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Hyperfine Studies of Site Occupation in Ternary Systems

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The analysis of spin-echo spectra of V, Mn, Co, Ru, Rh, Os, and Ir in Fe_3Si shows that these impurities unexpectedly enter one of the two available Fe sites in a selective manner. Those impurities to the left of Fe in the periodic table prefer the Fe site with eight first-neighbor Fe atoms. Those beneath and to the right of Fe in the periodic table enter the Fe site with four Fe and four Si first neighbors.

From a pulsed NMR study of dilute transition-metal impurities in Fe_3Si and slightly iron-rich off-stoichiometric Fe_3Si, we report an unexpected selective site occupation. Fe_3Si exhibits long-range crystallographic order with a bcc structure and therefore two inequivalent iron sites. In Fig. 1 an element of the Fe_3Si structure is shown. Table I gives the near-neighbor configurations for both Fe and Si out to the third neighbor. Fe_3Si

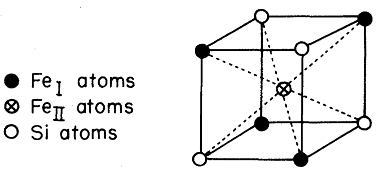

FIG. 1. An element of the Fe_3Si structure showing the Fe_I, Fe_{II}, and Si sites. One Fe site, Fe_I, is on the cube edge and has eight Fe first neighbors; the other Fe site, Fe_{II}, is at the body center and has four Fe and four Si first neighbors; Si is on a cube edge with eight first neighbors.

TABLE I. The first-, second-, and third-nearest-neighbor (nn) configurations for both the Fe and Si sites in Fe_3Si. We specify whether the Fe neighbors are in Fe_I or Fe_{II} sites. If the alloy is slightly Fe-rich, the extra Fe atoms occupy Si sites randomly, producing Fe_{II} sites with not only four but also five, six, and seven Fe first neighbors.

	1 nn	2 nn	3 nn
Fe_{II}	4 Fe_I 4 Si	6 Fe_{II}	12 Fe_{II}
Fe_I	8 Fe_{II}	6 Si	12 Fe_I
Si	8 Fe_{II}	6 Fe_I	12 Si

alloys have been investigated in a number of NMR,[1,2] Mössbauer,[3,4] and neutron-scattering studies.[5,6] Previously, it was believed that dilute concentrations of transition-metal atoms added to an Fe_3Si matrix would enter the two iron sites randomly. The NMR experiments reported in this paper for the 3*d* impurities V, Mn, and Co, the 4*d* impurities Ru and Rh, and the 5*d* impurities Os and Ir and Fe_3Si show for the first time that in each of these cases the impurity atoms enter only one of the two iron sites.

Small amounts of the desired ternary impurity were combined with master ingots of Fe_3Si and iron-rich off-stoichiometric Fe_3Si by arc melting to provide alloys of the desired concentrations. Care was taken to insure that little sample loss occurred during comixing. The resulting ingots were powdered by crushing and subsequently annealed at 600°C for 2 h and then slowly furnace cooled to produce well-ordered Fe_3Si. Homogenization of several Co samples prior to the ordering heat treatment indicated no significant difference in the results compared to samples not homogenized.

The spin-echo spectra were taken with a variable-frequency spectrometer at about 1.4°K. A measurement of the echo amplitude, when suitably corrected,[7] provides a measure of the hyperfine field distribution in the sample.

In Fig. 2, we show two previously published spectra important for the understanding of the new NMR results for the substitutional impurities.[1] Figure 2(a) shows a spectrum of Fe_3Si in which the peaks at 30.05, 31.47, and 46.57 MHz arise from the Fe_{II}, Si, and Fe_I sites, respectively. In Fig. 2(b), a spectrum for $Fe_{0.77}Si_{0.23}$ is presented. We note particularly that the peaks at 29.9, 37.0, and 42.7 MHz have been clearly identified as originating from Fe_{II} sites with four, five, and six Fe first neighbors.[1,2] We also note that a satellite on the Fe_I line at 47.2 MHz corresponds to Fe_I sites with a single Fe second neighbor.[2]

In Fig. 3(a), the spectrum arising from Co in $(Fe_{0.74}+Co_{0.01})Si_{0.25}$ is presented. Only a single sharp line with a center frequency of 195.0 MHz is observed. An intensive search from 10 to 420 MHz indicated that no other Co line was present. The spectra for Fe and Si (not shown) are similar to the spectra shown in Fig. 2(a) and confirmed that the alloys were well ordered and of approximately the desired composition. If Co entered the Fe_I site, the spectrum of the stoichiometric sample would show a clear Co-Co third-neighbor interaction. Furthermore, the spectrum of Co in the iron-rich off-stoichiometric sample would

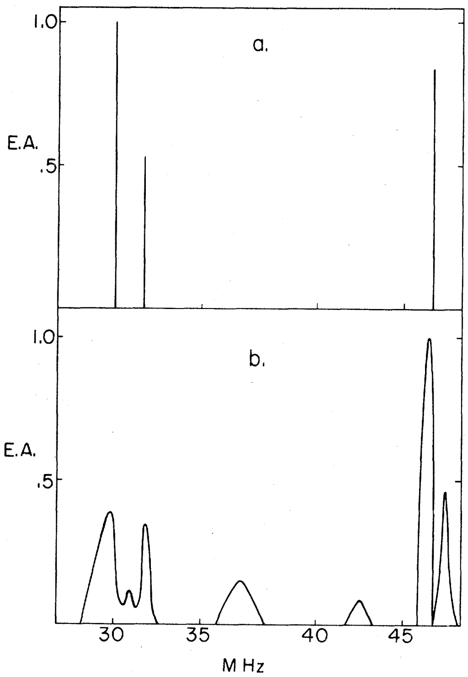

FIG. 2. Plots of the normalized echo amplitude versus frequency: (a) Fe_3Si; (b) $Fe_{0.77}Si_{0.23}$.

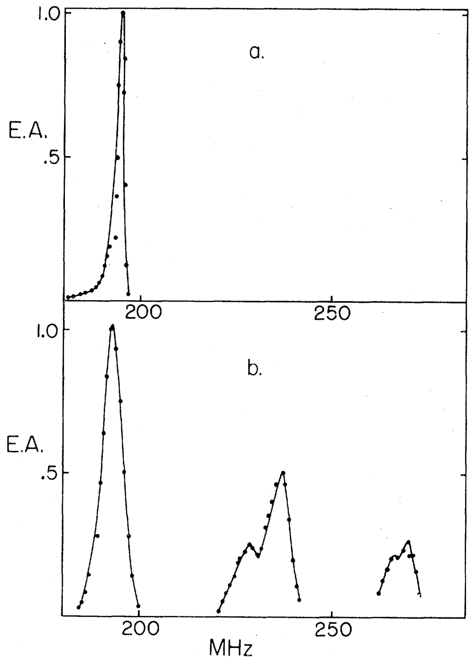

FIG. 3. Plots of the normalized echo amplitude versus frequency: (a) $(Fe_{0.74}+Co_{0.01})Si_{0.25}$; (b) $(Fe_{0.76}+Co_{0.01})Si_{0.23}$.

show a line arising from the Co atoms having as neighbors iron atoms which replace some Si. If Co entered the $\mathrm{Fe_{II}}$ site, the spectrum of Co in the stoichiometric sample should contain a single peak. The spectrum of Co in the off-stoichiometric sample should then contain peaks corresponding to first-near-neighbor configurations of four Fe and four Si atoms, five Fe and three Si atoms, and six Fe and two Si atoms. Figure 3(b) shows a spectrum of Co in $(\mathrm{Fe_{0.76}+Co_{0.01}})\mathrm{Si_{0.23}}$. The Co spectrum is similar in distribution and relative intensity to the spectrum of the $\mathrm{Fe_{II}}$ sites in this alloy and in the $\mathrm{Fe_{0.77}Si_{0.23}}$ spectrum shown in Fig. 2(b). Thus we identify the lines at 192.5, 237.5, and 270.0 MHz as arising from Co atoms which have entered the $\mathrm{Fe_{II}}$ sites and have four, five, and six Fe first neighbors in the off-stoichiometric sample.

Figure 4 shows a spectrum of Mn in $(\mathrm{Fe_{0.745}+Mn_{0.005}})\mathrm{Si_{0.25}}$. The spectrum shows a series of three almost equally spaced peaks. This spectrum can be explained only if Mn entered the $\mathrm{Fe_{I}}$ sites randomly.

For stoichiometric $(\mathrm{Fe}_{3-x}+\mathrm{Mn}_x)\mathrm{Si}$, an atom on an $\mathrm{Fe_{I}}$ site has eight $\mathrm{Fe_{II}}$ first neighbors, six Si second neighbors, and some combination of twelve $\mathrm{Fe_{I}}$ and Mn third neighbors (see Table I). The relative intensity of the lines in this spectrum is that of Mn in sites with zero, one, and two Mn third neighbors. This is also found in spectra of other stoichiometric alloys with different Mn concentrations. In Fig. 4(b), a spectrum of Mn in $(\mathrm{Fe_{0.76}+Mn_{0.01}})\ \mathrm{Si_{0.23}}$ is presented. The peaks at 273.2, 267.0, and 260.8 MHz are from Mn atoms with eight $\mathrm{Fe_{II}}$ first neighbors, six Si second neighbors, and zero, one, and two Mn third neighbors, respectively. The peak at 276.8 MHz is from Mn atoms with eight $\mathrm{Fe_{II}}$ first neighbors, five Si and one Fe second neighbors, and twelve Fe third neighbors. This satellite is similar to that produced by second-neighbor iron atoms at 47.2 MHz in the $\mathrm{Fe_{0.77}Si_{0.23}}$ spectrum shown in Fig. 2(b). Peaks corresponding to Mn atoms with eight $\mathrm{Fe_{II}}$ first neighbors, five Si and one Fe second neighbors, and eleven Fe and one Mn as well as ten Fe and two Mn third neighbors exist at about 270.6 and 264.4 MHz, respectively. However, these peaks lie underneath the main lines at 273.2 and 267.0 MHz and therefore are not evident.

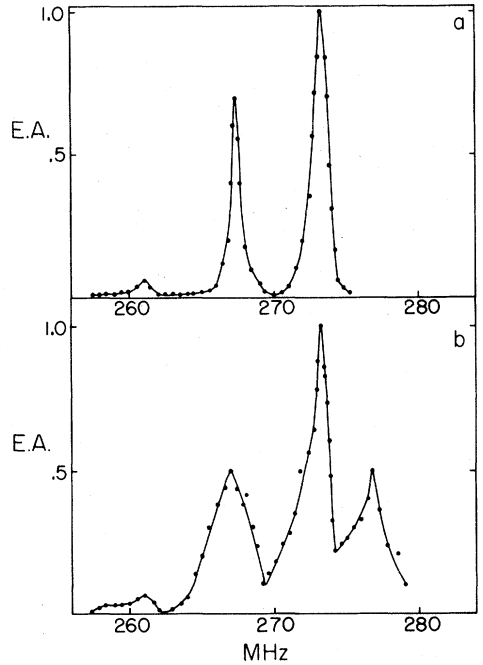

FIG. 4. Plots of the normalized echo amplitude versus frequency: (a) $(\mathrm{Fe_{0.745}+Mn_{0.005}})\mathrm{Si_{0.25}}$; (b) $(\mathrm{Fe_{0.76}+Mn_{0.01}})\mathrm{Si_{0.23}}$.

The spectra for V impurities in $\mathrm{Fe_3Si}$ alloys behave in the same way as those for Mn. Thus, for the 3*d* impurities we have studied, we conclude that those to the left of Fe in the periodic table enter the $\mathrm{Fe_{I}}$ site and those beneath and to the right enter the $\mathrm{Fe_{II}}$ site.

This observation can be confirmed by a neutron-scattering study of the site occupancy in the two magnetically inequivalent Fe sites. A preliminary study carried out in cooperation with Dr. S. Pickart of the U.S. Naval Ordnance Laboratory at the National Bureau of Standards reactor has already verified the selective site occupation deduced from the NMR spectra for the V, Mn, and Co substitutions.[8] Further neutron studies are in progress.

To explore further the possible systematics for the substitutional transition-metal impurities, we have found NMR signals arising from the 4*d* impurities Ru and Rh, and the 5*d* impurities Os and Ir. For both Ru and Rh, the spectra clearly suggest that they enter the $\mathrm{Fe_{II}}$ site as does Co. However, from studies of iron-rich off-stoichiometric samples, a strong preference is observed for the $\mathrm{Fe_{II}}$ site with four $\mathrm{Fe_{I}}$ first neighbors. We find that both Os and Ir enter the $\mathrm{Fe_{II}}$ site.

At present with the experimental results already obtained, we can clearly conclude that for the 3*d*, 4*d*, and 5*d* elements studied, those to the left of Fe on the periodic table enter the $\mathrm{Fe_{I}}$ site exclusively. Those beneath and to the right of

Fe on the periodic table enter the $\mathrm{Fe}_{\mathrm{II}}$ site exclusively, but different elements show different near-neighbor preferences in iron-rich off-stoichiometric samples. On the basis of these investigations, we conclude that an additional parameter which specifies the selective site occupation in $\mathrm{Fe}_3\mathrm{Si}$ when transition-metal impurities are added could shed some light on the ternary phase diagrams[9] of these systems.

The regularity of these results suggest a direct relationship to the large class of magnetic Heusler alloys.[10] If one writes $\mathrm{Fe}_3\mathrm{Si}$ as $(\mathrm{Fe}_{\mathrm{II}})_2\mathrm{Fe}_{\mathrm{I}}\mathrm{Si}$ the similarity to the Heusler structure, A_2BC, is clear.[11] In the known Heusler alloys, the transition metals most to the left in the periodic table prefer the B site, while those to the right enter the A site. Our results that V and Mn enter the Fe_{I} site whereas Co, Ru, Rh, Os, and Ir enter the $\mathrm{Fe}_{\mathrm{II}}$ site suggest a basis for the systematics of the transition-metal site occupancy of the known Heusler alloys. An interpretation of these results based on size and valency factors is actively being pursued.

During the course of this investigation, a similar conclusion for the $(\mathrm{Fe}_{3-x}+\mathrm{Mn}_x)\mathrm{Si}$ system was reached on the basis of a neutron experiment which concluded that Mn entered the Fe_{I} site.[12]

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Anomalous Small-Angle Magnetic Scattering from Amorphous TbFe_2 and YFe_2†

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Small-angle quasielastic neutron scattering measurements have revealed an intense magnetic component at low temperatures in amorphous TbFe_2 and YFe_2, in addition to a weak critical divergence at T_c in TbFe_2. These observations are interpreted as evidence that spatial fluctuations remain "frozen in" below the Curie point of TbFe_2, and that only short-range order is achieved in YFe_2.

Recent neutron scattering measurements on sputtered, amorphous magnetic alloys have provided information on the atomic and spin correlation functions[1] and excitation spectra[2] of these novel materials. Small-angle quasielastic scattering provides additional information about the longer-range, spatial fluctuations in the magnetization, particularly in the critical region near the transition temperature. We report here the observation by this method of an intense, strongly temperature-dependent small-angle component of magnetic origin in amorphous TbFe_2 and YFe_2, accompanied by a weak divergence near T_c in TbFe_2. We believe that these phenomena provide insight into the anomalous nature of the phase transition in amorphous magnets.

The measurements were taken at the National Bureau of Standards reactor with a double-axis