of the local *d*-spin and *d*-orbital susceptibilities[15]:

$$K_{(i)} = (\mu_B)^{-1} H_{\mathrm{hfs}}^{(i)} \chi_{(i)}^{zz}(0) \;, \tag{3.3}$$

$$T_{1(i)}^{-1} = k_B T(\mu_B)^{-2}\gamma_n^2 (H_{\mathrm{hfs}}^{(i)})^2 \lim_{\omega\to 0}[\mathrm{Im}\chi_{(i)}^{+-}(\omega)/\omega] \;, \tag{3.4}$$

where $H_{\mathrm{hfs}}^{(i)}$ are the appropriate hyperfine fields per Bohr magneton, γ_n is the nuclear gyromagnetic ratio, and the other symbols have their usual meaning. In the localized-spin-fluctuation regime, the susceptibilities may be obtained from the fivefold degenerate Friedel–Anderson model.[16,17] In the random-phase approximation (RPA) one obtains[18,19]

$$\chi_{(d)}^{zz}(0) = 2\rho_{(d)}\mu_B^2(1-\alpha_{(d)})^{-1} \;, \tag{3.5}$$

$$\chi_{(\mathrm{orb})}^{zz}(0) = 4\rho_{(d)}\mu_B^2(1-\alpha_{(\mathrm{orb})})^{-1} \tag{3.6}$$

and

$$\lim_{\omega\to 0}\chi_{(d)}^{+-}(\omega)/\omega = \tfrac{2}{5}\pi\hbar\rho_{(d)}^2\mu_B^2(1-\alpha_{(d)})^{-2} \;, \tag{3.7}$$

$$\lim_{\omega\to 0}\chi_{(\mathrm{orb})}^{+-}(\omega)/\omega = \tfrac{4}{5}\pi\hbar\rho_{(d)}^2\mu_B^2(1-\alpha_{(\mathrm{orb})})^{-2} \;, \tag{3.8}$$

where $\alpha_{(d)}$ and $\alpha_{(\mathrm{orb})}$ are the *d*-spin and *d*-orbital enhancement factors, respectively,

$$\alpha_{(d)} \equiv \tfrac{1}{5}(\overline{U}+4\overline{J})\rho_{(d)} \;, \tag{3.9}$$

$$\alpha_{(\mathrm{orb})} \equiv \tfrac{1}{5}(\overline{U}-\overline{J})\rho_{(d)} \;. \tag{3.10}$$

Here, $\overline{U}$ and $\overline{J}$ are effective intra-atomic Coulomb and Hund's-rule exchange interaction constants, respectively, and $\rho_{(d)}$ is the density of *d* states at the Fermi level for one spin direction. As pointed out previously,[19] $\chi_{(\mathrm{orb})} = 2\chi_{(d)}$ in the zero-enhancement limit (i.e., for $\alpha_{(d)} \approx \alpha_{(\mathrm{orb})} \approx 0$). In view of the large magnitude of the *d*-orbital hyperfine field relative to that of the *d*-spin hyperfine field ($-H_{\mathrm{hfs}}^{(d)} \lesssim 100$ kOe, $H_{\mathrm{hfs}}^{(\mathrm{orb})} \approx 600$ kOe for atomic Co),[14] it follows that the cobalt hyperfine constant will be dominated by the orbital interaction for sufficiently small values of the local enhancement factors. (In fact, the RPA Friedel–Anderson model has been used successfully to account for the positive impurity resonance shifts and rapid spin-lattice relaxation rates in *Cu*Co[10] and *Cu*Ni.[19]) However, since $\overline{U}+4\overline{J}$ is always greater than $\overline{U}-\overline{J}$ (i.e., $\alpha_{(d)} > \alpha_{(\mathrm{orb})}$) one expects the *d*-spin interaction to become dominant very rapidly with increasing $\alpha_{(d)}$. It is not surprising, therefore, that the net hyperfine field of magnetic as well as strongly exchange-enhanced nonmagnetic 3*d* impurities is generally negative in sign.[15] The experimental results for *Au*Co, however, do not follow this pattern since no reasonable choice of parameter values yields as large a positive shift as is observed. For example, a lower limit of 27×10^{-4} emu/g atom is obtained for $\chi_{(\mathrm{orb})}$, according to (3.3), by assuming that the orbital shift is equal to the experimental shift (i.e., $K_{(d)} = 0$) and that $H_{\mathrm{hfs}}^{(\mathrm{orb})}$ is given by the atomic value[14] 599 kOe. The absence of local-moment formation requires that $\alpha_{(d)} < 1$; we may also take $\overline{U}+4\overline{J} = 6$ eV[19,20] and hence conclude that $\rho_{(d)} < 0.83$ eV^{-1}. Using (3.6), this upper bound on $\rho_{(d)}$ implies $\alpha_{(\mathrm{orb})} \gtrsim 0.96$. Thus, according to (3.10), $\overline{U}-\overline{J} > 5.8$ eV, which is unrealistically large when compared to more typical values of 2–3 eV.[19,20] Smaller values of $H_{\mathrm{hfs}}^{(\mathrm{orb})}$, nonzero *d*-

spin contributions to K, and a more realistic value of $\alpha_{(d)}$ would all lead to even larger values of $\bar{U}-\bar{J}$.

The failure of the RPA Friedel–Anderson model, as applied to *Au*Co, can also be demonstrated by a comparison of the resonance shift and spin-lattice relaxation rate. We base this comparison as usual on the local d-spin and d-orbital Korringa relations,[19] which follow directly from (3.3) and (3.10):

$$K^2_{(d)}T_{1(d)}T = 5\mathcal{S} , \tag{3.11}$$

$$K^2_{(\mathrm{orb})}T_{1(\mathrm{orb})}T = 10\mathcal{S} , \tag{3.12}$$

where

$$\mathcal{S} \equiv (\gamma_e/\gamma_n)^2(\hbar/4\pi k_B) . \tag{3.13}$$

Finally, using (3.1) and (3.2), one obtains for the experimental Korringa product

$$K^2T_1T = 10\mathcal{S}(1+\xi)^2/(2+\xi^2) , \tag{3.14}$$

where

$$\xi \equiv K_{(\mathrm{orb})}/K_{(d)} . \tag{3.15}$$

Thus, $K^2T_1T/\mathcal{S}$ can range from 0 to 10, depending on the relative magnitude of $K_{(d)}$ and $K_{(\mathrm{orb})}$. Experimental values of $K^2T_1T/\mathcal{S}$ are shown in Table I for *Au*Co as well as *Cu*Co, *Cu*Ni, and *Au*Ni. It is apparent that the model is applicable to the weakly enhanced alloys *Cu*Co and *Cu*Ni, although the former may represent a marginal case. The more strongly enhanced gold alloys, however, are characterized by $K^2T_1T/\mathcal{S}$ values which fall well above the allowed range. In the case of *Au*Ni, it has been suggested[19] that crystal field splitting of the e_g and t_{2g} orbital levels might be responsible for the large magnitude of $K^2T_1T/\mathcal{S}$. If the d states at the Fermi level have pure e_g character the d-spin and d-orbital Korringa relations assume RPA solutions of $2\mathcal{S}$ and ∞, respectively.[19] The latter result is a direct consequence of the well-known fact that all matrix elements of the orbital angular momentum vanish within the e_g manifold and therefore cannot contribute to nuclear relaxation; any orbital contribution to the impurity susceptibility and resonance shift is then of the Van Vleck type.

TABLE I. Summary of low-temperature (1–4 °K) impurity NMR data for dilute copper and gold alloys. (Parentheses indicate the estimated uncertainty in the preceding digit.)

	K (%)	$\gamma_N^2 T_1 T$ (10^6 sec^{-1} °K Oe^{-2})	$K^2T_1T/\mathcal{S}$
Cu^{59}Co[a]	+5.2(2)	0.80(20)	11
Cu^{61}Ni[b]	+1.28(2)	6.8(7)	6
Au^{59}Co	+29.2(2)	0.11(2)	49
Au^{61}Ni[b]	+2.55(2)	6(2)	21

[a] Reference 10.

[b] Reference 19.

It is likely that the relatively slow impurity spin-lattice relaxation rate in *Au*Co can be attributed to a disproportionally large e_g character at the Fermi level as was done for *Au*Ni. However, in view of the very large magnitude of the *Au*Co impurity resonance shift, it is doubtful that our experimental observations can be rationalized entirely on the basis of cubic crystal field effects. For example, the neglect of spin-orbit coupling is probably not justified in *Au*Co. We also note that the interaction constants $\bar{U}$ and $\bar{J}$ in the Friedel–Anderson model do not satisfy the Slater sum rules; more accurate parametrizations of local electron-electron interactions have been shown[21] to lead to smaller differences between $\alpha_{(d)}$ and $\alpha_{(\mathrm{orb})}$ than indicated in (3.9) and (3.10), respectively.

Although we are unable to offer a quantitative interpretation of our results, several qualitative conclusions concerning the applicability of the RPA Friedel–Anderson model suggest themselves. The model obviously has its greatest validity in the extreme nonmagnetic limit where the great width of the virtual impurity d levels is the dominant feature, correlation effects being relatively unimportant. With decreasing level width (i.e., increasing $\rho_{(d)}$) the local correlations become stronger, and the assumption that spin and orbital effects can be treated independently becomes suspect. This is particularly true when crystal field interactions cannot remove the orbital degeneracy as in the case of divalent cobalt in cubic environments (in contrast to V^{2+}, Cr^{3+}, and Mn^{2+} whose ground states are orbital singlets in fields of cubic symmetry). As the magnetic limit is approached, we may speculate that the correlations on the impurity site take on strong atomic character. In this regime the detailed predictions of the RPA Friedel–Anderson model, such as the spin and orbital Korringa relations, are of questionable significance. However, for orbital-singlet impurities the spin-Korringa relation may continue to be qualitatively correct; the fact that the orbital contribution to the nuclear spin-lattice relaxation rate vanishes in this case [thus invalidating the orbital Korringa relation (3.12)] is of little consequence in the analysis of nuclear resonance data (since the relaxation rate is strongly dominated by the d-spin interaction in this regime). This would account for the apparent success which has been achieved[7] in separating the experimental impurity-resonance shifts of strongly enhanced alloys such as *Al*Cr and *Al*Mn into spin and orbital contributions. The failure of this approach in the case of *Au*Co emphasizes the serious difficulty which orbital degeneracy introduces into the problem of nearly magnetic impurities in metals.

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Statistical Mechanics of the Half-Filled-Band Hubbard Model[*]

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We have calculated thermodynamic properties of the half-filled-band Hubbard model for a ring of $N=4$ atoms. Our results resolve serious discrepancies between similar calculations which have appeared. For weak interactions, a new kind of smooth magnetic transition (nonantiferromagnetic) is found at low temperature. For strong interactions, properties are approximately independent of N when the grand canonical ensemble is used, enabling contact to be made with recent experimental work on N-methyl phenazinium tetracyanoquinodimethan (NMP)(TCNQ); the comparison suggests strongly that the Hubbard model is seriously deficient as a means of description of these experiments.

There has been considerable interest recently[1–3] in the Hubbard model for electrons in a half-filled band. Since exact results are extremely limited, particularly in the intermediate temperature range and for bandwidth b of the order of the Coulomb interaction U, we began a study of exact numerical solutions for small numbers of atoms. Since that time three papers[4–6] have appeared giving results of similar calculations. Their results disagree with each other in several important qualitative respects: in the region of large b/U one group[4] (SP) found one peak in the specific-heat-vs-temperature curve, the other group[5,6] (HM) finding three peaks; for $b/U \simeq 1$, the groups again disagree as to the number of peaks found. (These statements concern the four-atom ring, the only case common to both groups.)

Here we resolve these important theoretical discrepancies. We agree with the number of specific-heat peaks found by HM; however, numerical comparison is not possible because of inconsistencies in their results. We also disagree with their interpretation of these peaks and find instead a new kind of smooth magnetic transition. Further, the extrapolation to large systems as to the existence of the low-temperature peaks for large b/U is shown to be not possible on the basis of the four-atom results in disagreement with HM: whenever one-half the number of atoms is even, we show that there is a low-T peak for large b/U which does not scale with the size of the system. The behavior for small b/U does not appear to be spurious in relation to macroscopic systems, and we therefore carefully examined the susceptibility to compare with recent experimental results.[7] Whereas the previous calculations were made using the canonical ensemble, we have also made calculations in the grand canonical ensemble, as motivated below.

We consider a system of four atoms at the cor-