Large increase of magnetic hyperfine fields of 5*sp*-shell impurities in ferromagnets after vacancy trapping

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Vacancy trapping by ^{119}Sb impurities implanted in Ni, Co, and Fe gives rise to large changes of the magnetic hyperfine fields B_{hf} of the ^{119}Sn daughter nuclei. We have measured the following values for the normal substitutional and the vacancy-associated impurity hyperfine fields (in T):

	Sn*Ni*	Sn*Co* (fcc)	Sn*Fe*
$B_{hf}^{(subs)}$	+2.06(2)	−1.89(2)	−8.60(2)
$B_{hf}^{(vac)}$	+4.7−7.1	+7.3−14.5	−2.8(2)

In all cases, the vacancies associated with the impurities could be "frozen in" up to high temperatures by decoration with post-implanted helium atoms. The substantial increase of the fields can be understood in terms of the conduction-electron polarization model of Blandin and Campbell.

The magnetic hyperfine fields of dilute impurities in ferromagnetic metals and alloys have been systematically studied, both experimentally and theoretically, over a number of years. One of the characteristic features of the behavior of the field as a function of the impurity atomic number is a change of sign of the field for *sp*-shell impurities near the middle of the shell. For the case of the 5*sp*-shell impurities in Ni, Co, and Fe this is shown in Fig. 1. This phenomenon has been interpreted in two different ways: in terms of conduction-electron polarization (CEP)[1–3] and in terms of overlap polarization.[4] Our data show that large changes of the fields are caused by vacancy trapping at Cd impurities in Ni and at Sn impurities in Ni, Co, and Fe and that these can be interpreted by the CEP model of Blandin and Campbell.[1] For the first time we have seen that vacancy association can lead to a large *increase* of the absolute value of the impurity hyperfine field, namely, for Sn in Ni and Co. For other cases studied so far, in particular those of Te, I, and Xe impurities in Fe and Ni, a *decrease* of the field after vacancy trapping was always found.[5]

In our investigations of vacancy association of impurities implanted in various metals we have recently observed marked effects of the "decoration" of these vacancies by post-implanted helium: helium decorated vacancies are trapped at impurities to a much higher degree and they remain "frozen" there to a much higher temperature than undecorated vacancies.[6] This phenomenon has facilitated the observation of changes of the magnetic hyperfine field caused by vacancy trapping.

The experimental method used in our investigations is the following: sources of ^{119}Sb are prepared by the reaction ^{121}Sb$(p,3n)^{119m}$Te$\rightarrow^{119}$Sb, using 45-MeV protons from the Groningen cyclotron. The 38-h ^{119}Sb activity, chemically separated from 4.7-d ^{119m}Te, is introduced into our isotope separator and sources are implanted to strengths of 20–100 μCi.

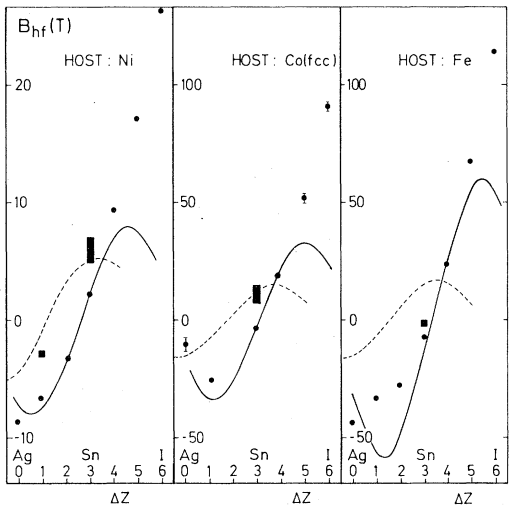

FIG. 1. Magnetic hyperfine fields vs impurity-host valence difference ΔZ for 5*sp* shell impurities in Ni, Co, and Fe hosts. Circles: substitutional impurities. Rectangles: vacancy associated impurities. Full lines: calculated dependence of field on ΔZ for substitutional impurities; phase and amplitude adjusted to experimental data (see text). Broken lines: calculated behavior of field for vacancy associated impurities.

The Sb-ion energy is 120 keV and the total implanted Sb dose $(0.5-2)\times10^{13}$ atom/cm^2. The sources can be post-implanted with 10-keV He ions to a dose of 2×10^{16} atom/cm^2. The helium-ion energy is chosen such that the maximum helium concentration occurs at the same depth as the maximum Sb concentration. Mössbauer spectra of the 23.9-keV γ transition of ^{119}Sn, following the electron capture decay of ^{119}Sb have been taken at 4.2 K, using SnO_2 or $BaSnO_3$ absorbers. All sources were subjected to annealing sequences in order to bring out the vacancy-associated sites. Helium decoration often allows us to bring almost 100% of the impurities in the high-field vacancy-associated site. The following results have been obtained:

1. *^{119}SbNi sources without helium*

The ^{119}Sn spectrum before annealing mainly shows one magnetically split component, with $B_{hf}^{(1)} = +2.06(2)$ T [see Fig. 2(a)]. Upon annealing, a second component[2] with an average hyperfine field $B_{hf}^{(2)} = +7.1(3)$ T, and Lorentzian spread of ±2.5 T grows in the spectrum. It vanishes when annealing above 540 K. A typical two-component spectrum is shown in Fig. 2(b).

2. *^{119}SbNi(He) sources (post-implanted with 2×10^{16} atom/cm^2 of helium)*

The Mössbauer spectra of these sources undergo a drastic change only when annealed above 600 K, due to extensive trapping of helium decorated vacancies by the Sb impurities. In Fig. 2(c) a case is shown where almost 100% of the spectrum corresponds to a site with a field $B_{hf}^{(2)} = 6.2(1)$ T, after a 30-min anneal at 820 K. Different sources yield different field values, from 4.7 to 6.2 T, indicating the sensitivity of the field for differences in defect configuration. The original spectrum, with $B_{hf}^{(1)} = 2.06$ T, is fully restored only after annealing to at least 1400 K [Fig. 2(d)].

A measurement with a ^{119}Sb*Ni*(He) source in an external field of 2.5 T shows an increased splitting of both the low- and the high-field component, proving that both fields are positive.

3. *^{119}SbFe(He) sources*

Spectra recorded before annealing can be fitted with one magnetically split component, yielding the absolute value $|B_{hf}^{(1)}| = 8.50(4)$ T for the tin impurity field. From other measurements,[7] this field is known to be negative. After annealing at temperatures between 800 and 900 K, this field "collapses" to a much lower absolute value. Combination with a measurement in an external field shows that this field

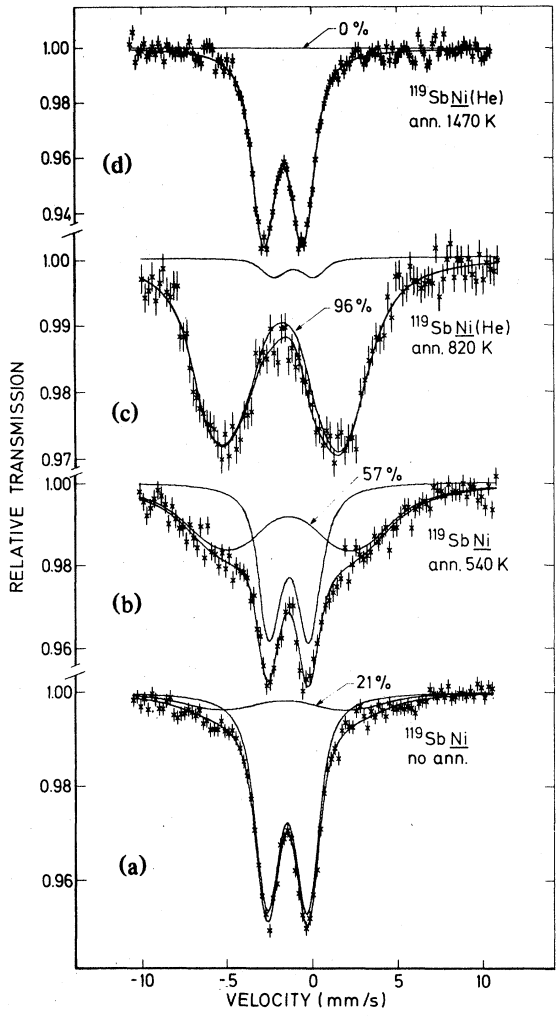

FIG. 2. Mössbauer spectra obtained with sources of ^{119}Sb implanted in nickel and a $BaSnO_3$ absorber, both at 4.2 K. (a) Unannealed ^{119}Sb*Ni* source, (b) ^{119}Sb*Ni* source annealed at 540 K, (c) ^{119}Sb*Ni*(He) source annealed at 820 K and (d) ^{119}Sb*Ni*(He) source annealed at 1470 K.

is negative: $B_{hf}^{(2)} = -2.8(6)$ T. It resumes its original value only after annealing at 1300 K.

4. *^{119}SbCo and ^{119}SbCo(He) sources*

The spectra of these sources are more complex, due to the presence of the hcp and the fcc phase in cobalt at room temperature [Fig. 3(a)]. We find from a two-component fit to the spectrum of an unannealed ^{119}Sb*Co* source $|B_{hf}^{(hcp)}| = 5.72(7)$ T and $|B_{hf}^{(fcc)}| = 1.89(2)$ T. From other measurements[8] these fields are known to be negative. After annealing a helium post-implanted source to 820 K a widely split spectrum appears [Fig. 3(b)]. A measurement in an external field proves that 80–90% of this spec-

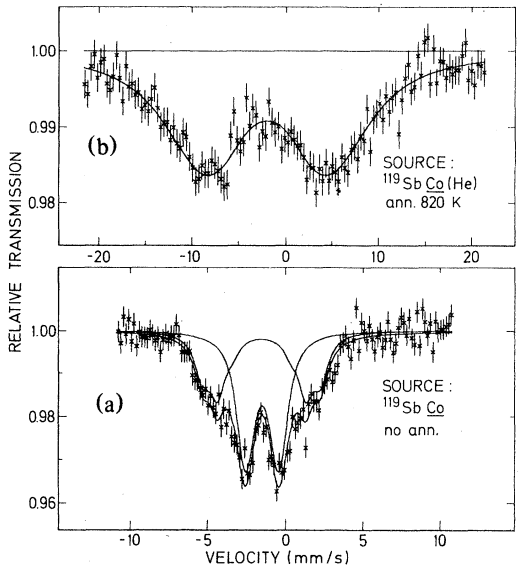

FIG. 3. Mössbauer spectra obtained with sources of ^{119}Sb implanted in cobalt and a $BaSnO_3$ absorber, both at 4.2 K. (a) Unannealed ^{119}Sb*Co* source, (b) ^{119}Sb*Co*(He) source annealed at 820 K. *Note the different velocity scales for spectra* (a) and (b).

trum originates from components with positive fields. The average field is 10.9(2) T, with a Lorentzian spread of ±3.6 T. This spread may be partly due to the coexistence of the fcc and hcp phases of the host metal.

In order to interpret the above results quantitatively, knowledge is required about the geometric configuration of the vacancy clusters trapped at the impurities. For this purpose, we refer to the results of Hohenemser *et al.*[9] who obtained strong evidence from time-differential perturbed angular-correlation spectra of ^{111}In implanted in Ni that a site exists in which the In impurities are surrounded by tetrahedra of vacancies in the nearest-neighbor shell [see Fig. 4(a)]. The annealing behavior of this site (called site 2) is very similar to that found from our Mössbauer spectra for the high field site (2) of ^{119}Sb impurities in Ni. For this reason we assume that for Sb impurities in Ni, site (2) also consists of Sb impurities tetrahedrally surrounded by vacancies. Disregarding relaxation of the host atoms, the distance between Sb atoms and nearest-neighbor Ni atoms in this site would be 0.43 Å larger than the Sb–Ni distance in a pure substitutional alloy (2.49 Å). Such an increase of the impurity-host atom distance apparently leads to a 3.5-fold *increase* of the hyperfine field. The increase of the site (2) field in the helium decorated sources is also large: 2.2- to 3-fold, indicative of similar vacancy configurations around the impurities. For the fcc phase of ^{119}Sb*Co*(He), which has a lattice constant very close to that of nickel, we may apply the same argument.

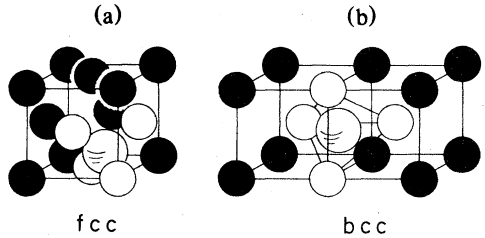

FIG. 4. Tetrahedral vacancy configurations. (a) Around an impurity at $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$ in fcc nickel or cobalt. (b) Around an impurity at $(0,\frac{1}{4},\frac{1}{4})$ in bcc iron.

In bcc iron, the vacancy configurations are, of course, different from those in the fcc metals, but also in this case a (distorted) tetrahedron is one of the possible nearest-neighbor vacancy environments for an impurity [see Fig. 4(b)]. This configuration has a large (calculated) binding energy per vacancy,[10] and it has been invoked earlier for explaining the hyperfine interaction of vacancy associated impurities in iron[11] and molybdenum.[12]

In Fig. 1 the hyperfine fields for vacancy associated impurities, including the case of ^{111}Cd in Ni are added to plots of the hyperfine fields of normal substitutional 5*sp* impurities in Fe, Co, and Ni. In each case we observe that the field increases when the impurity is surrounded by vacancies, corresponding to a shift of the hyperfine field plot to the left.

The vacancy configurations around the impurities are certainly not uniquely established by the considerations just presented. In the context of this paper, however, we shall limit ourselves to the tetrahedral configurations shown in Fig. 4. Our calculations will be based on the CEP model proposed by Blandin and Campbell.[1] According to this model the magnetic hyperfine field of a nonmagnetic impurity in a conducting lattice of ordered magnetic moments can be written

$$B_{\rm hf}=\alpha(\Delta Z)\sum n_i \frac{\cos[2k_F r_i+\frac{1}{4}\pi\Delta Z+\eta(r_i)]}{r_i^3}. \qquad (1)$$

The coefficient $\alpha(\Delta Z)$ varies slowly with ΔZ, the impurity-host valence difference, r_i is the distance between the impurity and one of the ith neighbor magnetic host atoms, n_i the number of such atoms, and k_F the Fermi-level wave number. The phase term $\eta(r_i)$ introduces an extra "proximity" phase shift. Following Jena and Geldart,[2] we take this shift inversely proportional to r and write

$$\eta(r_i)=\eta_0/(r_i/r_1)\ , \qquad (2)$$

where r_1 is the first-neighbor distance.

We first calculated the sum in Eq. (1) for substitutional impurities, neglecting relaxation and using a free-electron estimate $(2k_F r_1)/\pi=2.18$ (Ni, fcc Co)

or 2.15 (Fe), for the first six-neighbor shells. The resulting cosinelike function is fitted to the experimental data by adjusting η_0 so as to make the cosine function zero where the experimental B_{hf} vs ΔZ plot goes through zero and by choosing the amplitude such that the slope of the function equals that of the B_{hf} vs ΔZ plot near $B_{hf} = 0$ (full lines in Fig. 1). The result follows the data around the region of interest but also illustrates the limitations of the simple approach used here, with a constant coefficient $\alpha(\Delta Z)$.

For the tetrahedral vacancy-associated impurity-site configurations the distances r_i and the numbers n_i can be easily determined if lattice relaxation is disregarded. With the η_0 values found above the sums in Eq. (1) are now completely determined. The resulting cosinelike functions are given in Fig. 1 by broken lines. For the Ni and Co hosts, the measured hyperfine fields of the vacancy associated impurities (closed rectangles) are in good agreement with the simple model. For Fe, however, we can only say that the field change is in the right direction.

We must emphasize that the interpretation presented here does not pretend to give a fully quantitative description of the observed phenomena. The model of Blandin and Campbell does not provide a sufficient basis for this. Various simplifying assumptions in this model, such as the use of a free-electron RKKY approach and the simple additivity of contributions of different shells are certainly not justified in ferromagnetic metals with complicated band structures. In addition, we should remark once more that the geometrical arrangement of the vacancies surrounding the impurity is not yet uniquely established.

On the other hand, we do not see how alternative models,[4] based on direct overlap polarization of impurity orbitals, can explain our observations for vacancy associated $5sp$ impurities near the middle of the shells. The sharp rise of the field for the heavier substitutional impurities (Te, I, and Xe), on the other hand, may well be due to such an overlap contribution.

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