

Localized Magnetic Moments in Metals

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A simple model is used to obtain information about localized magnetic moments in metals from Mössbauer (or nuclear magnetic resonance) experiments. The formulation emphasizes the explicit dependence of the hyperfine field on the spin S' of the Fe atom and shows why the temperature dependence of the hyperfine field follows a Brillouin function of the total localized spin S (with $S \neq S'$). The moment of Fe atoms in dilute concentrations of Pd, Rh, and Mo are determined and the apparent contradiction between Mössbauer and susceptibility measurements for Rh and Mo is discussed.

LARGE magnetic moments associated with Fe atoms dissolved in nonmagnetic $4d$ metals have been extensively studied by means of susceptibility measurements¹. [At the Pd end of the series, the moments are found to be large, i.e., $\sim 9\text{--}12 \mu_B$ (Bohr magnetons).] Theoretical interpretations have emphasized the localized nature of these moments.^{1,2} Recently reported Mössbauer measurements by Craig *et al.*³ on dilute solid solutions of Fe⁵⁷ in Pd have confirmed the magnitude of the moment reported earlier¹ and have demonstrated that the moment associated with the Fe impurity acts, at low temperatures, like an isolated magnetic moment in an external magnetic field. However, for the cases of Fe in Rh and Fe in Mo, Craig *et al.* find no hyperfine splitting due to a localized moment in apparent contradiction with the susceptibility experiments which give a moment of 2.2 and 2.1 μ_B , respectively. The magnitude of the moment on the Fe atoms themselves has not been measured and, hence, the magnitude and spatial distribution of the magnetization of the localized states has not been determined.

This note is concerned with these aspects of the problem of the observed localized moments in metals. Starting with a basically simple idea, we show that measurements of the hyperfine field (e.g., by means of Mössbauer or nuclear magnetic resonance methods) can give this information—whereas, susceptibility measurements cannot—and that the nature of the coupling between the spin on the Fe atom and the polarization of its surrounding can be inferred. In addition, the temperature dependence of the hyperfine field is derived and is shown to agree with experiment. However, in contrast with earlier work,³ our formulation emphasizes the explicit dependence of the hyperfine field H_{int} on the spin S' of the Fe atom and demonstrates why H_{int} vs temperature follows a Brillouin function of the total localized spin S (with $S \neq S'$).

We assume, as is generally done,⁴ that the internal field is proportional to the time-average value of the z

component of the spin on the Fe atom,

$$H_{\text{int}} = A \langle S'_z \rangle. \quad (1)$$

This relationship is valid for the Fermi Hamiltonian for a free atom with $L=0$ [in which case $A \propto |\psi(0)|^2$], and appears to hold, at least qualitatively, for a number of cases in metals and alloys.⁴ While an exact visualization of the origin of A is not necessary, it is perhaps reasonable to assume that, for the case at hand, A arises mostly from the polarization of the s electrons in the core and conduction bands by the localized (3d) spin density on the iron atom. Since contributions to H_{int} from the polarized host atoms are also proportional to S' these may also be included in A .

For paramagnets, thermal relaxation times are so fast, relative to the γ -ray lifetime, that in the absence of an externally applied field H the average value of the spin $\langle S'_z \rangle$ is zero and, hence, no hyperfine splitting is observed in a Mössbauer measurement. When $H \neq 0$, one has the usual case of the alignment of the spins of the paramagnetic atoms and a thermal average of S'_z which is given by

$$\langle S'_z \rangle_T = S' B_{S'}(x). \quad (2)$$

Here, $B_{S'}(x)$ is the Brillouin function for spin S' , the parameter x is $g\mu_B S' H / kT$, and g is the gyromagnetic ratio (which we take to be 2 in what follows). For small x , i.e., large T or very small H , $B_{S'}(x)$ given by $(S'+1)x/3S'$. The field at the nucleus, H_n , as a function of temperature is then

$$H_n = H + H_{\text{int}} = H + A \langle S'_z \rangle_T = H + A S' B_{S'}(x). \quad (3)$$

Since H is an additive constant, it is convenient to subtract H from the observed H_n and to discuss the remainder, i.e., H_{int} . (Since $H_n < 0$ Craig *et al.*³ actually “added” H to H_n to obtain H_{int} .) For “ordinary” paramagnets, i.e., those for which the spin which gives rise to the hyperfine field and the spin which gives rise to the susceptibility are one and the same, Eq. (3) has previously been used successfully to explain⁵ the observations⁶ with the Mössbauer effect.

⁴ See, for example, R. E. Watson and A. J. Freeman, Phys. Rev. **123**, 2027 (1961) and, more recently, a number of articles in *The Mössbauer Effect*, edited by D. M. J. Compton and A. H. Schoen (John Wiley & Sons, Inc., New York, 1962).

⁵ Given independently by G. B. Benedek and A. J. Freeman (unpublished).

⁶ N. Blum and L. Grodzins, Bull. Am. Phys. Soc. **7**, 39 (1962).

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¹ A. M. Clogston, B. T. Matthias, M. Peter, H. J. Williams, E. Corenzwit, and R. C. Sherwood, Phys. Rev. **125**, 541 (1962) and references therein to earlier work.

² P. W. Anderson, Phys. Rev. **124**, 41 (1961); P. A. Wolff, *ibid.* **124**, 1030 (1961); and A. M. Clogston, *ibid.* **125**, 439 (1962).

³ P. P. Craig, D. E. Nagle, W. A. Steyert, and R. D. Taylor, Phys. Rev. Letters **9**, 12 (1962).

Consider now a spin S' rigidly coupled to its polarized surroundings, the system forming a resultant spin S . (In general, this coupling can be ferromagnetic or antiferromagnetic in nature, but we shall assume in what follows that the coupling is ferromagnetic.) Suppose we take a collection of such spins S to form a paramagnetic system. In an external field, $\langle S_z \rangle_T$ is of course given by a Brillouin function for the spin S . Because of the rigid coupling, S' "follows" S , and so $\langle S'_z \rangle_T$ is now given by

$$\langle S'_z \rangle_T / S' = \langle S_z \rangle_T / S = B_S(x), \quad (4)$$

instead of by Eq. (2), which holds only for a system of free spins S' . Therefore, we have that

$$H_{\text{int}} = A \langle S'_z \rangle_T = A S' B_S(x), \quad (5)$$

which, in the region of small x , is given by

$$H_{\text{int}} = A S' \left[\frac{(S+1)}{3k} g \mu_B \frac{H}{T} \right]. \quad (6)$$

Equations (5) and (6) display: (1) the physical origin of H_{int} through S' and A and (2) the temperature dependence of H_{int} through the usual susceptibility factor (which is concerned with the total spin S).

It follows from Eq. (5) that the saturation value of H_{int} is given by

$$H_{\text{sat}} = A S' \quad (7)$$

and so we may, therefore, write

$$\frac{H_{\text{int}}}{H_{\text{sat}}} = \frac{(S+1)}{3k} g \mu_B \frac{H}{T}. \quad (8)$$

Equation (8) is the phenomenological expression used by Craig *et al.* to fit their data for Pd in the linear region and to determine S and, hence, μ . (They find that $\mu \approx 12.6 \mu_B$ and $S \approx 13/2$.) Hence, we may take the agreement of our derived expression with experiment to indicate that our simple model is consistent with experience.

The above formulation allows us to determine S' provided we can obtain the value of A . Mössbauer measurements⁷ at low temperatures ($T=4^\circ\text{K}$) for Fe^{57} in a widely varying range of Co concentration (3

to 100%) in Co-Pd alloys give a value for A of ≈ -300 kG (which is also the value for Fe^{57} in metallic iron). Using this value of A as a reasonable approximation for the case of Fe^{57} in Pd and the observed H_{sat} value of -295 kG, we find that $S' \approx 1$ and $\mu \approx 2 \mu_B$.

Equation (6) also allows us to reconcile the apparent contradiction between the Mössbauer and susceptibility measurements for Rh and Mo referred to earlier. This expression shows that although the total spin S may be large (as determined by susceptibility measurements), the hyperfine field will be small if S' is small. Since A depends on environment⁴ it will, in general, not have the same value as estimated above; this effect on H_{int} is probably smaller than the variation in S' . We believe that the negative Mössbauer results for these cases are attributable to a very small moment ($\mu < 0.3 \mu_B$) on the iron atoms yielding an H_{int} which is unresolved in the range of H/T at which the measurements were made.

It is not yet clear how the induced moment, about $10.6 \mu_B$ per Fe atom, is distributed among the Pd host atoms. Theoretical calculations are, of course, exceedingly difficult to do.² A much more likely approach is to do either NMR or Mössbauer measurements on the host nuclide, or neutron diffraction measurements on the less dilute (i.e., 1% Fe) alloys. The simplest and most naive model, which assumes a polarization of only the nearest-neighbor Pd atoms, gives a moment of approximately $0.9 \mu_B$ and a spin of $\frac{1}{2}$ per Pd atom. The inclusion of second nearest neighbors, which is more realistic, reduces the induced Pd moments to $0.5 \mu_B$ per Pd atom. It is surprising that even this crude an estimate can yield a not too unreasonable result.

The rigid coupling, which we may now take as an experimental datum, arises from the direct and indirect interactions between d electrons on different atoms. However, detailed many-electron theoretical calculations involving these interactions are about as difficult to do for these systems as they are for the cases of ferromagnets and antiferromagnets.⁸

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⁸ See P. W. Anderson, reference 2; A. J. Freeman and R. E. Watson, *Phys. Rev.* **124**, 1439 (1961); and C. Herring, *Rev. Mod. Phys.* **34**, 631 (1962) and references therein for a discussion of the complexities of a *priori* determination of exchange interactions.

⁷ D. E. Nagle, P. P. Craig, P. Barrett, D. R. F. Cochran, C. E. Olsen, and R. D. Taylor, *Phys. Rev.* **125**, 490 (1962).