

## Hyperfine fields on nonmagnetic elements in ferromagnetic metal hosts

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It is suggested that there is no experimental evidence that the hyperfine fields on nonmagnetic elements in ferromagnetic metal hosts depend simply on the atomic volumes of the elements.

It is now well established experimentally that the hyperfine fields at nonmagnetic impurities in a transition-metal ferromagnetic host change from negative for impurities at the beginning of an  $s$ - $p$  series to positive at the end of an  $s$ - $p$  series. It is also known that elements at the end of an  $s$ - $p$  series have large atomic volumes. In a series of articles,<sup>1-3</sup> it has been suggested that the former is a direct consequence of the latter—that the positive hyperfine fields observed are due to the excess atomic volume of the corresponding impurities. Thus it is suggested phenomenologically that the hyperfine field on a nonmagnetic impurity contains two terms; one is a negative conduction-electron polarization contribution and the other a positive “misfit” term proportional to  $V_i - V_0$ , where  $V_i$  is the atomic volume of the impurity and  $V_0$  is a constant approximately equal to the atomic volume of the host. To obtain an estimate for the hyperfine field of each element an expression is proposed of the form

$$H_i/A_i = p + \alpha(V_i - V_0), \quad (1)$$

where  $A_i$  is the atomic hyperfine coupling constant of the element considered,  $p$  is a constant representing the conduction-electron polarization, and  $\alpha$  is another constant.  $p$  and  $\alpha$  are taken to be independent of the impurity.

In fact, even calculations using simple models<sup>4,5</sup> show that the conduction-electron polarization contribution to an impurity hyperfine field must depend strongly on the impurity charge, and that the impurity site polarization can change sign because of this effect alone. It is certainly incorrect to assume a constant  $p$  independent of impurity valence in the real physical situation which is undoubtedly more complicated than the models. Nevertheless, we will consider Eq. (1) as it stands; it is a completely phenomenological relation and thus can be tested only on purely empirical grounds.

As all of the physical properties of the elements vary regularly across the periodic table, virtually any two parameters chosen at random will correlate to some extent if values for all elements are

plotted together. The overall correlation between hyperfine field and atomic volume is rather poor (the correlation between the boiling point of the element and the hyperfine field is better) unless the data are represented on logarithmic plots in such a way that factors of the order of 10 tend to escape notice.

In order to test seriously the assertion that Eq. (1) is valid, it is not enough to compare hyperfine fields at elements having similar volumes and similar positions in the periodic table; we must compare hyperfine fields on elements having *similar* atomic volumes but *dissimilar* positions in the periodic table. If Eq. (1) is really valid, the hyperfine fields (normalized by the atomic constants  $A_i$ ) should be similar; if, on the other hand, the hyperfine field is not a function of atomic volume but depends on atomic structure in a different

TABLE I. Atomic volumes and hyperfine fields at impurity elements in Fe, showing selected examples of sets of elements having similar atomic volumes but different positions in the periodic table.  $H_i$ : experimental hyperfine field in Fe.  $A_i$ : estimated atomic coupling constant (Ref. 3). The values of atomic volume for P correspond to different allotropic forms; in metallic compounds the P atomic volume is always small, and P reduces the lattice constant of Fe solid solutions.

| Element | Atomic volume<br>(at. wt./density) | $H_i$<br>(kOe) | Reference | $10^2 (H_i/A_i)$ |
|---------|------------------------------------|----------------|-----------|------------------|
| Al      | 10.0                               | -55            | 6         | -6               |
| P       | 11.5-17                            | +133           | 7, 8      | +6               |
| As      | 13.1                               | +344           | 8, 9      | +4               |
| Cd      | 13.1                               | -366           | 10        | -5               |
| Se      | 16.5                               | +690           | 11        | +7               |
| In      | 15.7                               | -295           | 12        | -3               |
| K       | 45.3                               | -150           | 13        | -27              |
| Ca      | 29.9                               | -100           | 14        | -11              |
| Ba      | 39                                 | -85            | 15        | -3               |
| Sc      | 18                                 | -135           | 7         | -15              |
| Lu      | 17.8                               | -575           | 16        | -10              |
| Te      | 20.5                               | +676           | 17        | +3.5             |
| I       | 25.7                               | +1144          | 18        | +6               |
| Xe      | 37                                 | (+)1510        | 19        | +5               |

way, then the hyperfine fields can be expected to be dissimilar. In Table I, we give results for such sets of elements in solution in Fe.

(i) Al and P both have small atomic volumes, but the former has a strong negative field while the latter has a strong positive field. Similarly, the pairs of elements As and Cd, Se and In have very similar atomic volumes, but in both cases the former has a strong positive field and the latter a strong negative field.

(ii) Elements at the beginning of the transition series (K, Ca, Ba, Sc, Lu) have large atomic volumes and strong negative hyperfine fields,<sup>20</sup> while the elements at the end of the *s-p* series (Te, I, Xe) also have large atomic volumes, but have strong positive hyperfine fields.

There are thus numerous examples of cases where Eq. (1) does not represent even an approximate empirical guide to the behavior of the hyperfine fields. Small atoms can have positive fields, and large atoms can have negative fields. Any rough correlation that can be observed between the hyperfine fields and atomic volumes for some elements seems to stem only from the fact that both properties vary with position in the periodic table. Where it is possible to isolate change of volume from change of valence, there are enough counter-

examples to provide strong evidence against a simple cause and effect relation of the form of Eq. (1).

In fact, it is possible to summarize the observed trends in nonmagnetic impurity hyperfine fields in Fe and Ni without making any reference whatsoever to atomic volume. Elements with less than about 3.5 *s-p* electrons (including nonmagnetic transition elements K, Ca, Ba, Sc, Hf, and Lu) have negative fields while impurities with more than 3.5 *s-p* electrons have positive fields. For the entire periodic table, the solitary exception to this rule is Cs in Fe.<sup>21</sup> This regularity is not at all what would be expected from Eq. (1), but a plausible explanation of the behavior can be obtained from models where the emphasis is placed on the effect of the conduction electron screening at the impurity site.

We conclude that the "volume misfit" analysis fails to provide a phenomenological rationalization of known hyperfine fields. We do not suggest that direct overlap is never an important contribution to hyperfine fields at nonmagnetic sites; it may possibly dominate for halogen or rare-gas impurities in Fe or Ni. However, there seems to be no justification for any simple scaling of this term with "volume misfit" or for ignoring charges in the local conduction-electron polarization with impurity valence.

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<sup>20</sup>The only exceptions are Cs in Fe (Ref. 21) and an early measurement on Y in Fe (Ref. 22); as the fields on Y in Y-Fe ferromagnetic compounds are negative (Ref. 23) and the fields on Sc (Ref. 7) and Lu (Ref. 16) (lying above and below Y in the periodic table) are definitely negative, it seems that FeY should be re-investigated. The field on Y in Ni is negative (Ref. 24).

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