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Local atomic order in *Au*Fe

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An average value of the first atomic order parameter $\overline{\alpha}_1$ has been determined by Mössbauer spectroscopy for a series of *Au*Fe alloys (5–20 at.% Fe). The alloys are found to exhibit either clustering of iron atoms or atomic short-range ordering depending on their metallurgical state and heat treatment. The variation of $\overline{\alpha}_1$ with annealing temperature is consistent with a vacancy mechanism for diffusion.

The aim of this Rapid Communication is to outline the behavior of the atomic short-range order in *Au*Fe alloys (5–20 at.% Fe). The first atomic order parameter α_1 has been determined from analysis of room-temperature Mössbauer spectra in a systematic study of heat-treated samples.

The interplay of chemical short-range order and magnetic order in the development of magnetic clusters and the spin-glass state has been emphasized recently by Mydosh.[1] As outlined below, several investigations of the atomic order in *Au*Fe have been carried out using a variety of experimental techniques. However, there remains a lack of agreement between results with values determined for α_1 differing considerably. In the present work, which is an extension of earlier Mössbauer measurements on 5 and 10 at.% Fe alloys,[2] we show that the type of atomic short-range order observed in *Au*Fe—clustering as indicated by positive α_1 or atomic ordering by negative α_1—depends on the sample state. These quantitative findings are relevant to the recent discussions[3–5] stemming from the earlier reporting of two different chemical environments in *Au*Fe alloys containing 10.5–33 at.% Fe (Ref. 6) (see also Ref. 7).

The extent to which the magnetic behavior of *Au*Fe alloys depends on the local atomic order was demonstrated by Crane and Claus[8] in their systematic study of the effects of annealing temperature on the magnetic ordering temperatures of 14 and 15 at.% Fe alloys. The degree of atomic order was not quantified, but the influence which the quenching rate of samples has in determining the bulk magnetic behavior was noted. Comparison of available x-ray diffuse scattering data shows that whereas one study[9] derived negative α_1 and positive α_2 values for a 25 at.% Fe alloy, the other[10] resulted in positive α_1 and negative α_2 for 14.4 and 15.4 at.% Fe alloys as deduced by Morgownik and Mydosh.[11] The position is similar for Mössbauer-effect measurements: Violet and Borg[12] reported that *Au*Fe alloys containing 1.7–10.5 at.% Fe are random solid solutions, whereas our earlier study of 5 and 10 at.% Fe alloys showed slight, but significant deviations from randomness.[2] More recently, Violet and Borg[6] have criticized other workers for assuming a random solid solution and have stated that short-range order is known to exist. As evidence for this they cited the changes induced in a 17 at.% Fe alloy on annealing at high temperatures or irradiating samples at room temperature with neutrons.[13] The increase which they observed in the magnetic ordering temperature after annealing or neutron irradiation was taken as an indication of clustering in this alloy. Since all other concentrations of their study[13] (8, 13, 20, 24, and 32 at.% Fe) failed to respond to similar treatments, they assumed that the 17 at.% Fe alloy is in a critical compositon region with regard to variations in atomic order (see also, Ref. 7). As no quantitative information concerning the atomic order in *Au*Fe is available over the concentration range which spans the spin-glass and ferromagnetic regions of interest, we report the results of a systematic investigation of the dependence of $\overline{\alpha}_1$ in *Au*Fe. $\overline{\alpha}_1$ is an average value of the first atomic short-range order parameter. A complete report of the diffusion and aging effects in *Au*Fe alloys outlined here will be presented elsewhere.[14]

*Au*Fe alloys containing 5, 10, 15, and 20 at.% Fe were prepared and examined as described previously.[2,14,15] Room-temperature Mössbauer-effect data were obtained for foils in an as-rolled state (AR) and after heat treatment in vacuum at temperatures between 100 and 950 °C for periods of 1 and 7 days. After heat treatment, all samples were quenched (~ 3 s) into water at room temperature. The present discussion is concerned mainly with samples heat treated at 550 °C for 1 day (HT); the formation of α-Fe precipitates in these samples is not a problem at this aging temperature.[15] The Mössbauer spectra recorded from these alloys, and their detailed spectral analysis have been presented and discussed elsewhere.[2,14]

Analysis of spectra obtained from all AR and HT alloys gave spectral components having fractional areas which are different from those expected on the basis of random alloys. Previously[2] the occupancy of the first nearest-neighbor shell and hence $\overline{\alpha}$, were determined solely from the fractional area of the spectral component due to the isolated iron atom site, A_0. However, in the present work $\overline{\alpha}_1$ was calculated by comparing combinations of the areas of all main spectral components with the corresponding combinations of binomial probabilities of iron nearest-neighbor configurations.[14] This improved method minimized errors in determining $\overline{\alpha}_1$ for alloys of low iron concentration and allowed $\overline{\alpha}_1$ to be determined for alloys of higher concentration in which the component A_0 becomes less significant.

The results of this analysis for *Au*Fe alloys are shown in Fig. 1. All alloys display a deviation from randomness, with AR alloys having a positive $\overline{\alpha}_1$ and HT alloys a negative $\overline{\alpha}_1$ value. The magnitude of $\overline{\alpha}_1$ increases with iron concentration for both sample conditions. Clearly, *Au*Fe alloys with 5–20 at.% Fe in both sample states are not random. The

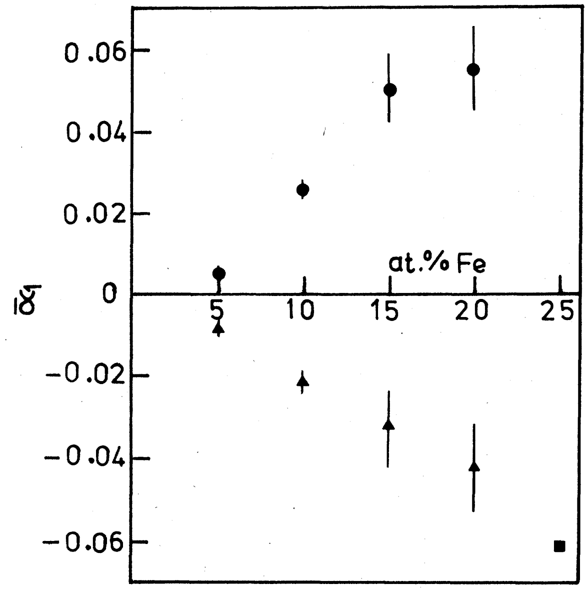

FIG. 1. Variation of $\bar{\alpha}_1$, an average value of the first atomic order parameter, for *Au*Fe alloys [● as rolled sample state; ▲ heat treated at 550 °C for 1 day plus water quench; ■ heat treated at 900 °C for 30 min plus oil quench (Ref. 9)]. For a random alloy $\bar{\alpha}_1 = 0$.

AR alloys in this concentration range indicate a clustering of iron atoms within the fcc matrix, whereas the HT alloys exhibit the opposite tencency towards atomic short-range order. While the $\bar{\alpha}_1$ values demonstrate this slight deviation of *Au*Fe alloys from atomic randomness, it should also be noted that they represent average values over the whole sample. For example, Fig. 2 of Whittle and Campbell[2] demonstrates how the $\bar{\alpha}_1$ values of a 10 at.% Fe alloy in the AR and HT conditions are reflected by the differing contributions of the spin-glass matrix or cluster glass regions (as labeled in the magnetic phase diagram of Sarkissian[16]) to the 4.2 K Mössbauer spectrum.

It was also found that changes from positive $\bar{\alpha}_1$ values to negative $\bar{\alpha}_1$ values occurred as the AR 5 and 10 at.% Fe alloys were subjected to heat treatments at successively higher annealing temperatures T_A. $\bar{\alpha}_1$ changes sign at $T_A \sim 175\,^{\circ}\mathrm{C}$ with an increase in magnitude at higher T_A values until ~ 225 and $\sim 330\,^{\circ}\mathrm{C}$ for the 5 and 10 at.% Fe alloys, respectively. $\bar{\alpha}_1$ was found to remain unchanged on annealing at higher temperatures. This constancy in $\bar{\alpha}_1$ is considered to result from the atomic ordering which takes place on cooling the sample. The changes which occurred in the spectral areas of a 10 at.% Fe sample (HT) on long-term aging at room temperature showed that diffusion occurs primarily by a vacancy mechanism, in agreement with the results of tracer studies.[17] Samples which are quenched from high temperatures do not retain the equilibrium vacancy concentration, but rather, exhibit properties characteristic of a sample annealed at the temperature, T_V, at which the hopping time of the iron atoms is similar to the time available for cooling—atomic redistribution therefore takes place during the quench with samples reflecting the metallurgical state around the temperature T_V for heat treatments carried out above T_V. T_V was calculated from the changes in the spectral components of the 10 at.% Fe sample (HT) before and after aging at room temperature and found to be $\sim 325\,^{\circ}\mathrm{C}$, in good agreement with the annealing temperature above which $\bar{\alpha}_1$ is constant for this alloy. The HT condition of Fig. 1, is therefore more correctly described as corresponding to a sample state following heat treatment at the appropriate value of T_V. The metallurgical state of *Au*Fe alloys annealed at high temperatures is therefore seen to be dependent on the quench time, which in turn depends on the sample size, ejection speed, quenching medium, and so on.

Also shown in Fig. 1 is the α_1 value obtained by Sundahl, Siversten, and Chen[9] from x-ray diffuse scattering measurements on a 25 at.% Fe cold-rolled foil (~ 2.5 mm thick) which was heat treated at 900 °C for 30 min and oil quenched. Even though this sample would be expected to experience a slower quench[14] than that of the typically 10-μm foils used in the present study, consistent behavior in the variation of α_1 for annealed foils is found. As already noted, positive values for α_1 of $+0.075$ and $+0.064$ were obtained for annealed single crystal 14.4 and 15.4 at.% Fe samples.[10,11] Although these data disagree with the values reported here, the discrepancy may be attributed to the large sample volume ($\sim 1\ \mathrm{cm}^3$) of the original heat-treated crystals, and therefore comparatively slow quench. It is stressed that quench rate, as well as concentration and annealing temperature, should be considered in comparing results for *Au*Fe alloys.

Changes in chemical order are reflected in both the bulk[8] and microscopic low-temperature magnetic behavior.[2] Borg and Dienes[13] report an increase in the ordering temperature T_0 for a 17 at.% Fe alloy from 50 to 75 K after annealing. Such a heat treatment for this alloy is well within the two-phase region of the equilibrium phase diagram[18] and the increase in T_0 may be linked with an early state of α-Fe precipitation.[15,19] We have carried out a detailed low-temperature study of the variation of the magnetic hyperfine splittings with temperature for the present 5 and 10 at.% Fe alloys in the AR and HT states: no detectable change in $T_0 \sim 26$ K was obtained on annealing the 5 at.% Fe alloy, although a slight increase from $T_0 \sim 38$ to ~ 41 K was observed in the 10 at.% Fe sample. (The 5 and 10 at.% Fe alloys are well within the single-phase region of the equilibrium phase diagram.[18]) This trend is similar to that reported for a 17 at.% Fe alloy[13] although the opposite trend—decrease in T_0 with annealing—was obtained in ac magnetic susceptibility studies of 14 and 15 at.% Fe alloys.[8] Both of these sets of workers[13,8] interpreted their observations as evidence for atomic clustering—the former an increase in clustering and the latter a decrease—although the present work shows that single-phase alloys which are heat treated exhibit tendencies towards short-range atomic order or anticlustering. The slight increase in T_0 observed on heat treatment of the present 10 at.% Fe alloy suggests that the more regular array of atoms with its corresponding regularity in magnetic spins, enhances the strength of the magnetic interactions between the finite clusters which exist in this region of the magnetic phase diagram.[16]

Mössbauer spectra which we have recorded at 4.2 K for the set of *Au*Fe alloys (5–20 at.% Fe) can be described as comprising essentially two broadened sextets.[20] The relative proportions of these components depend on the atomic order.[2] These spectra cannot be described well by two six-line subspectra using Lorentzian line shapes. Rather, because of the distributions of hyperfine parameters,[3,20] we found it necessary to model the distributions associated with each spectral component by using pseudo-Lorentzian line shapes during the fitting. The intensity ratios of the six lines in each subspectrum were allowed to vary in the ratios 3:*b*:1. Quantitative information concerning the two broadened sextets was extracted, and the response of these two components to an applied magnetic field was studied for samples at various temperatures. For the 20 at.% Fe sample, which is above the critical composition $c_p \sim 15.7$ at.% Fe for the onset of long-range ferromagnetic order, a field responsive ferromagnetic component and an unresponsive glasslike component were identified at 4.2 K in agreement with other workers.[21] The mean hyperfine parameters of magnetic hyperfine field, isomer shift, and quadrupole splitting which we obtain for the two subspectra of the 5 to 20 at.% Fe alloys are in good agreement with those reported by Violet and Borg[6] for 10.5 to 33 at.% Fe alloys. The striking feature of a plot of both sets of these isomer shift values against iron concentration for the two subspectra, H_h for the high-field component and H_l the low, is a decrease from an approximately constant value of $\delta(H_h) \sim +0.65$ mm s^{-1} (with respect to α-Fe) for alloys in the range 5 to 26 at.% Fe to $\delta(H_h) \sim +0.15$ mm s^{-1} for the 33 at.% Fe alloy. By comparison, the isomer shift of the low-field component remains approximately constant at $\delta(H_l) \sim +0.75$ mm s^{-1} over the concentration range 5 to 33 at.% Fe. The tendency of the $\delta(H_h)$ value for the 33 at.% Fe alloy to approach that of α-Fe is consistent with the presence of α-Fe as reported by Violet and Borg.[5,19] Conversely the constant, non-α-Fe–like value for $\delta(H_h) \sim +0.65$ mm s^{-1} at lower concentrations is in accord with the evidence for magnetic homogeneity in such alloys as explained by Monod and Campbell.[3] Our variable temperature measurements on the 5 and 10 at.% Fe alloys in the AR and HT conditions show that the magnetic hyperfine fields for each sample reduce to zero at essentialy a unique temperature; that this behavior occurs in alloys in either a clustered or an atomically ordered state is further evidence in support of the conclusion[3] that the magnetic correlation length is greater than the extent of the atomic short-range order.

In summary, we have shown that the atoms in *Au*Fe alloys containing 5–20 at.% Fe are not distributed randomly. Alloys examined as foils which are cold rolled from the arc-melted ingot exhibit clustering of iron atoms, whereas atomic short-range order is induced on heat treatment. Diffusion of iron atoms occurs primarily by a vacancy mechanism and the degree of the local atomic order has been found to depend on the quench time for annealed samples; this occurs as a result of the atomic reordering which takes place during the quench. Although changes in the magnetic behavior of *Au*Fe alloys can be discerned for samples of differing atomic short-range order, the intrinsic microscopic details of the magnetic behavior of, for example, the spin-glass matrix or the magnetic clusters, as monitored by their magnetic hyperfine splittings, are relatively unaffected.

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