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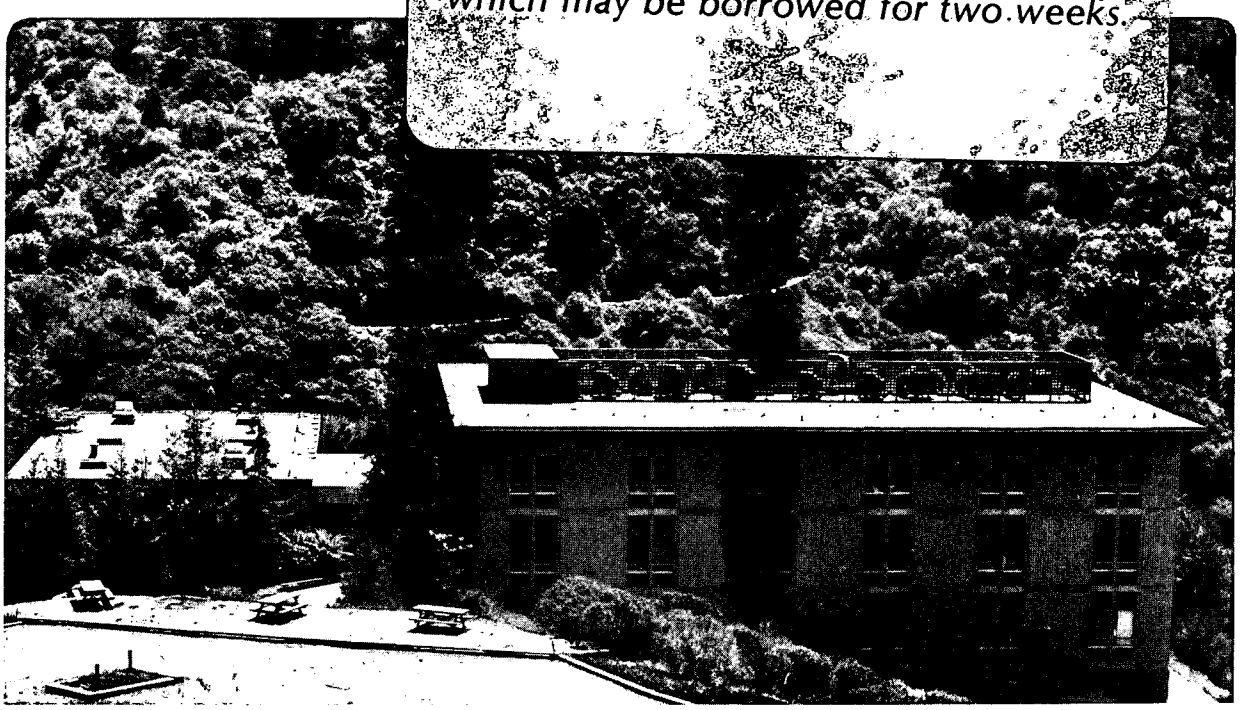

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THE TEMPERATURE DEPENDENCE OF THE ^{57}Fe HYPERFINE MAGNETIC FIELD DISTRIBUTION IN Fe-Ni

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The temperature dependence of the ^{57}Fe hyperfine magnetic field (hmf) in Fe-Ni is stronger than the temperature dependence of the ^{57}Fe hmf in pure Fe. By analyzing the shape of the ^{57}Fe hmf distribution, and with the help of experiments with Si in Fe-Ni, we deduce that this anomalous temperature dependence originates from a large thermal sensitivity of the magnetic moments at those Fe atoms with more Ni nearest neighbors. A strong temperature dependence of the recoil-free fraction was also observed in Fe-Ni alloys. We suggest that a large mean square thermal displacement of Fe atoms in Fe-Ni is the cause of the anomalous temperature dependence.

1. BACKGROUND

For many solutes the temperature dependence of the hyperfine magnetic field (hmf) at ^{57}Fe nuclei near solute atoms is little different from that at ^{57}Fe nuclei in pure Fe. However, for bcc Fe-Ni alloys the hmf at ^{57}Fe nuclei near Ni atoms is found to be anomalous in that it decreases more rapidly with temperature than for ^{57}Fe nuclei in pure Fe /1-4/. In this paper we qualitatively discuss the temperature dependence of the ^{57}Fe hmf in Fe-Ni.

Specimen materials of 99.99% purity were prepared by melting measured amounts of Fe, Ni and Si in new alumina crucibles under a backpressure of helium gas. A martensitic microstructure with a uniform 10 μm grain size was produced after further homogenization and austenitization heat treatments. Foils of about 10 μm thickness were used in transmission geometry with a constant acceleration spectrometer. A ~100 mCi ^{57}Co in Rh and a ~100 mCi ^{57}Co in Pd radiation source at room temperature were used during the course of this work. The ratio of recoil-free fractions at two temperatures was found by comparing the areas of spectra from the same specimen and experimental configuration at two different temperatures.

2. THE ^{57}Fe HMF IN Fe-Ni

A neighboring Ni atom changes the magnetic moment at a ^{57}Fe atom by changing its balance of 3d↑ and 3d↓ electrons. This causes a spatial redistribution of s- and p- electron spin around the ^{57}Fe nucleus, and a change in the ^{57}Fe hmf in proportion to the change in magnetic moment at the ^{57}Fe atom. From theoretical /2,5/ and experimental /6,7/ work, the change in the ^{57}Fe hmf due to a change in the number of unpaired 3d electrons local to the ^{57}Fe atom, ΔH_L, is:

$$\Delta H_L = (\alpha_{CP}+\alpha_{CEP}) \sum_{r'} \delta(r')\, g_{Ni}^{Fe}(r-r') \quad \text{where} \quad \alpha_{CP}+\alpha_{CEP} = -90\ \text{kG}/\mu_B \ . \tag{1}$$

The constants α_{CP} and α_{CEP} refer to the mechanisms of core polarization and conduction electron polarization, respectively. The Kroneker delta function equals 1 if the site is occupied by a solute atom, and equals 0 if it is occupied by an Fe atom. We use the variable $g_{Ni}^{Fe}(r)$ to represent the change in magnetic moment of an Fe atom when it has an Ni atom in its rth coordination sphere. The additivity of $\{g_{Ni}^{Fe}(r)\}$ parameters is expected only for dilute Fe-Ni alloys. All perturbations of Fe magnetic moments are referenced to the magnetic moment of an Fe atom in pure Fe, μ_{Fe}, and all perturbations of the Ni magnetic moments are referenced to the magnetic moment of an isolated Ni atom in an Fe matrix, μ_{Ni}. The ^{57}Fe atom is located at the origin of our bcc lattice.

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We use two terms to account for how the non-localized 4s electrons are spin-polarized at the ^{57}Fe nucleus by magnetic moments at neighboring atoms. The first term comprises the contributions from those neighboring lattice sites occupied by solute atoms, ΔH_{DNL} (direct non-local), and the second term comprises the contribution from those neighboring lattice sites occupied by Fe atoms, ΔH_{INL} (indirect non-local):

$$\Delta H_{DNL} = \alpha_{CEP} \sum_{r}' \{ f(r)\, \delta(r) [\mu_{Ni} + \sum_{r'} \delta(r')\, g_{Ni}^{Ni}(r-r') - \mu_{Fe}]\} \tag{2}$$

$$\Delta H_{INL} = \alpha_{CEP} \sum_{r}' \{ f(r) [1 - \delta(r)] \sum_{r'} \delta(r')\, g_{Ni}^{Fe}(r-r') \} \tag{3}$$

where f(r) is the fraction of conduction electron polarization at the ^{57}Fe nucleus produced by a change in magnetic moment at r, with respect to the conduction electron polarization produced by the same change in magnetic moment at the ^{57}Fe atom /8/. For qualitative analysis it is acceptable to assume that one unpaired spin at an Fe atom and one unpaired spin at a Ni atom are equally effective in polarizing the 4s electrons.

3. RESULTS AND DISCUSSION

The first and sixth peaks of Mössbauer spectra from Fe-9Ni and pure Fe at different temperatures are shown in Fig. 1. At 4 K the Fe-Ni peaks are broadened and shifted towards larger velocities with respect to the pure Fe peaks. Reductions in this broadening and shift are observed at 290 K. A qualitative change is seen in the Fe-Ni peaks at 773 K, which are shifted towards smaller velocities with respect to pure Fe, and have become observably narrower. From 773 K to 873 K the Fe-Ni peaks are further shifted toward smaller velocities, but have begun to broaden again.

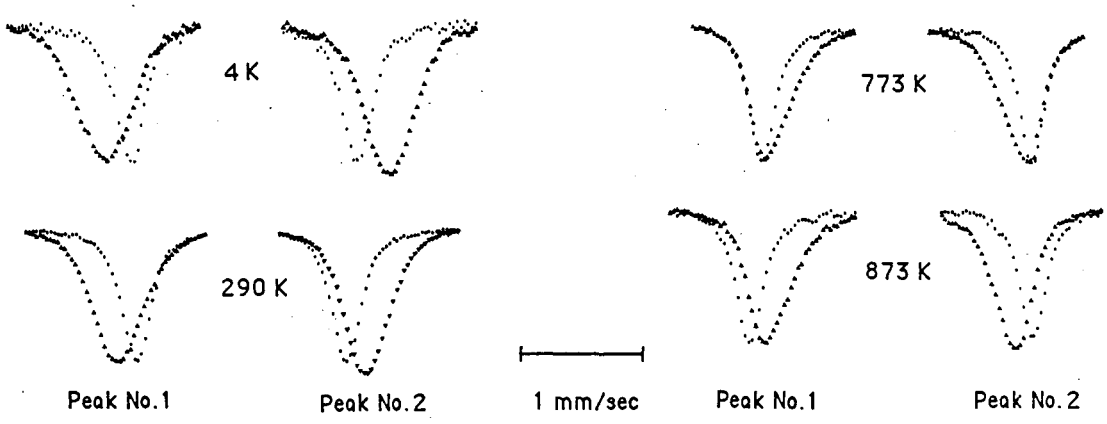

Fig. 1. Spectral peaks from Fe-8.86Ni (triangles) positioned with respect to pure Fe peaks (dots) at the same temperature.

Alloys of Fe-1.5at.% Si, Fe-6.02Ni-1.5Si and Fe-8.86Ni-1.4Si were prepared for our measurements of the set $\{\alpha_{CEP}\, f(r)\}$ from 4 K to 873 K. Si atoms develop no magnetic moment in bcc Fe, so the parameters $\{g_{Si}^{Si}(r)\}$ and $(\mu_{Si} - \mu_{Fe})$, which determine ΔH_{DNL}, are known to be 0 and -2.22 μ_B, respectively. Furthermore, since $\{g_{Si}^{Fe}(r)\} \sim 0$ /9/, the effects of Si on ΔH_L and ΔH_{INL} can conveniently be neglected. Mössbauer spectra from dilute Fe-Si and Fe-Ni-Si alloys show well-defined "satellite peaks" that can be associated with a Si atom in each nearest neighbor shell. Measuring the positions of these satellite peaks determines the set $\{\alpha_{CEP}\, f(r)\}$. We observed that the positions of the "Si satellites" changed rather little with Ni concentration or with temperatures in the range from 4 K to

873 K /10/. The $\{\alpha_{CEP} f(r)\}$ parameters, $\{-11.5, -3.5, +2.5, 0 \ldots\}$kG/$\mu_B$, adequately accounted for the observed "Si satellites" in Fe-Ni-Si alloys at 4 K, 77 K, 290 K and at 773 K. The parameter α_{CP} is not expected to be temperature dependent because it describes spin polarization mechanisms involving tightly-bound electrons.

Eqns. 1 - 3 can account for the average temperature dependence of the ^{57}Fe hmf in Fe-Ni alloys if either μ_{Ni} or $\{g_{Ni}^{Fe}(r)\}$ is reduced more rapidly with temperature than μ_{Fe}. However, if μ_{Ni} were to decrease with temperature, the width of the distribution of ΔH_{DNL} and the widths of the spectral peaks should increase. The opposite experimental systematics are observed from 4 K to 773 K [1]. We attribute most of the temperature dependence of the ^{57}Fe hmf to a temperature dependence of the $\{g_{Ni}^{Fe}(r)\}$ parameters, whose reduction should reduce the mean and width of the ΔH_{NL} and the ΔH_{INL} distributions. Using Eqns 1 - 3 and magnetic moment data from Stearns /11/, the mean hmf of Fe-9Ni will be reduced to that of pure Fe if the net enhancement of Fe moments caused by one Ni solute atom is reduced from 1.8 μ_B to 0.7 μ_B. This is a large change in the $\{g_{Ni}^{Fe}(r)\}$ parameters, and since the average Fe-Ni hmf becomes even less than that of Fe the average $g_{Ni}^{Fe}(r)$ parameter must become nearly zero at higher temperatures.

The recoil-free-fractions of pure Fe and of a Fe-9Ni alloy are shown as functions of temperature in Fig. 2. We suggest that the large temperature dependence of the $\{g_{Ni}^{Fe}(r)\}$ parameters originates with the large thermal motions of ^{57}Fe atoms in Fe-Ni alloys, which change the spin-dependent charge transfers between Fe and Ni neighbors. We now discuss the origin of such an effect. The Fourier components of the lattice periodic potential, U_k, will be reduced with mean squared thermal displacement, $<\rho^2>$, as: $\exp\{-k^2 <\rho^2> / 3\}$, and the $\{g_{Ni}^{Fe}(r)\}$ parameters will be similarly reduced. The recoil-free fraction is reduced as: $\exp\{-k_\gamma^2 <\rho^2> / 3\}$, where k_γ is the wavevector of the γ-ray. Since the $\{g_{Ni}^{Fe}(r)\}$ parameters are more temperature dependent than the recoil-free fraction, the important k-vectors for the charge transfers should be greater than k_γ. Since k_γ is about 7 Å^{-1}, the spin-dependent charge transfers seem sensitive to short-range interactions. The spin-dependent charge transfers are sensitive to the radial separation between the Fe and Ni atoms. Only a small dependence of these charge transfers on $d/dr\, g_{Ni}^{Fe}(r)$ is expected because the differences in thermal expansion between pure Fe and Fe-Ni are small. However, when we thermally average a Taylor approximation for $g_{Ni}^{Fe}(r+\rho)$, the term $<\rho^2>/2\, d^2/dr^2\, g_{Ni}^{Fe}(r)$ is non-vanishing. The $g_{Ni}^{Fe}(r)$ can decrease more rapidly than μ_{Fe} if $d^2/dr^2\, g_{Ni}^{Fe}(r)$ is strongly negative. It may be argued that thermal broadening of the Fermi surface may reduce the imbalance of 3d↑ and 3d↓ electrons when the densities of states near the Fermi surface of these electrons depend in a strongly different way on energy. This seems unlikely for bcc Fe-Ni.

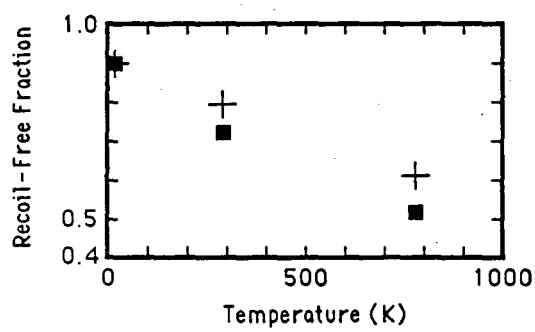

Fig. 2. Temperature dependence of the recoil-free fraction of Fe-8.86Ni (squares) and of pure Fe (crosses). A recoil-free fraction of 0.90 at 4K was assumed.

1 The increasing width of the hmf distribution from 773 K to 873 K may suggest some reduction in μ_{Ni} over this temperature range.

4. CONCLUSIONS

A marked difference was observed between the temperature dependence of the ^{57}Fe hmf distribution in Fe-Ni alloys and the temperature dependence of the ^{57}Fe hmf in pure Fe. It seems that this temperature dependence originates with the effects of Ni solutes on host Fe magnetic moments, although a rapid reduction in μ_{Ni} may be important at higher temperatures. It was also found that the recoil-free fraction had a stronger temperature dependence in Fe-Ni alloys than in pure Fe. We suggest that the large thermal displacements responsible for the low recoil-free fraction of Fe-Ni alloys are also responsible for the temperature dependence of the effects of Ni on the host Fe moments.

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References

/ 1 / P. J. Schurer, K. W. Maring, F. van der Woude and G. A. Sawatzky, Int. J. Mag. 4 (1973) 291, 297.
/ 2 / F. van der Woude and G. A. Sawatzky, Phys. Repts. 12 (1974) 335.
/ 3 / I. Vincze and G. Grüner, Phys. Rev. Lett. 28 (1972) 178.
/ 4 / P. C. Reidi, J. Phys. F: Metal Phys. 8 (1978) L201.
/ 5 / K. J. Duff and T. P. Das, Phys. Rev. B 12 (1975) 3870.
/ 6 / M. B. Stearns, Phys. Rev. B 4 (1971) 4069, 4081.
/ 7 / T. Yang, A. Kreshnan and N. Benczer-Koller, Phys. Rev. B 30 (1984) 2438.
/ 8 / I. Vincze and I. A. Campbell, J. Phys. F: Metal Phys. 3 (1973) 647.
/ 9 / G. G. Low, J. Appl. Phys. 39 (1968) 1174.
/ 10 / B. Fultz and J. W. Morris, Jr., to be published.
/ 11 / M. B. Stearns, Phys. Rev. B 9 (1974) 2311. M. B. Stearns, Phys. Rev. B 13 (1976) 1183.

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