Theory Relating NMR Satellite Data to the Structure of Iron-Group Impurities in Copper

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We report model calculations of NMR satellite spectra for Cr, Mn, and Fe atoms in Cu which provide, for the first time, a tractable method for relating the experimentally observed Knight shifts to the structure of the magnetic atoms. Based on a three-parameter one-electron screened potential with exchange, the model is also consistent with bulk susceptibility and high-temperature resistivity measurements. We determine the position and widths of the conduction-electron scattering resonances, and the number of 3*d* electrons on the magnetic atoms.

The theoretical understanding of the electronic structure of the 3*d* elements in nonmagnetic metal hosts remains one of the major unsolved problems of magnetism. At one extreme is the Friedel-Anderson model,[1] which, like a band theory of ferromagnetism, permits nonintegral numbers of *d* electrons. At the other extreme is the Hirst picture,[2] which says that the atoms are similar in many ways to ions in insulators, with an integral number of 3*d* electrons, and well-defined orbital and spin quantum numbers L and S obeying Hund's rules.

Determination of the electronic structure of these systems has largely eluded conventional experimental techniques [ESR and ENDOR (electron-nuclear double-spin resonance)] which have been so useful when the host is an insulator. Ho However, NMR studies of the Co nucleus in Mo and W by Narath[3] and in Au by Dupree, Walstedt, and Warren[4] have shown that in both cases Co acts much like a Co^{2+} ion. A largely unexploited set of data is the measurements of Knight shifts of Cu nuclei which are near neighbors to the various 3*d* atoms in Cu, so-called "satellite" resonances.[5] Since these Knight shifts arise from the spin-dependent scattering of conduction electrons by the magnetic atom, it is evident that they contain substantial information about the magnetic atom. Extensive new measurements of the host NMR for Cr, Mn, and Fe in copper single crystals[6] have recently made it possible to identify the crystallographic position of the nuclei giving rise to a number of the observed satellites, but heretofore little progress has been made in developing a workable theoretical approach to extract conclusions from the data.

In this Letter we describe a simple model which provides a tractable method for relating experimentally observed Knight shifts to the structure of the magnetic atom. We deduce the positions and widths of Friedel-Anderson–like scattering resonances, and determine the number of 3*d* electrons to be nearly integer, 4.2 for Cr, 4.9 for Mn, and 7.0 for Fe. In this way we demonstrate the intimate connection of the satellite data to electronic properties of the impurity.

The unique feature of our calculation is a one-electron potential sufficiently simple that the parameters can be varied to obtain a fit to the data. Specifically, we solve numerically a scattering model, based on a screened atomic-like potential with exchange to represent the magnetic impurity, for electrons throughout a spherical "host-metal" conduction band. Integration of the radial Schrödinger equation gives the scattering phase shifts versus energy, and we find an up- and down-spin scattering resonance similar to the Hartree-Fock solution of the Anderson model.[1] However, our approach works readily across the iron group in contrast to the pioneering work of Jena and Geldart[7] who use the Anderson model directly but whose approach yields a tractable form only for nearly empty or nearly full *d*-electron spin subshells.[8] Our model also includes the scattering deep within the band which gives an important contribution to the spin density at the near neighbors. We do not include the lattice potential. Holzwarth[9] treats the latter in detail and, although her theory in its present form deals only with scattering at the Fermi surface, as she points out extension of her methods could provide a suitable framework for treating such effects.

The potential is taken to a constant (zero) for distance r outside a Wigner-Seitz radius, $r_c = 2.67$ bohr, corresponding to the bottom of the conduction band. For $r < r_c$ the potential is taken to be

$$V(r) = [V_A(r) + C \pm C_{\mathrm{exch}}]e^{-\alpha r}, \qquad (1)$$

where $V_A(r)$ is the atomic potential for the free atom given by Herman and Skillman.[10,11] C gives the displacement of this potential relative to the bottom of the band. Since $V_A(r)$ includes an average spin-independent Slater-exchange potential, C_{exch} explicitly denotes the spin-dependent d-wave interaction due to the partially filled d levels of the impurity (± for up and down spin, respectively). The parameter α allows for screening within the core region itself.

The two kinds of screening represented by C and α give enough freedom in determining $V(r)$ that d-wave scattering "resonances" can be generated at any given position in the band, with any given width, as a result of conduction electron tunneling into a potential well whose transmission characteristics and depth are determined by the two parameters. α is found to be consistent with Thomas-Fermi screening contributed by one electron, lying in the range 0–0.1. In general, slightly different values of C and α would apply to the s- and p-wave scattering.

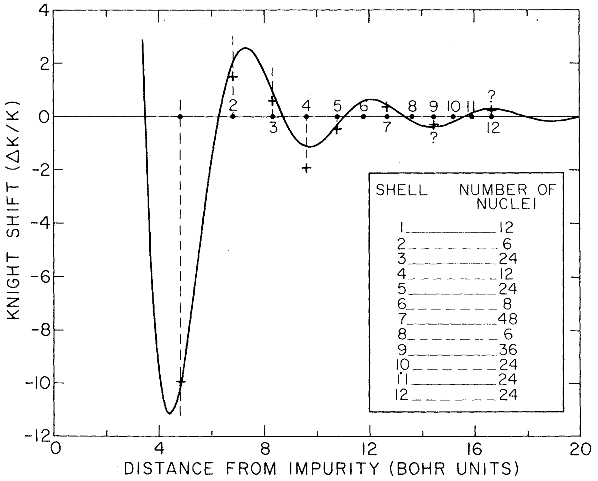
Once the potential has been parametrized, phase shifts are calculated numerically and the Knight shifts, $\Delta K/K$, at the neighboring copper atoms are obtained from[12]

$$\frac{\Delta K}{K}=\frac{\chi_{\text{imp}}(T)}{\chi_s^e}\,\frac{2\pi}{[\delta_{2\uparrow}(k_{\text{F}})-\delta_{2\downarrow}(k_{\text{F}})]}\sum\nolimits_\sigma m_0\int\rho_1(W_k)\,dW_k\,f(W_k,T)$$
$$\times\{[n_2^2(kr)-j_2^2(kr)]\sin^2\delta_{2\sigma}(k)-2n_2(kr)j_2(kr)\sin\delta_{2\sigma}(k)\cos\delta_{2\sigma}(k)]\} \qquad (2)$$

in the notation of Ref. 12. Expressing the satellite Knight shifts as ratios to the pure-metal Knight shift, K, allows one to use free-electron wave functions neglecting the enhancement that comes from orthogonalization of these wave functions to the copper core states. An especially interesting feature of the model is that it enables us to determine the number of d electrons on the magnetic atom. Since we know the wave function in the core region for each k, a properly normalized integral over the band of the square of the core functions gives us the charge density as a function of r. Having used the free-atom potential, the radial dependence of the charge density closely resembles that of the free atom, allowing us to determine in a straightforward way the number of d electrons associated with the impurity *as distinct from* the total d-wave screening.

The system *Cu*Mn provided an illustration. The three parameters of the model are constrained to produce the observed spin of 2 determined by bulk susceptibility measurements[13,14] and varied to obtain a best fit to the Knight-shift data (Fig. 1). The corresponding d-wave density of states is shown in Fig. 2 and clearly displays scattering resonances for up- and down-spin electrons. Figure 3 compares the d-wave charge density given by the model in the impurity region with that to five atomic Mn d electrons.[15] This allows us to assign 4.9 d electrons to the Mn atom. Since the Friedel sum rule produces a total d-wave screening of 5.5 d electrons, this implies a charge of about 0.6 d electrons in the screening cloud outside the atom. Uncertainties in experimental quantities and the spread of parameters obtainable in using different fitting criteria yield an uncertainty ± 0.2 electrons in these results. Phase shifts at ϵ_{F} give a high-temperature resistivity value of 2.1 $\mu\Omega$ cm/at.% versus the experimental value of 2.76 $\mu\Omega$ cm/at.%.[16]

Similar calculations for the systems *Cu*Cr and *Cu*Fe, using spin values of 1.5 and 1.25, respectively,[17,18] give reasonable agreement to the



SHELL	NUMBER OF NUCLEI
1	12
2	6
3	24
4	12
5	24
6	8
7	48
8	6
9	36
10	24
11	24
12	24

FIG. 1. *Cu*Mn Knight shifts, $\Delta K/K$, vs distance from impurity: experiment and theory. Positions of the first twelve nearest-neighbor shells are indicated. Staellites at the fifth and seventh neighbors are assigned on the basis of intensity and those shown at the ninth and twelfth are *not* identified experimentally. The table giving number of nuclei for each shell may explain why certain neighbor shells are not observed. Parameters used in the model are $C = 0.9664$ Ry, $C_{\text{exch}} = 0.1788$ Ry, and $\alpha = +0.05$.

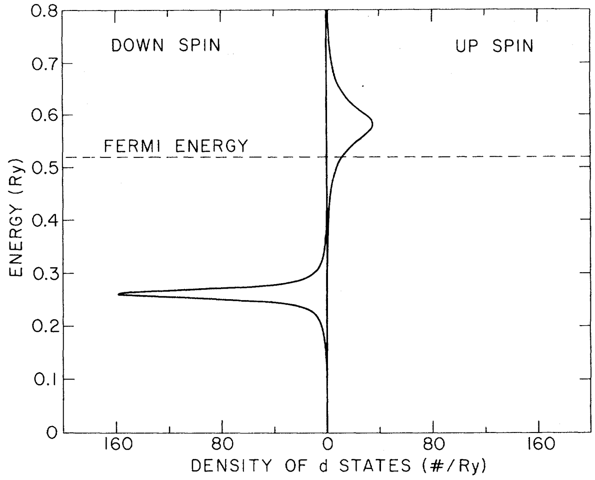


FIG. 2. *Cu*Mn density of *d* states vs energy above the bottom of the conduction band for up and down spins. Positions, shapes, and widths of resonances are determined entirely from integration of the Schrödinger equation. Thus in this model the resonances for up and down spins have different widths.

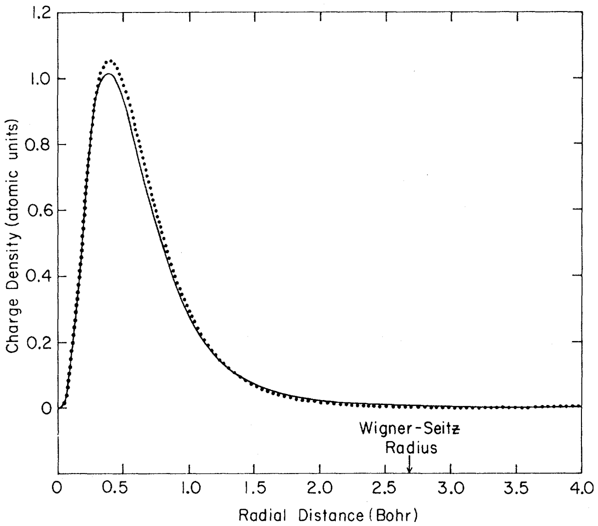


FIG. 3. Total (angular averaged) *d*-wave charge density in core region of magnetic atom vs radial distance as given by model for *Cu*Mn (solid line) compared to five Mn 3*d* electrons obtained from Hartree-Fock wave functions of the free atom (dotted line).

Knight shifts and high-temperature resistivity data.[19] The charge density yields 4.2 ± 0.3 and 7.0 ± 0.2 electrons for the impurity species, respectively, in agreement with recent findings by Abbas by configurational arguments.[20] The integral number of *d* electrons and change of two *d* electrons from Mn to Fe provides strong support to Hirst's concept[2] that the iron-group atoms behave much the same in a metal as they do in insulators.

In addition to the isotropic Knight shift produced by the Fermi contact interaction, the single-crystal studies have also determined the anisotropic "pseudodipolar" component at three neighbors to *Cu*Mr and *Cu*Cr and two neighbors to *Cu*Fe.[6] This interaction can be calculated from our model wave functions with no additional adjustable parameters and thus gives a valuable *independent* experimental check on these results. In most cases we account for both the correct sign and magnitude to within a factor of 2 of the axial component of the pseudodipolar tensor (the only exception occurs at the third neighbor of *Cu*Fe).

Despite its success and simplicity, our model omits two physical effects which, as the NMR data show, are important: (1) The nonuniform part of the lattice potential,[21] and (2) the Hund's-rule coupling within the magnetic atom. We believe that our calculations provide the clear demonstration that more sophisticated calculational efforts will be justified by the present state of experimental data and that satellite NMR is a uniquely valuable tool for study of structure of magnetic atoms in metals.

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Phys. Rev. 181, 662 (1969), based on the interpolation formula of Jena and Geldart (Ref. 7) is incorrect due to a sign error in Eq. (27). With the correct sign, no reasonable fit can be obtained either for *Cu*Fe or the other alloys. A full discussion of this matter will appear at a later date.

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[14] The susceptibility-measured spin includes the exchange-coupled polarization of the extended conduction-electron wave functions and it is this *total* S that is reflected in the scattering phase shifts.

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[19] 6.5 $\mu\Omega$ cm/at.% calculated versus 5.5 $\mu\Omega$ cm/at.% measured for *Cu*Cr; 9.2 $\mu\Omega$ cm/at.% calculated versus 8.7 $\mu\Omega$ cm/at.% measured for *Cu*Fe.

[20] D. Abbas, Ph.D. thesis, University of Illinois, 1977 (unpublished).

[21] The existence of a nonaxial pseudodipolar interaction has suggested the importance of including a crystal field in those calculations. We obtain a nonaxial tensor by including a crystal-field parameter in $V(r)$, but the asymmetries are at most a few percent, much smaller than is found experimentally in *Cu*Mn and *Cu*Fe.