11, 3535 (1975).
[12]T. Schneidel and E. Stoll, Phys. Rev. B 13, 1216 (1976).
[13]P. A. Fleury, in *Light Scattering in Solids*, edited by M. Balkanski *et al.* (Flammarion, Paris, 1975), p. 747.
[14]Y. Makita, T. Yagi, and I. Tatsuzaki, Phys. Lett. 55A, 437 (1976).
[15]J. D. Axe, S. M. Shapiro, G. Shirane, and T. Riste, in *Anharmonic Lattice, Structural Transition and Melting*, edited by T. Riste (Noordhoff, Leiden, 1974), p. 23.

Evidence for Crystalline Electric Field and Spin-Orbit Splittings for Co Impurities in Au

R. Dupree,* R. E. Walstedt, and W. W. Warren, Jr.
Bell Laboratories, Murray Hill, New Jersey 07974
(Received 22 October 1976; revised manuscript received 2 February 1977)

High-temperature ^{59}Co NMR data are presented for dilute alloys of Co in Au. A four-parameter ionic model, including Kondo condensation effects, is shown to account for the anomalous properties of this system.

Although many cases of 3*d* ions in simple metals can be understood in terms of the Friedel-Anderson model theory,[1-3] ionic structure on a finer scale than the virtual-bound-state width ~ 0.5–1.0 eV is excluded from consideration in this picture. In the conceptual framework developed by Hirst,[4] however, fine-grained ionic structure will survive the mixing interaction V_{kd} if other ionic configurations are well removed in energy. Because of the Kondo effect and other complications, analyses of such cases have been slow in appearing.

In this Letter we present and discuss evidence for the occurrence of ionic structure in the impurity state of dilute Co in Au. New high-temperature NMR data are presented. These, combined with susceptibility[5,6] and low-temperature NMR data[7] from the literature, are then analyzed with an ionic (Co^{2+}) model T_{1g} ground state, split by spin-orbit coupling. The system is further presumed to undergo Kondo condensation. With this picture we can account for all available data in at least semiquantitative fashion, while traditional models[8,9] cannot.[10] To our knowledge this is the first successful analysis of crystal-field and spin-orbit splittings for an orbitally degenerate 3*d* series ground state in a metal. A study of the related orbital singlet case of Co in W has recently appeared.[11]

Susceptibility and specific-heat measurements[5] on *Au*Co alloys show that isolated Co atoms are "magnetic" with an apparent Kondo temperature of 200–300 K. Nuclear orientation[12] and NMR[7] studies revealed the presence of an extremely large, positive Knight shift of 29.2% at 4.2 K. Since *d*-spin core-polarization hyperfine fields are generally negative, we conclude that the hyperfine coupling is dominated by the orbital term.[7] However, the relaxation associated with this shift is much weaker than expected by current models.[7,9,13,14] Studies of concentrated *Au*Co alloys[15] suggest that the *d*-spin hyperfine field is negligibly small in the dilute limit; we shall assume this to be the case throughout.[16]

We have studied the NMR shift and relaxation time of ^{59}Co in this system at temperatures in the vicinity of the melting point. Figure 1 shows the inverse shift K^{-1} vs T for alloys of concen-

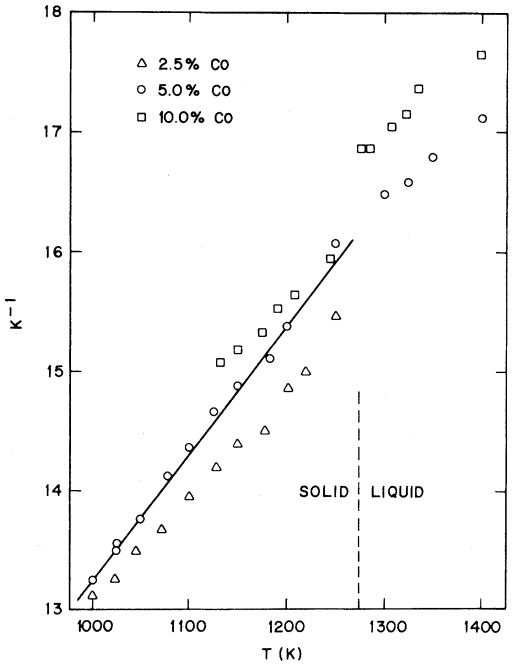

FIG. 1. Inverse of shift K vs T for three concentrations of Co in Au. Solid line shows behavior analyzed in text.

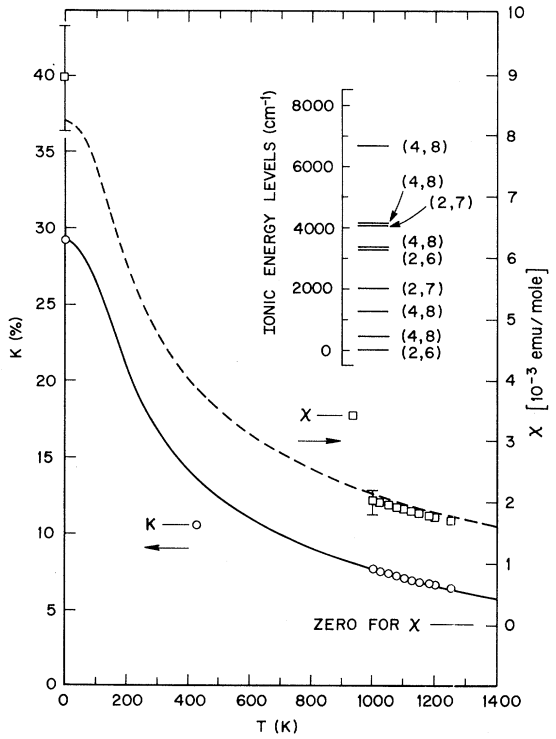

FIG. 2. Susceptibility χ and shift K vs T with model theory fits. Inset shows ionic levels for parameters given in text, with degeneracy m and symmetry Γ_n given as (m,n).

tration 2.5, 5, and 10 at.% Co. The shift has dropped by a factor ~ 4 from its $T = 0$ value and depends only weakly on concentration. It can be fitted to a Curie-Weiss law with $\theta = 250$ K in the solid phase for the 5-at.% alloy (for which θ is experimentally the most reliable). It is important to note that it has not been feasible to observe the ^{59}Co resonance in these alloys between 4.2 and ~ 1000 K.[17]

Data for the impurity susceptibility[6] $\chi(T)$ and shift $K(T)$, plotted in Fig. 2, are seen to vary in close correspondence. The ratio K/χ is smaller by a factor 2–3 than the expected orbital shift coefficient, leading us to conclude that χ is fairly evenly divided between spin and orbital contributions. This inference is in serious conflict with local-enhancement theories, which predict much larger spin than orbital enhancement effects.[8]

Measured high-temperature relaxation times T_2^* (assumed equal to T_1) show a weak concentration dependence. At 1350 K T_2^* extrapolated to zero concentration is $2.4^{+1.0}_{-0.3}$ μsec. This gives $T_1T = 3.2$ msec K as compared with 2.7 msec K at helium temperatures.[7] In contrast, K^2T_1T changes by a factor > 20 over this temperature range, so that a simple Korringa law is not valid.

Our ionic-model theory is based on the Hamiltonian (in standard notation)

$$H = (\Delta/60)(O_4^0 + 5O_4^4) + \lambda \vec{L}\cdot\vec{S} + H_{ex} \quad (1)$$

as applied to the ground $^4F(3d^7)$ term of the Co^{2+} ion. Δ is taken to have its normal, i.e., "point-charge," sign for an fcc lattice,[18] leaving the orbital triplet T_{1g} state lowest. The exchange coupling H_{ex} consists of several terms such as

$$H_{ex} = J_S\vec{S}\cdot\vec{s} + J_L\vec{L}\cdot\vec{l} + J_{LS}\vec{S}\cdot\vec{s}\vec{L}\cdot\vec{l} + \ldots, \quad (2)$$

where $\vec{s}$ and $\vec{l}$ are conduction-electron angular momentum operators. The first two terms of H can be diagonalized straightforwardly, but the treatment of H_{ex} leads into phenomena of enormous complexity. For simplicity we limit our treatment of H_{ex} to (a) Kondo condensation of the moment at low temperatures, (b) polarization of host band and associated scaling of χ, and (c) thermal fluctuations of the local moment. To treat these effects we use available results from model theories.

The spin (χ_S) and orbital (χ_L) susceptibilities are calculated using the first two terms of (1). χ_L and χ_S each consist of Curie-like and Van Vleck–like terms from matrix elements within and between degenerate manifolds, respectively. χ is thereby divided into four components: $\chi_{S,C}$, $\chi_{S,VV}$, $\chi_{L,C}$, and $\chi_{L,VV}$ in an obvious notation. Curie terms are then assumed to vary as $(T + T_K)^{-1}$ apart from exponential occupation factors. For $T \ll T_K$, we include the T^2 region in the Kondo susceptibility,[19,20] thereby reducing $\chi_{S,C}(0)$ and $\chi_{L,C}(0)$ by ~ 13% below their Curie-Weiss projections. The scale factor is applied uniformly to all all susceptibility contributions. The Van Vleck terms are also made to approach $(T + T_K)^{-1}$ behavior as they become Curie-like at high temperatures. As they must also approach $T = 0$ K with zero slope, we let T_K for these terms vary as $T_K'(T) = 2T - T^2/T_K$ for $0 \le T \le T_K$ and $T_K'(T) = T_K$ for $T \ge T_K$. While this is arbitrary, none of our conclusions depends on the shape of this function.

In fitting our model to the data, the parameters λ, Δ, and T_K are adjusted to meet the conditions that (a) the ratio $\chi_L(1000)/\chi_L(0)$, and (b) the Curie-Weiss intercept of $\chi_L(T)$ between 1000 and 1200 K be equal to experimental values derived from $K(T)$, i.e., 0.26 and 250 K, respectively. These requirements can be satisfied with values of λ ranging from – 400 to – 700 K. For $\lambda = -400$ K one has $\Delta > 600$ K, with a rather poorly defined upper limit. For $\lambda = -700$ K one has $\Delta \sim 280$ K.

Over the total range of fits $T_K = 400 \pm 50$ K. A typical fit of $\chi_L(T)$ to the temperature dependence of $K(T)$ is shown in Fig. 2 (solid line), corresponding to $\lambda = -500$ K, $\Delta = 370$ K, and $T_K = 430$ K. In any case λ is found to be strongly enhanced over the atomic value[21] $\lambda = -250$ K. One possible mechanism for this would be an admixture effect between the Co^{2+} $3d$ orbitals and the filled Au $5d$ band, similar to that calculated for *Cu*Cr by Yafet.[22] However, a detailed evaluation of this is beyond the scope of the present work.

The fitting of $\chi_L(T)$ to $K(T)$ yields a value for the orbital shift coefficient $\beta = K/\chi_L$. The parameters of the previous paragraph lead to $\beta = 79$ (emu/mole)$^{-1}$. This is rather smaller than the Co^{2+} value $\beta = 134$ (emu/mole)$^{-1}$ derived from atomic calculations[23] using $\beta = 2\langle r^{-3}\rangle/N_0$, where N_0 is Avogadro's number. A diminished value of β is expected because of conduction-electron screening effects.

The scale factor is estimated by fitting the calculated total susceptibility to the experimental data. In Fig. 2, $\chi(T)$ is seen to fall slightly more rapidly than predicted by the model (dashed line), where the model fit shown corresponds to a mean of scale factors for the high-and low-temperature data. The observed discrepancy may well be experimental error, since the high-and low-temperature χ data are from different sources, and $\chi(0)$ is derived rather indirectly from experiment.[5] We might also note that there is no significant variation in the temperature dependence of $\chi(T)$ over the range of fitting parameters discussed above. The scale factor for $\chi(T)$ is given by $(1 - |J|\rho)$ in simple theories,[3] where ρ is the host-band density of states for one spin direction. For the case shown in Fig. 2 one has $|J\rho| = 0.40$. This is a reasonable value and is in fact the same as that derived for *W*Co from nuclear-relaxation studies.[11]

Consideration of the nuclear spin-lattice relaxation provides additional support for the ionic model. On this picture the low-temperature relaxation rate is expected to be dominated by the fluctuations of the ground-state Kramers doublet, which are nearly the same for spin and orbital hyperfine fields because of the large spin-orbit energy. We calculate T_1 with the dynamic susceptibility derived for an $S = \frac{1}{2}$ Kondo system by Götze and Schlottmann (GS),[20] assuming $\chi_{L,VV}''$ to be of negligible importance for $T \ll T_K$. Only that portion of $\chi_{L,C}$ which is generated by the orbital perturbation is effective for T_1.[24] We denote this term $\chi_{LL,C}$, where $\chi_{L,C} = \chi_{LL,C} + \chi_{LS,C}$. Assuming that $\chi_{LL,C}''(\omega)$ is very nearly Lorentzian,[20] one has $[\chi_{LL,C}''(\omega)/\omega]_{\omega\to 0} = \chi_{LL,C} T_{1e}$, where T_{1e}^{-1} is the width parameter. For a typical case GS find $\hbar/T_{1e} = 1.2 k_B T_K$ at $T \ll T_K$. The fluctuation-dissipation theorem then yields

$$1/T_1 T = 1.6\hbar\gamma_n^2 N_0 \beta^2 \chi_{LL,C}/T_K. \quad (3)$$

Using $\chi_{LL,C}(0)$ from our model in Eq. (3) gives $T_1 T = 4.9$ msec K, which is almost twice the experimental value. Similar estimates are reached equating the shift to $\beta\chi_{LL,C}(0)$ in Korringa relations from the literature[9,13,14] (for $L = 0$, $S = \frac{1}{2}$). In view of this discrepancy, our neglect of $\chi_{L,VV}''$ may not be justified. One may speculate, for example, that $\chi_{L,VV}$ has significant dynamic character at low temperatures because of the comparable values of $k_B T_K$ and the energy splitting of the first excited state.

The high-temperature relaxation rate is similar to that of Eq. (3), where the dynamic part of $\chi_{L,VV}$ is now included in a fashion similar to $\chi_{LL,C}$, and T_{1e} must be given its high-temperature value. Replacing $\chi_{LL,C}$ with $\chi_{LL} = \chi_{LL,C} + \chi_{LL,VV}$ and substituting the calculated value of $\chi_{LL}(1350)$, T_{1e} from the GS[20] results (GS, Fig. 8) and other appropriate parameter values, one finds $T_1 T = 7.6$ msec K, again about twice the measured value $3.2^{+1.3}_{-0.4}$ msec K. In both cases, then, one finds a rough agreement with experiment which is considered satisfactory in view of the approximations made.

In conclusion, a simple four-parameter ionic model is found to give a reasonable account of the impurity state of Co in Au. In particular, the anomalous properties of weak nuclear spin-lattice relaxation and comparable values of spin and orbital susceptibility are well accounted for. The ionic picture for *Au*Co is also supported in that the system satisfies Hirst's configurational stability criterion.[4] We anticipate that the ideas presented will find application to a variety of other impurity systems, among which we mention *Au*V and *Cu*Co. Discussion of these cases is deferred to a future publication.

The authors whish to thank Dr. Y. Yafet for many informative discussions and Dr. J. Gardner for permission to quote his data before publication.

*Present address: Physics Department, University of Warwick, Warwick, England.

[1]J. Friedel, Adv. Phys. 3, 446 (1954), and Nuovo Cimento Suppl. 7, 287 (1958).

[2]P. W. Anderson, Phys. Rev. 124, 41 (1961).
[3]For a general review see *Magnetism*, edited by H. Suhl (Academic, New York, 1973), Vol. V.
[4]L. L. Hirst, Phys. Kondens. Mater. 11, 255 (1970); L. L. Hirst, in *Magnetism and Magnetic Materials —1974*, AIP Conference Proceedings No. 24, edited by C. D. Graham, Jr., G. H. Lauder, and J. J. Rhyne (American Institute of Physics, New York, 1975), p. 11.
[5]E. Boucai, B. Lecoanet, J. Pilon, J. L. Tholence, and R. Tournier, Phys. Rev. B 3, 3834 (1971).
[6]J. Gardner, to be published; see also H. J. Guntherodt and H. A. Meier, Phys. Kondens. Mater. 16, 25 (1973).
[7]A. Narath and D. C. Barham, Phys. Rev. B 7, 2195 (1973).
[8]B. Caroli, P. Lederer, and D. Saint-James, Phys. Rev. Lett. 23, 700 (1969).
[9]L. Dworin and A. Narath, Phys. Rev. Lett. 25, 1287 (1970).
[10]See also the extension of the Anderson model developed by Malmström and C. Blomberg, J. Phys. F 5, 1197 (1975).
[11]A. Narath, Phys. Rev. B 13, 3724 (1976).
[12]R. J. Holliday and W. Weyhmann, Phys. Rev. Lett. 25, 243 (1970).
[13]L. Dworin, Phys. Rev. Lett. 26, 1372 (1971).
[14]H. Shiba, Prog. Theor. Phys. 54, 967 (1975).
[15]R. Dupree and W. W. Warren, Jr., to be published.
[16]Even a substantial d-spin hyperfine field would have only a minor effect on our results.
[17]Shift results reported in Ref. 7 at 120 and 300 K have subsequently been identified as spurious; further efforts to observe the ^{59}Co NMR in this range of temperature have proved fruitless. A. Narath, private communication.
[18]We note that the complementary case $\underline{Au}\,V^{2+}(d^3)$ must have the opposite sign of Δ. From the contrast in behavior between these systems [see A. Narath and A. C. Gossard, Phys. Rev. 183, 391 (1969)] it is clear that the sign taken for Δ is correct.
[19]K. D. Schotte and U. Schotte, Phys. Rev. B 4, 2228 (1971).
[20]W. Götze and P. Schlottmann, J. Low Temp. Phys. 16, 87 (1974).
[21]G. Andersson, Acta Chem. Scand. 10, 623 (1956).
[22]Y. Yafet, J. Phys. Chem. Solids 30, 1957 (1969).
[23]A. Freeman and R. Watson, in *Magnetism*, edited by G. Rado and H. Suhl (Academic, New York, 1965), Vol. IIA.
[24]Analysis of a similar case is given by R. E. Walstedt and A. Narath, Phys. Rev. B 6, 4118 (1972).

COMMENTS

Exponent Inequalities at the Roughening Transition

Robert H. Swendsen*
Institut für Festkörperforschung der Kernforschungsanlage Jülich, D-517 Jülich, Germany
(Received 30 July 1976)

The exponents describing the divergence of various measures of the width of an interface between two phases in an Ising ferromagnet at the roughening transition are shown to satisfy a set of rigorous inequalities.

In this Letter, I derive a set of inequalities for the roughening transition in an interface between two phases in an Ising ferromagnet.[1] The roughening transition is characterized by the divergence of various measures of the interface width at a temperature, T_R, below the bulk critical temperature, T_c, and is of great interest in the theory of crystal growth.[1,2] The inequalities that I present are useful in checking calculations of interface properties and, in particular, show that the published values of the roughening exponents obtained from low-temperature expansions are not self-consistent.[3,4]

I consider a three-dimensional (3D) Ising ferromagnet with (not necessarily isotropic) nearest-neighbor exchange. A 2D interface perpendicular to the z axis is imposed by some appropriate boundary conditions (antiperiodic in the z direction, for example) and the concentration of up spins in the nth layer (x-y plane) is denoted by $c_n \in [0, 1]$. For sufficiently low temperatures, the interface is localized[5,6] and the layer magnetization, $2c_n - 1$, takes on positive values on one side of the interface and negative values on the other. One can number the layers so that $c_n > \frac{1}{2}$ for $n \leq 0$ and $c_n < \frac{1}{2}$ for $n \geq 1$. Far from the interface, the magnetization takes on its bulk value, $\sigma = c_{-\infty} - c_{\infty}$.

We are primarily interested in the measures of the interface width given by the absolute moments

$$\langle |n|^k \rangle = \sum_{n=-\infty}^{\infty} |n|^k (c_n - c_{n+1}). \quad (1)$$