Local Atomic Arrangements in $Fe_{63.2}Ni_{36.8}$ Invar from Diffuse X-Ray Scattering Measurements

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X-ray measurements show that $Fe_{63.2}Ni_{36.8}$ has a slight tendency toward $L1_0$ and/or $L1_2$ ordering with a preference for weakly ordered {100} platelets. This bias for Fe-Ni first neighbor pairs decreases the number of Fe atoms with eight or more Fe nearest neighbors. Such Fe rich regions are strongly correlated to the alloy's Invar properties. The mean separation of Fe-Fe first neighbor pairs is expanded relative to the average lattice, and the amount of expansion increases upon cooling from 293 to 60 K. This expansion supports the large moment–large volume explanation for the Invar effect. [S0031-9007(99)08748-7]

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Historically, the "Invar effect" has referred to magnetic alloys exhibiting an anomalously small or negative coefficient of thermal expansion over a broad temperature range [1]. Many explanations exist for this and for other unusual variations of the magnetization, electrical resistivity, heat capacity, and elastic moduli with respect to composition, temperature, pressure, and applied magnetic field [1,2]. Of particular interest is the strong correlation observed between the characteristic magnetic properties and lattice parameter (volume/atom) with concentration [2,3] (number of Fe-Fe nearest neighbor pairs). Because of this unusual behavior as well as the technological importance of Invar alloys, an extensive body of literature detailing their bulk properties has developed since their discovery in 1896 [4]. Little is known, however, about the local atomic environments present in these alloys and how they relate to the anomalous bulk properties. We report on the measurement of the local atomic configurations and show their importance to our understanding of the Invar effect which occurs in both ordered and disordered crystalline materials, as well as in amorphous alloys.

The small coefficient of thermal expansion observed over a wide temperature range below the Curie temperature T_C in Invar alloys is currently best understood as a volume increase associated with increasing magnetization/spin alignment as the alloy is cooled below T_C. This volume increase, termed spontaneous volume magnetostriction, opposes the usual Gruneisen lattice contraction. The prevailing explanation is that as the alloy is cooled or an external magnetic field is applied, the increasing alignment of the magnetic spins causes the Fe-Fe nearest neighbors (NN) to push apart thus occupying a larger volume and creating an internal "pressure" which expands the lattice [1,2]. This interpretation has evolved from Weiss' earlier proposed explanation for the strong correlation between large average moments $\langle\mu\rangle$ and large magnetostriction. He postulated that Fe in fcc alloys can exist in one of two spin states: a high spin state (large moment–large volume) or a low spin state (small moment–small volume) [5]. In this Letter we report new detailed information on the chemical short-range order (SRO) and temperature dependence of the mean species-dependent static displacements between pairs of atoms to address the lack of direct and consistent information [6] on the local atomic environments in this alloy.

Many Fe-Ni Invar properties closely follow the compositional dependence of the fraction of Fe atoms with an Fe rich local environment indicated by the yellow band in Fig. 1. This region is bounded by solid red lines that denote the fraction of Fe atoms with eight or more and with ten or more Fe NN. The dashed red line shows the fraction of Fe-Fe NN pairs as a function of composition. The number of Fe atoms with 8–10 NN closely follows the steep rise in the compressibility B^{-1} [7], the spontaneous volume magnetostriction $\omega_{s,o}$ [8], and the deviation of $\langle\mu\rangle$ from the Slater-Pauling curve [9]. A similar dependence is found for the lattice parameter, Curie and martensitic transformation temperatures, electronic specific heat, Debye temperature, and high field susceptibility [10,11]. The reduction of $\langle\mu\rangle$ with increasing Fe content can be explained by the Fe rich regions remaining paramagnetic and/or developing a noncollinear spin alignment and/or becoming antiferromagnetic. Indeed, a tendency for unlike neighbors (Fe-Ni NN pairs) will decrease the occurrence of Fe rich regions and suppress [12] the Invar properties. Knowledge of the preference for like or unlike neighbors provides insight into the dependence of the Invar properties on the Fe concentration.

The $Fe_{63.2}Ni_{36.8}$ fcc single crystal was annealed at 753 K and then quenched to room temperature. Because atomic diffusion in this alloy is quite slow at room temperature, the crystal is in a metastable homogeneous single-phase Invar state. X-ray diffuse scattering data were collected on beam line X-14 at the National Synchrotron Light Source. Measurements were made at both 293 and 60 K and at three x-ray energies chosen to vary the scattering contrast between Fe and Ni to enhance the sensitivity of the measurement to the *local* atomic structure [13]. X-ray

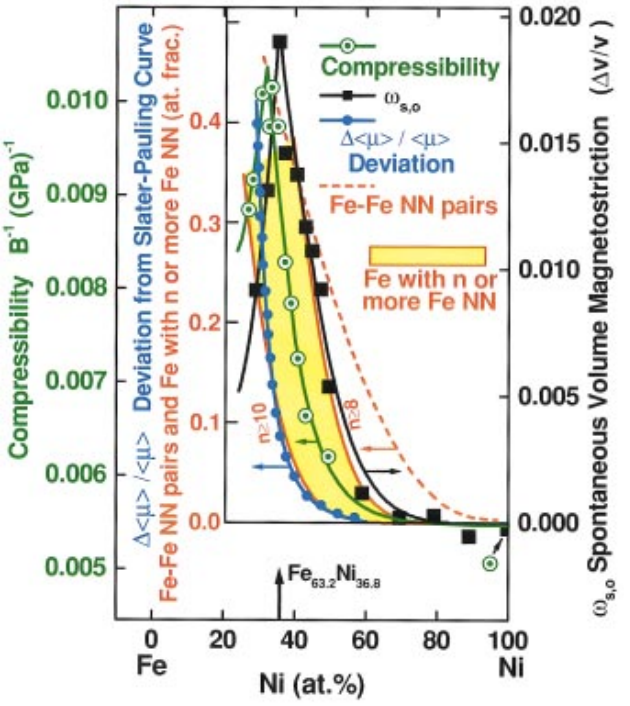

FIG. 1(color). The concentration dependence of the compressibility B^{-1}, volume magnetostriction $\omega_{s,o}$, and deviation of $\Delta\langle\mu\rangle/\langle\mu\rangle$ from the Slater-Pauling curve are plotted to show the correlation with the fraction of Fe-Fe NN pairs and even stronger correlation with the fraction of Fe atoms with $n \geq 8$ Fe NN. The curves drawn for B^{-1}, $\omega_{s,o}$, and $\Delta\langle\mu\rangle/\langle\mu\rangle$ are guides to the eye.

data collected at 30 K confirmed that none of the sample had martensitically transformed [14].

Details of the data collection, reduction, and analysis are substantially the same as in previous investigations of Fe-Ni alloys [13]. The chemical short-range order and the first-order mean static displacements were recovered using a nonlinear least squares refinement. The SRO is expressed in terms of the Warren-Cowley SRO parameters α_{lmn}, defined by $\alpha_{lmn} = 1 - P_{lmn}^{\mathrm{NiFe}}/c_{\mathrm{Fe}} = 1 - P_{lmn}^{\mathrm{FeNi}}/c_{\mathrm{Ni}}$, where P_{lmn}^{NiFe} is the conditional probability of finding an Fe atom at site lmn given a Ni atom at the origin [15]. The first-order static displacement (size effect) parameters, $\Delta_{lmn}^{\mathrm{FeFe}}$, $\Delta_{lmn}^{\mathrm{NiNi}}$, and $\Delta_{lmn}^{\mathrm{FeNi}}$, describe the mean species-dependent deviations of the atomic positions relative to the average lattice. The Δ_{lmn} are vectors, so it is actually the individual Cartesian components of the displacement vectors that are recovered from the least-squares analysis.

The first six recovered α_{lmn}'s are given in Table I. The fact that $\alpha_{000} \approx 1.0$ indicates that the data sets collected at the three x-ray energies are internally self-consistent. Both α_{110} and α_{200} show significant deviation from randomness, while the remaining α_{lmn}'s tend to zero. There is a slight preference for unlike first neighbors and for like second neighbors indicative of $L1_0$ (AuCu) and/or $L1_2$ ($AuCu_3$) ordering. This tendency for unlike first neighbors is less than for higher Ni content Fe-Ni alloys [13]. The α_{lmn}'s recovered from the 60 K data were indistinguishable from those at 297 K because of negligible diffusion at such low temperatures. Thus only one set of α_{lmn}'s is reported.

TABLE I. Warren-Cowley short-range order coefficients α_{lmn} for $Fe_{63.2}Ni_{36.8}$ Invar. The numbers in parentheses are the standard deviations based on our best estimates of the total error.

lmn	α_{lmn}	lmn	α_{lmn}
000	1.002(53)	211	−0.003(2)
110	−0.058(3)	220	0.000(2)
200	0.052(2)	310	−0.006(2)

The largest observed α_{lmn} values are those of the form $l00$ and $lm0$ which when coupled with the small out of plane α_{lmn}'s, especially the α_{211}, indicate that the chemical order is strongest in the {100} planes. Reverse Monte Carlo simulations [16] were performed which distribute the Fe and Ni atoms on an fcc lattice to match the recovered α_{lmn}'s. A tendency for Fe atoms to form {100} platelets was found. A majority of the Ni nearest neighbors to the Fe atoms of the platelets occupy adjacent {100} planes above and below. From the shape of the chemical short-range order intensity, e.g., the (100) peak profile shown in Fig. 2, we conclude that these small locally ordered platelets average about three unit cells or ~9 Å in diameter. Broad shoulders at the base of the peak are consistent with an average thickness of about 1.3 lattice planes. Neutron small-angle scattering (SANS) studies [17] on similar Invar compositions have reported variations in the magnetic scattering density due to regions of varying spin alignment and spin density of approximately 6 to 12 Å in size. The similarity in size suggests that the chemical fluctuations we observe are associated with these magnetic variations. However, we find that the chemical fluctuations are platelike as opposed to the spherical magnetic models used to interpret the SANS measurements.

Figure 3 shows the magnitude of the radial component of the mean static displacements. This is the deviation in Å of the pair separation distance from the average lattice for each type of atomic pair. Upon cooling from room temperature to 60 K the pattern of displacements is unchanged, but their magnitude increases by as much as a factor of 2. For Fe-Fe and Fe-Ni pairs, only the first and second neighbors show significant displacement. The displacements for Ni-Ni pairs are smaller but persist to much greater distances. Also, the displacements for the Fe-Fe and Fe-Ni neighbor pairs tend to oscillate in sign, whereas all the Ni-Ni pairs except for the 310 are negative indicating that most Ni-Ni pairs are compressed relative to the average lattice. Similar behavior of the displacements has been found in Fe-Ni alloys with different composition; however, no temperature dependence was observed [13]. The large

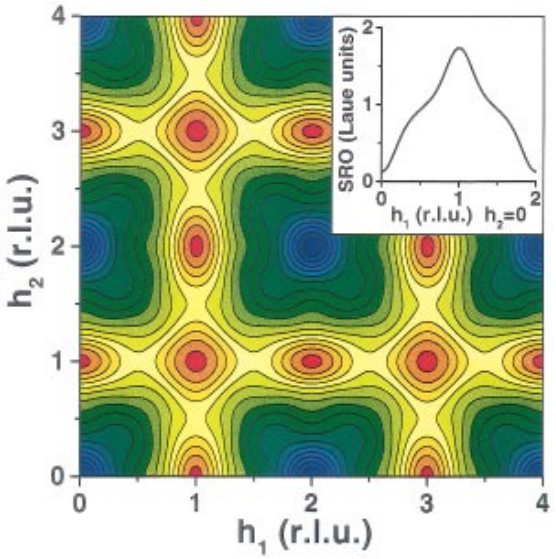

FIG. 2(color). Two dimensional plot of the short-range order scattering with contours in Laue units. Intensities are reconstructed from the recovered α_{lmn}'s. The dark blue contour indicates the minimum (0.13) and red the maximum (1.83) value. The shape of the (100) diffuse peak along $\{h_1 00\}$ associated with the chemical short-range order intensity is shown in the inset. The sharp central peak and broad base of the profile are associated with the thickness and diameter of the platelets, respectively.

temperature sensitivity of the static displacements observed for $Fe_{63.2}Ni_{36.8}$ but undetectable in $Fe_{46.5}Ni_{53.5}$ [13] can be understood in terms of the larger ($\times 5$) volume magnetostriction for $Fe_{63.2}Ni_{36.8}$ and its greater relative cooling below T_C. Because of the difference in their T_C's, 529 K for $Fe_{63.2}Ni_{36.8}$ and 830 K for $Fe_{46.5}Ni_{53.5}$, the Invar composition $Fe_{63.2}Ni_{36.8}$ recovers about 21% of its average magnetic moment compared with only 5% for $Fe_{46.5}Ni_{53.5}$ upon cooling from 293 to 60 K [9]. Thus the Invar composition would have undergone a change in $\omega_{s,o}$ 21 times ($5 \times 21/5$) greater than that for $Fe_{46.5}Ni_{53.5}$ upon cooling, and hence a much larger change in the displacements associated with the increased magnetization.

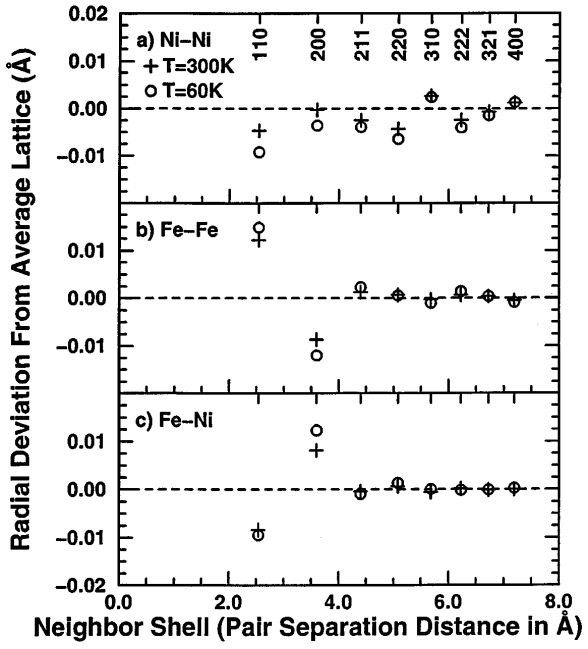

FIG. 3. Species dependent radial components of the first moment of the mean static displacements for the first eight near neighbor shells. Experimental uncertainty from both statistical and systematic errors is smaller than the size of the symbols.

The large temperature-dependent Fe-Fe NN spacing supports the large moment–large volume model for explaining the properties of $3d$-element Invars [1,5]. The average spacing between the different pairs is an equilibrium position between the magnetic interaction causing the Fe-Fe NN pairs to expand and neighboring pairs resisting the expansion. It has been predicted by theory [18] that a large Fe volume or Fe-Fe spacing is necessary to support ferromagnetism in fcc Fe. However, the large Fe-Fe NN spacing is not wholly of magnetic origin. Part of the Fe-Fe NN displacement is simply the result of the larger size of the Fe atoms which accounts for about one-half of the observed expansion and the other originates from the ferromagnetic exchange of the Fe-Fe pairs.

Though a majority of the Fe-Fe NN are ferromagnetically coupled, only a small perturbation (temperature and Fe content) has a large effect on their magnetic alignment. The drop in $\langle\mu\rangle$ and lattice parameter near the $Fe_{65}Ni_{35}$ composition is commonly associated with the increasing number of Fe rich environments. Using a binomial distribution modified by our observed chemical order, we find that 9.5% or fewer of the Fe atoms are in an environment of ten or more Fe NN as shown in Fig. 1. For $Fe_{63.2}Ni_{36.8}$ the estimated drop in the average moment from the Slater-Pauling curve is 8%. Thus, 8% of the Fe atoms could be in such Fe enriched neighborhoods so as to be coupled antiparallel. Evidence exists for a partial transformation near 20 K to the antiferromagnetic state for alloys near the $Fe_{65}Ni_{35}$ Invar composition [19]. Of course differing local environments of Fe-Fe NN, especially the distance between atoms, will cause variations in the magnetic exchange. Rather than 8% of the Fe atoms being coupled antiparallel, a larger fraction of Fe atoms could participate in the deviation of $\langle\mu\rangle$ from linearity with composition by being in various disordered local moment arrangements. These could range from small inclinations of their spins from a collinear ferromagnetic arrangement to a completely antiparallel alignment. Such an arrangement of varying noncollinear spins has been theoretically predicted [20]. Both theoretical treatments and phenomenological observations indicate that for Fe-Ni Invar alloys, Fe atoms with eight to ten or more Fe nearest neighbors will be in the low spin (small volume) noncollinear environment [18,20].

We have observed a large Fe-Fe NN separation which increases upon cooling and conclude that this results from both increased ferromagnetic spin alignment of the

Fe atoms and an increase in their individual moments. (About one-third of the change in the average moment on cooling below T_C is associated with a change in the individual Fe moments [21,22]). This is direct evidence that increased moment and spin alignment account for the large spontaneous volume magnetostriction. The resulting increase in the volume occupied by the Fe atoms with decreasing temperature opposes the usual thermal contraction of the lattice giving rise to the anomalously small coefficient of thermal expansion. Because of the anisotropic nature of the platelike chemical and magnetic order and the large size and directionality of the Fe-Fe first and second nearest neighbor displacements, new insight is given into the directionality of the magnitude properties [23]. Observation of the partially ordered platelike domains and the temperature sensitivity of the mean pair displacements provides a basis for better computational models and for testing of theoretical advancements. This information will aid in the interpretation of neutron diffuse scattering measurements of the spin-spin correlation function in these alloys.

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