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Hyperfine fields at nonmagnetic elements in ferromagnetic metal hosts

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It is shown that there is strong experimental evidence that the hyperfine fields at nonmagnetic solute atoms in ferromagnetic metal hosts depend on the atomic volume of the impurities. Charge-perturbation models are discussed and shown to be in disagreement with the hyperfine-field data.

Upon observing the variation of the hyperfine fields (hff) at impurities in Fe, Co, and Ni, it was proposed[1] that the hff at nonmagnetic impurities, H_Z, consists of two terms, (i) a negative contribution H_{C}^Z due to s-like conduction-electron polarization (sCEP) from all neighboring host moments and (ii) a positive contribution H_v^Z which occurs because of the volume misfit of the impurity atom. The value of H_{C}^{Fe}, for Fe as the host, can be obtained either from measurements of the sCEP in dilute Fe alloys[2] or from the hff value measured at small impurity atoms. Both methods give $H_Z^{\text{Fe}} \simeq -150$ kG. The H_{C}^Z values can then be obtained from H_{C}^{Fe} by simply scaling by the atomic hyperfine coupling constants A_Z (or equivalently the Knight shifts). Thus $H_{\text{C}}^Z = A_Z H_{\text{C}}^{\text{Fe}}/A_{\text{Fe}}$. Since Fe has about one $4s$-like conduction electron, $H_{\text{C}}^{\text{Fe}}/A_{\text{Fe}} = p_{\text{Fe}}$ can be interpreted as the net sCEP at a nonmagnetic impurity due to neighboring Fe atoms. Thus for Fe as the host p_{Fe} is a constant "background" contribution independent of the impurity atom. We will see later why it is unaffected by the valence of the impurity atom.

The origin of the H_v^Z term is as follows: Impurity atoms which possess two valence s electrons in the atomic state are assumed to contribute a conduction-electron density equivalent of 1 to the conduction band of Fe and a density equivalent of 1 (along with the other valence p or d electrons of the atom) remains in the vicinity of the impurity, screening its excess charge. This screening s-like electron picks up a polarization p_v from the surrounding Fe atoms which is proportional to its volume misfit in the Fe lattice. The H_v^Z contribution is then given by

$$H_v^Z = p_v A_Z = \alpha (V_Z - V_0) A_Z, \tag{1}$$

where V_Z is taken as the atomic volume of the impurity atom in its elemental solid state and α and V_0 are constants for a given host. For the alkali metals, which have only one s electron, and the rare gases, where the s electrons are tightly bound, we expect the H_v^Z term to be less positive than indicated by Eq. (1). The hff at an impurity atom is thus given by

$$H_Z = A_Z H_{\text{C}}^{\text{Fe}}/A_{\text{Fe}} + \alpha (V_Z - V_0) A_Z \tag{2a}$$

or

$$H_Z/A_Z = p_{\text{Fe}} + \alpha (V_Z - V_0), \tag{2b}$$

as in Eq. (1) of the previous comment.[3]

In Fig. 1 we show the values of H_Z/A_Z plotted as a function of Z. The open circles indicate cases where the sign is not measured. The ◇ sign is used for impurities that develop a moment (this moment is usually in the same direction as that of Fe and then gives a negative contribution to the hff; in a few cases, e.g., V, it is opposite to the Fe moments so that the core contribution is positive) and are not of interest here. We show the value of $p_{\text{Fe}} = H_{\text{C}}^{\text{Fe}}/A_{\text{Fe}}$ as the dashed line, so the polarization p_v is simply given by using this value as the origin, as indicated by the scale on the right-hand side. On the top of Fig. 1 we indicate the excess valency ΔZ between the impurity atom and the Fe host. Fe is assumed, as usual, to have a valency of 1. As has been noted many times,[5] H_Z/A_Z has a very regular behavior. In particular, the hff values of a given sd series decrease from large positive values to negative values as ΔZ increases, while the sp-series elements show the opposite behavior, i.e., their hff values rise from negative to positive values as ΔZ increases. Since the hff in Fe is predominately due to s electrons, whose behavior should not depend on whether the other valence electrons are p or d electrons, it appears obvious that the predominant behavior of the hff at impurity atoms does not depend on ΔZ.

In Fig. 2 we show the variation of the atomic volume V_Z as a function of Z. We see that the behaviors of p_v and V_Z are strikingly similar, even on linear plots. Only three elements, K, Ca, and possibly Sc, do not vary in a similar manner on the two graphs and these do not fit any model. On the other hand, 35 elements do vary similarly (22 in the sp series and 13 in the sd series). A more quantitative fit to Eq. (2) is made in Ref. 1 and is, in general, very good. Naturally, all of the elements do not fit Eq. (2) exactly; there are a number of reasons for this: (i) As mentioned earlier, the alkali metals and rare earths are expected to be less positive than indicated by Eq.

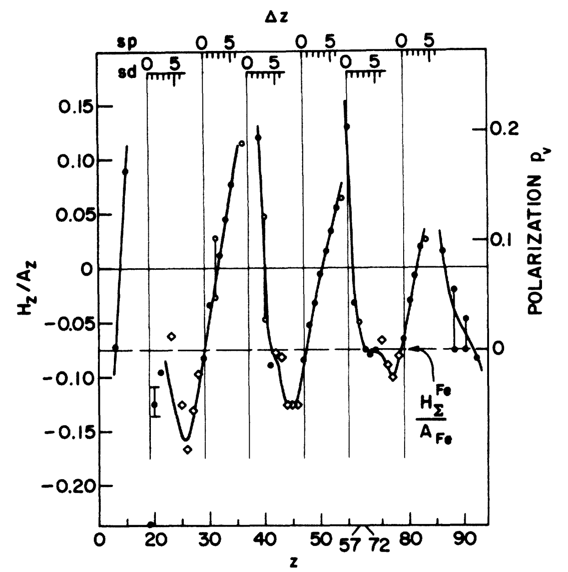

FIG. 1. H_Z/A_Z as a function of Z. ●: sign measured; ○: sign not measured; ◊: impurity has a moment. The H_Z values used here are from Refs. 1 and 4.

(1); (ii) some of the measurements are not very accurate or reproducible, and in a few cases the atoms may possibly be in interstitial rather than substitutional sites; (iii) for many elements the A_Z values are only approximate and calculated from the Fermi-Segre formulas as discussed in Ref. 5; these values may be in error, especially at low Z; and (iv) since this simple model encompasses only average behavior, detailed atomic structure may cause quite large deviations from average behavior.

There are undoubtedly effects other than atomic misfit that affect the hff; however, at this stage we are looking for the predominant effect. There do seem to be systematic differences between Figs. 1 and 2 that could be reduced with additional assumptions, e.g., if the estimated A_Z values increase less rapidly with Z or, alternately, if V_0 were taken not as constant but as increasing linearly with Z. However, for the sake of simplicity we have taken the simplest model possible.

Thus it seems that the strikingly similar variations in Figs. 1 and 2 are strong experimental evidence that there is a positive contribution to the hff which is proportional to the volume misfit of the impurity atom. Even more subtle features, such as the rapid decrease of the hff values for the *sd* series and the slower increase for the *sp* series, are evident on both graphs.

Discussing whether or not a particular impurity has a positive or negative hff, as in the previous Comment, is irrelevant. The meaningful question is whether a positive contribution remains after subtraction of the negative H_Σ^Z term. We see that within the accuracy with which H_Σ^{Fe}/A_{Fe} is known (~10%) this is so in all cases except for K and Ca. However, as seen from Fig. 1, the H_Z/A_Z values of K and Ca are anomalous; they lie far below any other nonmagnetic impurities and K is below even the magnetic impurities that are known to have large negative core contributions. The K and Ca fields were measured[7] using the perturbed angular correlation technique, which is known to sometimes give stopping sites other than substitutional sites.

Other models have been proposed which attribute the hff variations in the *sp* series to the charge perturbations caused by the impurity atoms. A phenomenological model was proposed by Daniel and Friedel[8] which had a hff variation as a function of ΔZ which was similar to that of the *sp* series. It, of course, could not fit the nonmagnetic *sd* elements. This model assumed that the charge-perturbation potential V_0 of the impurity had a spin dependence $\pm\epsilon$ caused by exchange interactions, i.e., in a ferromagnetic host, V_0 became $V_0^\pm = V_0 \pm \epsilon$. The magnitude of ϵ was shown to be proportional to the net polarization of the conduction band. Since this is very small in Fe,[1,9] because of the competition between the positively polarizing *s-d* direct exchange interaction and the negatively polarizing *s-d* hybridization interaction, it is easy to see why the charge-dependent contribution might be very small, as indicated by the hff data.

Another model, by Caroli and Blandin,[10] can be identified with the *s-d* hybridization contribution to H_Σ^{Fe}. A later model of Blandin and Campbell[11]

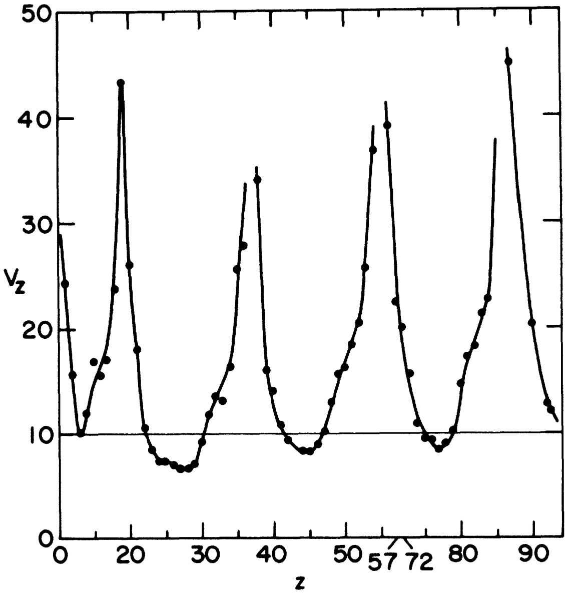

FIG. 2. Atomic volume (at. wt./density) as a function of Z. Values are taken from Ref. 6.

strangely does not contain the usual $\sin(\delta_0^+ - \delta_0^-)$ factor which is proportional to the spin polarization $Z_0^+ - Z_0^-$ of the s conduction electrons ($\propto \epsilon$ in the Daniel-Friedel model), where $\delta_0^\pm$ are s-wave phase shifts due to the modified charge-perturbation potentials $V_0^\pm$. This factor would lead to very little contribution of the charge-perturbation term as in the Daniel-Friedel model. Without this factor, this model indicates that the total H_Σ^{Fe} is modulated by only a phase factor $2\delta_0$, where δ_0 is the phase shift due to the pure charge-perturbation potential V_0. Thus it gives hff's varying as $\sum_i \cos(2k_F r_i + 2\delta_0)/r_i^3$, i.e., a sinusoidal variation is expected, or at least a leveling off of the hff as ΔZ increases. Assuming $\delta_0 = \delta_1$, as in Ref. 11, and assuming the most favorable condition to make the hff cross zero as late as possible while still increasing continually with ΔZ (i.e., $2k_F r_i \sim \pi$), this gives hff variation which crosses zero around $\Delta Z = 2$ and saturates around $\Delta Z = 4$. Using the phase shifts obtained by Blatt[12] from the residual resistivity of Cu and Ag alloys we find (again for the most favorable case) that for fourth-row impurities (Cu–Se) the hff goes through zero at $\Delta Z \simeq 1.5$ and starts flattening out around $\Delta Z = 3$. For the fifth-row impurities the hff goes through zero at around $\Delta Z = 2$ and starts flattening out around between $\Delta Z = 3–4$. This is in disagreement with the observed hff values, which go through zero at $\Delta Z \simeq 3$ for rows four and five and show essentially no tendency to flatten out through $\Delta Z = 6$. Using the phase shifts of Kohn and Vosko[13] gives even worse agreement with experiment; the hff values go through zero at about $\Delta Z = 1$ and saturate at $\Delta Z = 2$. However, this set of phase shifts is unreal, since it corresponds to more than two s-valence electrons per impurity atom. As seen in Fig. 1 the data shows no tendency to a sinusoidal shape but is quite linear between $\Delta Z = 0–6$. Thus this model not only fails in explaining the sd-series data but also does not give the variation seen in the sp series.

I therefore disagree with the statement in the preceding Comment that it has been shown that the CEP contribution to the impurity hff depends strongly on the impurity charge.

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