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Local and nonlocal isomer shifts in bcc Fe- X alloys ($X = \text{Al, Si, Ga, Ge}$)

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We measured Mössbauer spectra from bcc alloys of compositions near Fe_3Al , Fe_3Si , and Fe_3Ge , and reanalyzed older data from Fe_3Ga . All four alloys developed some $D0_3$ chemical order, and their Mössbauer spectra were qualitatively similar. The local (first-nearest-neighbor) could be distinguished from the nonlocal (beyond the first-nearest-neighbor) contributions to the ^{57}Fe isomer shifts from the solute atoms owing to differences in their hyperfine magnetic fields. The nonlocal isomer shift contributions correlated best to the valence of the solute atom, and not to the atomic volume. The local isomer shift contributions were best attributed to a loss of Fe $3d$ electrons at the solute sites.

Isomer shifts (IS) and hyperfine magnetic fields (HMF) at ^{57}Fe nuclei in Fe- X alloys have been interpreted on the basis of chemical properties of the solute atoms such as charge,¹ atomic volume,² and electronegativity with electron density.³ For many solutes in the periodic table, Akai *et al.*⁴ recently compiled experimental data on local IS's at ^{57}Fe nuclei having one first-nearest-neighbor (1nn) solute atom. They found that the chemical trend correlated best with the calculated change in the number of s electrons at the ^{57}Fe atom; changes in the d -electron count were found to cause an almost negligible effect.⁵ It is interesting that this chemical trend for the local IS is not the same as the trend for the ^{57}Fe IS for Fe impurities in different host metals, even when these host-metal data are corrected for the atomic volumes of the host.⁶

We measured the Mössbauer spectra from bcc alloys of compositions near Fe_3Al , Fe_3Si , and Fe_3Ge , and examined previous data on Fe_3Ga .⁷ These bcc polycrystalline alloys were prepared initially as disordered solid solutions, and then annealed to develop $D0_3$ chemical order. In these ferromagnetic alloys, the HMF causes the dominant perturbation of ^{57}Fe nuclear energy levels. The chemical trends in solute-induced HMF perturbations are now understood to be largely independent of the solute properties that underlie alloy chemistry. Instead, local HMF perturbations originate from the magnetic moments in the alloy.^{8,9} For example, all nonmagnetic solutes that do not interact strongly with the $3d$ electrons of Fe cause very similar perturbations in the HMF at 1nn

^{57}Fe atoms. Similar HMF perturbations are found for all solutes of interest in the present study, so their Mössbauer spectra are expected to be similar.

The systematics of the ^{57}Fe HMF distribution can be used to identify the subspectral components from ^{57}Fe atoms with different 1nn solute configurations. The IS of each configuration can then be determined with at least some degree of independence. In this work we have identified separately the local IS perturbations caused by changes in the 1nn solute configuration, and the nonlocal IS perturbations at those ^{57}Fe atoms with no 1nn solute atoms. We show that the dominant trend in the nonlocal IS's for these four alloys correlates strongly with the number of valence sp electrons of the solute atom, and not with the atomic volume of the solute atom. We show that the dominant trend in the local IS's for these four alloys correlates best with the number of Fe atoms in the 1nn shell of the ^{57}Fe atom.

Samples of Fe 25 at. % Al, Fe 24 at. % Si, Fe 22 at. % Ge, and Fe 25 at. % Ge were prepared in different ways. Thin films of Fe 22 at. % Ge were deposited onto a quartz substrate by standard ion-beam sputtering. An alloy of Fe 25 at. % Al was prepared from materials of 99.99% purity by arc-melting under an argon atmosphere. Chemically disordered samples of Fe 25 at. % Al were obtained by piston-anvil quenching with an Edmund Bühler ultrarapid quenching apparatus. Alloys of chemically disordered Fe 24 at. % Si and Fe 25 at. % Ge were prepared from elemental powders of Fe and Si or Fe

and Ge by mechanical attrition in a Spex 8000 laboratory mill/mixer. A major concern with the ball-milling method is contamination from the vial and the balls. We used tungsten carbide vials and balls because tungsten carbide has a very high heat of formation, and so does not interdiffuse with our sample material. From energy dispersive x-ray spectrometry (EDXS) we found that the alloy composition was approximately Fe 24 at. % Si, evidently homogeneous, and the tungsten was essentially all confined to tungsten carbide fragments. No cobalt from the tungsten carbide vials was detected in the Fe-Si alloy.

All materials were examined by x-ray diffractometry to ensure that they were polycrystalline bcc, and that they developed DO_3 order after annealing at temperatures around 350°C in evacuated quartz ampoules. The development of DO_3 order in the Fe-Ge alloys may seem a bit surprising, since it is not an equilibrium state of order, but this was confirmed by x-ray diffractometry for both sputtered and ball-milled materials that were initially bcc solid solutions. Chemical compositions were measured by energy dispersive x-ray spectrometry (EDXS) on a Philips EM 430 transmission electron microscopy, by a Kevex energy dispersive x-ray spectrometer mounted on a JEOL 6800 scanning electron microscope, and by a JEOL 733 Superprobe electron microprobe spectrometer. Mössbauer spectra were obtained at room temperature using conventional constant acceleration spectrometers. Radiation sources were ^{57}Co in a Rh matrix. For the sputtered Fe-Ge alloy, conversion electron spectra were obtained with a He- CH_4 flow-gas detector. Spectra from the bulk Fe-Ge, Fe-Al, and Fe-Si alloys were obtained in conventional transmission geometry.

Specimens of Fe_3Al , Fe_3Si , and Fe_3Ge in their initial state as chemically disordered solid solutions gave very similar Mössbauer spectra, comprising a broad and featureless sextet of magnetically split peaks. After annealing, the spectra from all alloys tended towards the two sextets from the two sites of Fe in the DO_3 ordered structure; a minority site with zero 1nn solutes, and a majority site with four 1nn solutes. Again, the spectra from ordered alloys of Fe_3Al , Fe_3Si , and Fe_3Ge were qualitatively similar. To show the subspectra from ^{57}Fe atoms with 1, 2, and 3 solute neighbors (and to permit a comparison with the published spectrum from Fe_3Ga) we present Mössbauer spectra from specimens with partial order in Fig. 1. It is not expected that the intensities of the subspectra should be the same for all four spectra because the samples differ somewhat in their precise compositions and state of order.¹⁰ Nevertheless, the four spectra of Fig. 1 have similar subpeaks, and similar asymmetry that is best seen in the widths of the peaks near zero velocity. The positions of the subspectral peaks depend on both the IS and the HMF associated with a local ^{57}Fe chemical environment. The ^{57}Fe HMF distribution is expected to be similar in Al, Si, Ga, or Ge alloys,^{8,9,11} and this is seen in the results presented in Fig. 2. The features are qualitatively similar in all four HMF distributions, although the separations of the subpeaks in the HMF distribution are larger for the Si and Ge alloys than for the Al and Ga alloys. The HMF's associated with different numbers of solute nearest neighbors, such as

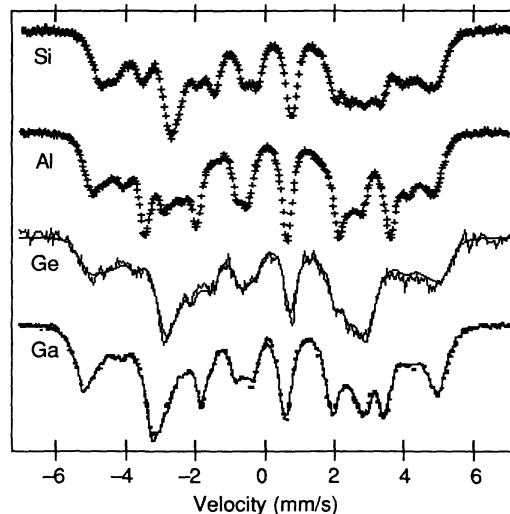


FIG. 1. Mössbauer spectra of Fe 25 at. % Al, Fe 24 at. % Si, Fe 25 at. % Ga (Ref. 7), and Fe 22 at. % Ge with approximately the same state of chemical short-range order.

shown at the top of Fig. 2 for the Fe-Si alloy, were conveniently identified by following the changes during annealing of the components in the HMF distribution.

In extracting the HMF distribution from the spectra by the method of Le Caër and Dubois,¹² the local IS's were determined. The IS, I , was assumed linearly dependent on the HMF, H , through the linear relationship: $I = AH + B$. Values for A and B were determined by optimizing the quality of fit of the recalculated spectrum to the experimental spectrum, and the results are presented in Table I. Using these values of A and B , and associating the various peaks in the HMF distribution with ^{57}Fe atoms having different numbers of solute neighbors (as in Fig. 2), we obtained the IS's for ^{57}Fe atoms with different

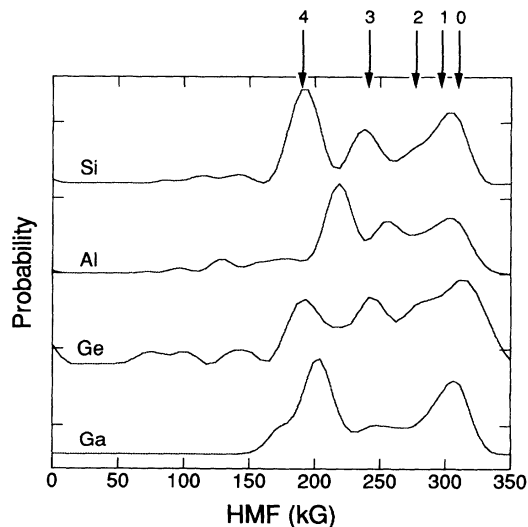


FIG. 2. HMF distributions extracted from the experimental spectra of Fig. 1 by the method of Le Caër and Dubois (Ref. 12). Numbers at top indicate specific numbers of solute atoms about the ^{57}Fe nuclei for the Fe 25 at. % Si alloy.

TABLE I. Parameters for the linear IS-HMF correlation: $I = AH + B$.

Fe-Al (disordered):	$A = -6.6 \times 10^{-4} \text{ mm s}^{-1} \text{ kG}^{-1}$	$B = +0.148 \text{ mm s}^{-1}$
Fe-Al (ordered):	$A = -1.25 \times 10^{-3} \text{ mm s}^{-1} \text{ kG}^{-1}$	$B = +0.336 \text{ mm s}^{-1}$
Fe-Si (ordered and disordered):	$A = -1.3 \times 10^{-3} \text{ mm s}^{-1} \text{ kG}^{-1}$	$B = +0.54 \text{ mm s}^{-1}$
Fe-Ge (ordered and disordered):	$A = -1.5 \times 10^{-3} \text{ mm s}^{-1} \text{ kG}^{-1}$	$B = +0.637 \text{ mm s}^{-1}$

numbers of solute neighbors. These data are presented in Fig. 3. For the local IS's of Fe_3Ga , the tabulated experimental data of Newkirk and Tsuei⁷ were used directly in Fig. 3. Also included as large points in Fig. 3 are linear extrapolations to 25% of data from Dubiel and Zinn for ^{57}Fe atoms with zero Al (Ref. 13) and zero Ge (Ref. 14) solute atom neighbors.

The HMF distributions were also determined from Mössbauer spectra of Fe-Ge by an alternative, independent method in which the HMF distribution was assumed to be a sum of Gaussian functions centered at HMF's characteristic of each 1nn environment. This fitting procedure is described elsewhere,¹⁵ but suffice to say that the local IS values so obtained were very similar to those from the method of Le Caër and Dubois.

Previous attempts have been made to isolate the local and nonlocal contributions to the isomer shifts at ^{57}Fe atoms with solute neighbors.^{13,14,16} In the dilute alloys used in this previous work, however, the nonlocal contributions are small and are hard to determine with precision. This difficulty contributed to the controversy about the relative importances of valence and atomic volume on the hyperfine parameters.^{16,17} The IS systematics found in this work with concentrated alloys of similar compositions (Fig. 3) are clear and easier to interpret, although they may not be directly applicable to the dilute alloy problem.

Chemical properties of the elements are presented in Table II. The electronegativity is that of Pauling.¹⁸ For our purposes we can use 1 for the number of sp electrons for Fe, although the actual number is about 0.8.¹⁹ The atomic volume was based on the Goldschmidt metallic radius²⁰ for the elements Fe, Al, Si, Ge.²¹ The element Ga does not have a high-symmetry crystal structure, so its volume was obtained by scaling the Goldschmidt metallic radius of Ge by the ratio of the atomic radii of Ga and

Ge. A second atomic volume for Ga was obtained with the same procedure with Al and Ga, and the results were averaged.

The *nonlocal* components of the IS data presented in Fig. 3 are strong. There is a strong positive IS for ^{57}Fe atoms with zero 1nn valence 4 solutes. This nonlocal component of the IS translates vertically the curves in Fig. 3, so it is similar for those ^{57}Fe atoms that do have solute neighbors. We expect such a nonlocal effect to originate with the $4s$ conduction electrons of the alloy. A comparison of the results in Fig. 3 with the chemical properties of Table II shows that the nonlocal IS correlates best with the number of valence electrons of the solute atom. The upper two curves for Si and Ge are for valence 4 solutes. The lower curves are for Al and Ga, which are valence 3 solutes. The IS correlates poorly with the difference in atomic volume of Fe and that of the solute atoms. We also found a poor correlation to atomic volume for the local isomer shift data reported in Ref. 14 (Fig. 9) when the Goldschmidt metallic radius was used. The positive nonlocal IS for the valence 4 solutes indicates that these solutes reduce the $4s$ electron density at the Fe atoms in the alloy. To understand this nonlocal component, we consider the valence 4 solutes as depleting the $4s$ states at Fe. Although charge transfers of $3d$ and $4s$ electrons in alloys tend to be of opposite sign, the $4s$ electron transfers tend to follow the trends of chemical electronegativity. The electronegativities of Si and Ge are greater than of Fe. On the other hand, the valence 3 solutes are less electronegative than Fe. They serve to donate electrons to the $4s$ states at Fe, so the IS is negative for ^{57}Fe atoms with zero 1nn Al or Ga atoms.

The *local* component of the IS data presented in Fig. 3 is also clear. For greater numbers of 1nn solute neighbors, the data of Fig. 3 show that the local IS becomes progressively more positive, and does so in about the same way for all four alloys. The slopes and curvatures of the four curves on Fig. 3 are the same within experimental error (except for the curve for disordered Fe_3Al , which does deviate from the others). The success of the linear relationship between local IS and HMF perturbation suggests a similar origin for the mechanisms by which 1nn solute atoms cause local ^{57}Fe HMF perturbations and local ^{57}Fe IS perturbations. For solutes that do

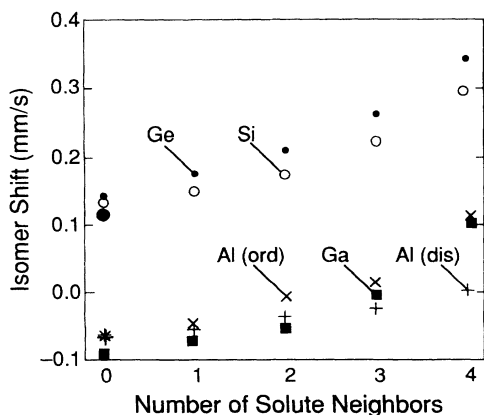


FIG. 3. Isomer shifts of the different iron environments in alloys of compositions near Fe_3X , where ($X = \text{Al, Si, Ge, Ga}$).

TABLE II. Properties of the elements Al, Si, Fe, Ga, and Ge.

Element	Metallic volume (\AA^3)	sp Electron count	Electronegativity
Fe	8.68	1	1.83
Al	12.21	3	1.61
Ga	13	3	1.81
Si	9.50	4	1.90
Ge	10.75	4	2.01

not disturb significantly the $3d$ electrons at Fe atoms, the local ^{57}Fe HMF perturbations correlate well with the magnetic moment at the solute site.^{8,9} An important feature of our solutes is that their magnetic moments are all zero, so they represent a loss of polarized Fe $3d$ electrons at the solute site. We propose that it is the loss of these $3d$ electrons that causes the local ^{57}Fe IS perturbations to be so similar for all sp solute atoms. The physical origin could be either the loss of Fe $3d$ spin at the solute site, or the loss of Fe $3d$ charge; either is capable of causing the IS disturbance at a neighboring ^{57}Fe atom.²² We suspect, however, that it is the change in Fe $3d$ charge that is most important, because the chemical trends for local isomer shifts from $3d$ and $4d$ transition-metal

solutes do not depend significantly on whether these solutes are magnetic.^{4,6} Finally, we believe that the nonlinear dependence of the local IS on the number of solute neighbors is real, but the origin of this nonlinearity is unclear. Stearns attributed the nonlinear trend in the local HMF perturbations to a saturation of the $4s$ spin polarization by the addition of further Fe atom neighbors.²³ The local IS's show that the charge disturbances around solute atoms are large, and this could be a source of the nonlinearity.

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