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Ionic Model for Cr, Mn, and Fe Impurities in Cu

D. C. Abbas,[(a)] T. J. Aton,[(b)] and C. P. Slichter
Materials Research Laboratory and Department of Physics, University of Illinois at Urbana–Champaign, Urbana, Illinois 61801

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We report studies of the temperature dependence of the Knight shift of Cu atoms near to Cr atoms in dilute *Cu*Cr alloys. Comparison with *Cu*Mn and *Cu*Fe leads us to propose electronic structures for these important systems. We confirm the general picture of Hirst: The atoms have integral numbers of $3d$ electrons and obey Russell-Sanders coupling, but the sign of the crystal field is opposite to that of Hirst, and Fe has seven rather than six $3d$ electrons.

We report NMR studies of the temperature dependence of the Knight shift of Cu atoms near to Cr atoms in dilute *Cu*Cr alloys. The results, together with those for *Cu*Mn and *Cu*Fe, leads to a detailed picture of the electronic structure of these important systems which also accounts for the magnetic susceptibility.

Differences in a fundamental description of the $3d$ atom are at issure here. Hirst argues a single configuration $3d^n$ describes the atom, the number of $3d$ electrons being integral. There are well-defined orbital and spin quantum numbers L and S given by Hund's rules. The Friedel-Anderson picture, on the other hand, permits nonintegral numbers of d electrons analogous to band theories of ferromagnetism, and as usually employed does not lead to Hund's rules.

Deductions about Co in metals have been made by Narath[1] and by Dupree, Walstedt, and Warren[2] who studied the Co Knight shift and spin-lattice relaxation time. Both found that Co acts much like a Co^{2+} $3d^7$ (^4F) ion in an insulator, thus supporting the Hirst picture. Our results add Cr, Mn, and Fe to Co as $3d$ atoms which obey the Hirst picture.

In the Hirst picture[3] the orbital and spin angular moment of the magnetic atom couple to those of the conduction electron through an interaction which in general form is written

$$H_{\text{mix}} = \sum_{\substack{k,m,\sigma,\\ k',m',\sigma'}} I_{kk'} a_{m\sigma}{}^{\dagger} a_{m'\sigma'} c_{k'm'\sigma'}{}^{\dagger} c_{km\sigma}, \tag{1}$$

where $a_{m\sigma}{}^{\dagger}$ creates an impurity electron, $c_{km\sigma}{}^{\dagger}$ creates a conduction electron with a wave vector of magnitude k, and m and σ specify the z component of orbital and spin angular momenta, respectively. $I_{kk'}$ gives the strength of the interaction. The Fermi contact interaction H_{F} couples the conduction electrons to the neighboring Cu nuclear spins and together with H_{mix} produces an extra Knight shift, ΔK. We find,[4] to a good approximation,

$$\Delta K/K = g(\vec{r})\chi^S(T), \tag{2}$$

where $\chi^S(T)$ is the spin susceptibility of the impurity. $g(\vec{r})$, which gives the spatial dependence, is independent of T. Thus measurement of ΔK enables one to deduce the temperature dependence of $\chi^S(T)$.

For *Cu*Cr we have followed the temperature variation of ΔK from 8.0 to 334 K for two neighbor shells and from 8.0 to 278 K for a third shell (Fig. 1). For *Cu*Fe[5] and *Cu*Mn[6] $\Delta K/K$ obeys a Curie-Weiss law; a plot of $K/\Delta K$ is a straight

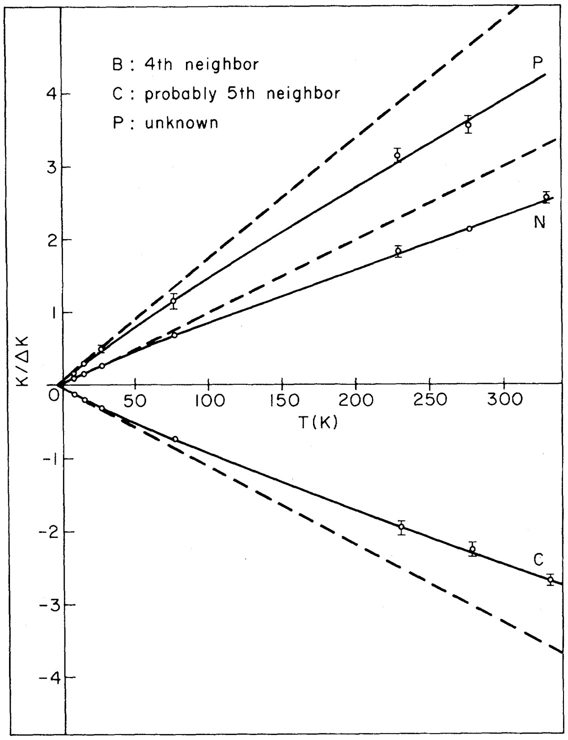

FIG. 1. A plot of the *Cu*Cr satellite data, $K/\Delta K$ vs T. The dashed lines represent a Curie-Weiss law fit to the low-temperature data. The solid lines are the fit to the model described in the text.

line similar to the dashed lines in Fig. 1. Although the data of Fig. 1 clearly deviate from a Curie-Weiss law, all three shells exhibit the *same* temperature dependence: $\Delta K_i = A_i f(T)$ for the ith satellite, where $f(T)$ is the same for all three satellites, and is very nearly the sum of a Curie-Weiss and a temperature-independent term. The fact that the same $f(T)$ works for three satellites shows that, like the Curie-Weiss term, the temperature-independent term also arises from H_F.

A temperature-independent susceptibility arises from the admixture of excited states into a degenerate ground manifold of states via the Zeeman interaction. If the magnetic atom has no spin-orbit coupling, the spin portions of the Hamiltonian may be solved separately and the temperature-independent spin susceptibility vanishes. Therefore, the data indicate that spin-orbit coupling must be included for Cr in contrast to Mn and Fe.

Spin-orbit coupling can be included in either the Anderson or Hirst models. The former gives a temperature-independent χ^s of order

$$\chi^s \simeq \lambda \mu_B^2/W^2, \tag{3}$$

where μ_B is the Bohr magneton, λ the one-electron spin-orbit coupling parameter, and W the width of the d-electron scattering resonance (a substantial fraction of an eV). Such a result is too small to account for the Cr result, and does not explain the large experimental difference between Cr and Fe which, since they should possess approximately four and six $3d$ electrons, respectively, should have spin-orbit effects roughly comparable in magnitude but opposite in sign.

We find we cannot explain the difference between Cr and Fe without a crystalline electric field. We do so readily in the Hirst model along lines he has suggested.

If the ground state is described by a single Hirst state with effective orbital and spin angular momenta $\vec{L}$ and $\vec{S}$, coupled to form an effective total angular momentum $\vec{J}$, the Zeeman coupling admixes states of different $\vec{J}$ but same $\vec{L}$ and $\vec{S}$ to contribute a temperature-independent χ^s of order

$$\chi^s \simeq \mu_B^2/|\lambda|. \tag{4}$$

If the ground-state orbital angular momentum is quenched but there is a spin-orbit multiplet of energy Δ higher due to the crystal field, there is a temperature-independent χ^s of order

$$\chi^s \simeq -\mu_B^2\lambda/\Delta^2$$

which should be smaller than Eq. (4) for reasonable crystal fields.

Hirst[7] suggests that Cr is a Cr^{++}, $3d^4$ configuration[8] split by an attractive crystal field to make the ground state a nonmagnetic E-orbital doublet. (Attractive means it is energetically favorable for a $3d$ wave function to point towards a neighbor.) $\chi^s(T)$ follows Eq. (5). He suggests that Fe is an Fe^{++}, $3d^6$ configuration split by the crystal field to give a T_2 triplet with an orbital magnetic moment. The spin-orbit coupling adds a term like Eq. (4) to χ^s. Such an assignment gives *Cu*Fe a larger temperature-independent contribution to χ^s than *Cu*Cr whereas the opposite is true and the sign of the temperature-independent contribution to the Cr χ^s [Eq. (5)] has the wrong sign. Detailed calculations verify these statements. If, however, we change the sign of the crystal field,[9] Cr corresponds to Eq. (4), Fe to Eq. (5), and we can explain the data.

We have solved the spin Hamiltonian for Cr with the repulsive sign of the crystal field. We allow for thermal population of the excited spin-orbit multiplets since λ for the free Cr ion (58 cm^{-1})[10] is about 80 K. We treat the Kondo effect by replacing T with $T+T_K$ in formulas for χ_s. The results are the solid curves in Fig. 1. The best fit gives a Kondo temperature of 2.9 ± 1.0 K. In solids, both the orbital g factor and λ are usually reduced from their free-atom values.[10] We find $\lambda = 48 \pm 32$ cm^{-1}, a reduction factor 0.8 ± 0.5, and an orbital g factor of 0.84 ± 0.19. The lack of precision in the spin-orbit parameter results from the strong interdependence of the parameters in obtaining a best fit.

The impurity magnetic susceptibility can be calculated from the assumed ground state but must be corrected for the antiferromagnetic exchange polarization of the conduction electrons, which also determines the Kondo temperature. From T_K, we get about a 10% susceptibility correction for *Cu*Cr.

Vochten, Labro, and Vynckier[11] have recently reported a bulk susceptibility study of *Cu*Cr at temperatures from 1.5 to 300 K. They fit their data from 300 K down to about 12 K with the sum of a Curie-Weiss term and a temperature-independent term with a Weiss temperature of 3.4 ± 0.3 K which agrees with our value. They point out strong anomalies in their data below 12 K which we lack space to discuss. Perhaps one should include additional effects such as a crystal-field splitting of the ground states or a Jahn-Teller effect. Their data indicate a high-temperature magnetic moment of $(3.7 \pm 0.4)\mu_B$ which agrees with the $(3.4 \pm 0.4)\mu_B$ that we calculate from our model after reduction due to H_{mix}. [Vochten, Labro, and Vynckier apply a correction to the concentration, which we feel should be omitted, to obtain a moment of $(3.99 \pm 0.04)\mu_B$.] We believe, therefore, that a simple Hirst configuration accounts well for *Cu*Cr.

The conventional Hirst picture of Mn as an Mn^{++}, $3d^5$ configuration with $L=0$ and $S=\frac{5}{2}$ is unaffected by the change of sign of crystal field. No spin-orbit effects are expected, in keeping with experiment,[6,12] and the magnetic moment, corrected for the negative exchange polarization, is $4.8\mu_B$ compared with $(4.9 \pm 0.3)\mu_B$ observed in experiment.[13] Again, a single Hirst configuration works.

With the repulsive crystal field, and Fe^{++}, $3d^6$ configuration gives a susceptibility 70% too large. An Fe^{+} $3d^7$ A_2-symmetry ground state yields good agreement with experiment, yielding temperature-independent contributions to orbital and spin susceptibilities. Comparing the ratio of the temperature-independent and temperature-dependent terms of the bulk susceptibility with the composite data assembled in Ref. 12 and assuming the spin-orbit parameter and orbital momentum are both reduced to about 80% of their free-atomic values, as for *Cu*Cr, we find the first excited crystal-field state lies 1850 cm^{-1} above the ground state, and predict that ΔK should show about a 2% deviation from a Curie-Weiss law at room temperature. Though ΔK can be well fitted without a temperature-independent contribution to the splittings,[5] inclusion of the small temperature-independent term improves the fit. The effective low-temperature moment including the correction for H_{mix} yields a low-temperature effective moment of $3.6\mu_B$ compared with $(3.54 \pm 0.08)\mu_B$ observed in experiment.[14] For this case, too, a single Hirst configuration gives a good account of experiment.

The configurations Cr ($3d^4$), Mn ($3d^5$), and Fe ($3d^7$) indicate a jump of two in the number of d electrons going from Mn to Fe such as Cohen[15] also finds is needed to fit the spatial form of the ΔK data. Such a jump, predicted by Hirst[16] between Ni and Cu, gives particularly strong support to the ionic picture.

The hyperfine fields calculated at the magnetic atoms are also reasonable.

Hirst based his original assignments of configurations and attractive sign of the crystal field on the pioneering observations by Monod and Schultz[17] (MS) of conduction-electron resonance by spin transmission (TESR) for *Cu*Cr and the lack of such observation for *Cu*Fe. They interpret their data using the Hasegawa equations, along lines used to interpret *Cu*Mn,[18] with Cr having a g value of nearly 2. Our picture, on the other hand, makes $g=1$.

Work subsequent to theirs suggests several points. (i) Anomalies in magnetic susceptibility[11] indicate *Cu*Cr behaves differently for $T<12$ K than for $T>12$ K. (ii) Our data are all above 8 K, the TESR all below 20 K; so we may not be comparing the same regime. (iii) If there is a low-T crystal splitting, the Hasegawa equations would need modification. (iv) Unlike *Cu*Mn, a direct ESR of Cr at $g=2$ has never been found. (v) As intimated by Monod and Schultz[17] the TESR data do not require $g=2$, but could result from an impurity which scatters conduction-electron spins and produces a Weiss molecular field since experimentally both linewidth and g shift are proportional to Cr concentration.

We believe there remain enough difficulties in comparing our data with those from TESR that our model may yet be found to be compatible with the TESR data.

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(a)Present address: Research Laboratories, Eastman Kodak Company, Kodak Park, Bldg. 81, Rochester, N. Y. 14650.

(b)Present address: Department of Physics, University of Virginia, McCormick Road, Charlottesville, Va. 22901.

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