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Nonuniqueness of the state of amorphous pure iron

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Amorphous pure Fe has been studied with ^{57}Fe Mössbauer spectroscopy by utilizing various Fe-based binary amorphous-alloy systems that have stable amorphous phases up to very high Fe concentrations and then extrapolating the properties toward those of amorphous pure Fe. The concentration dependence of the magnetic properties and the hyperfine interaction parameters of Fe–early transition metal (Ti, Zr, Hf, Nb, Ta, and Mo) and Fe-metalloid (B, Sb, Si, Ge) systems reveals different states of amorphous Fe which can be related to the theoretically proposed γ_1 and γ_2 states of fcc Fe.

Understanding of the magnetic and structural behavior of amorphous pure iron (a-Fe) is of theoretical and practical importance. The Fe-based amorphous alloys represent the most studied class of magnetic amorphous system,[1] and, in the Fe-rich region, their properties are closely related to those of a-Fe. Future fabrication of Fe-based amorphous alloys of practical interest also calls for a better understanding of a-Fe itself. This subject is particularly timely because of the recent advances achieved by first-principle total-energy calculations which clearly demonstrate the richness of the magnetic states of Fe.[2-6] Depending on the lattice structure, its lattice parameter, or atomic volume, Fe could be forming the well-known ferromagnetic bcc state (α-Fe), and more interestingly, the antiferromagnetic fcc state (γ_1-Fe) or the ferromagnetic fcc state (γ_2-Fe). Unfortunately due to its extreme structural instability, the pure a-Fe state cannot be maintained and is inaccessible to investigation. An attractive alternative to study a-Fe is to utilize various amorphous systems having a stable amorphous phase up to a very high Fe concentration and to extrapolate the properties towards a-Fe.

We have studied two important classes of Fe-based binary amorphous alloys: Fe–early transition metal (T_E) (T_E = Ti, Zr, Hf, Nb, Ta, and Mo) and Fe-metalloid (M) (M = B, Sb) systems, with the Fe concentration extended to the highest accessible value in each case.[7-10] The purpose of this work is to probe into the characteristics of a-Fe by a systematic study of the concentration dependence of magnetic properties and hyperfine interactions, such as magnetic hyperfine field, isomer shift (IS), and electric quadrupole splitting (QS). It is conclusive from our results that there exist *different* states of amorphous pure Fe.

All the samples studied in this work were prepared in a magnetron sputtering system under the same conditions. The vacuum prior to the sputtering was in the 10^{-8}–10^{-7}-Torr range. The films were all deposited onto liquid-nitrogen–cooled substrates of copper and Kapton with 4-m-Torr Ar as the sputtering atmosphere. A typical sputtering rate was in the range of 500–1000 Å/min and the sample thicknesses were about 15–20 μm.

An energy-dispersive x-ray spectrometer was used to ascertain the structure of the samples. The hyperfine interactions were studied by using a conventional Mössbauer spectrometer with a ^{57}Co in Rh source.

In Fig. 1, the concentration dependence of the effective magnetic hyperfine field (H_{eff}) at 4.2 K of four Fe-T_E systems are displayed, where H_{eff} is proportional to the average magnetic moment of the Fe atoms. All the crystalline

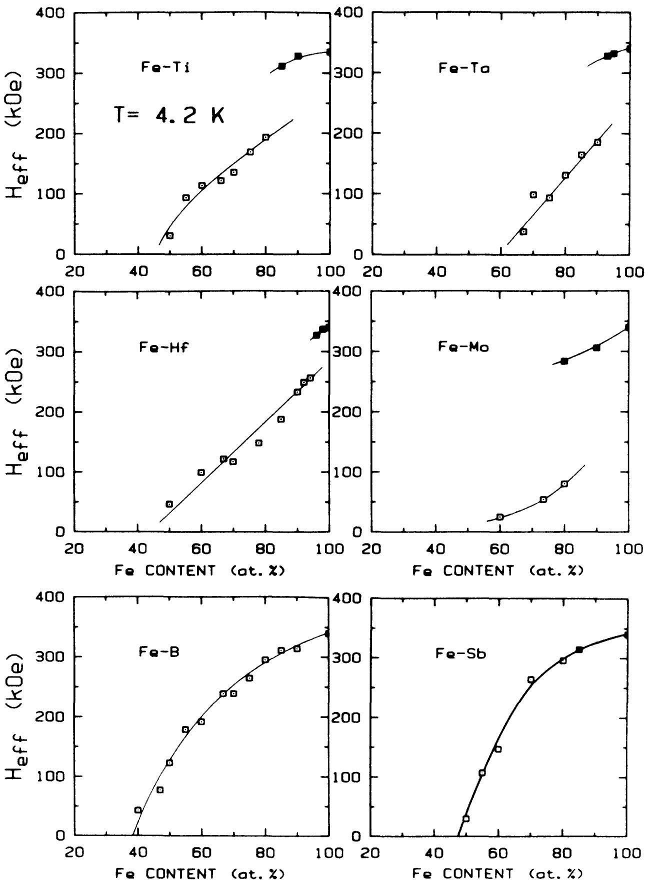

FIG. 1. Concentration dependence of effective magnetic hyperfine field at 4.2 K of Fe–early transition metal and Fe-metalloid amorphous systems. The open squares denote amorphous alloys and the closed squares, bcc crystalline alloys.

samples obtained with the same sputtering method have bcc structures and can be regarded as extensions of bcc α-Fe. A common feature shared by all Fe-T_E systems is that there is an abrupt change in the magnetic moment at the boundary separating the amorphous and crystalline phases (at about 80–93 at.% of Fe depending upon an alloy system). Extrapolating the $H_{\rm eff}$ of the amorphous phase to *a*-Fe, we find that the $H_{\rm eff}$ of *a*-Fe is much lower than that of bcc Fe. It was also found that the magnetic ordering temperatures of *all* the binary amorphous Fe-T_E alloys, regardless of composition, are below 300 K, whereas all the crystalline bcc alloys are strongly ferromagnetic with T_c in excess of 850 K. Thus, the magnetic properties are drastically different between the crystalline and amorphous states.

Quite contrary to the case of Fe-T_E, in Fe-M systems such as Fe-B, Sb, Si (Ref. 11), and Sn (Ref. 12) *no* discontinuity is observed in magnetic moment at the phase boundary, and the magnetic moment continuously approaches the moment of bcc Fe. Figure 1 also shows the concentration dependence of $H_{\rm eff}$ of two typical Fe-M systems, Fe-B and Fe-Sb, in which a smooth curve connecting the $H_{\rm eff}$ values of amorphous alloys to those of the bcc alloys is realized. These observations suggest that the short-range order in the Fe-rich Fe-T_E alloys is different from that in the Fe-M alloys and that the structure of amorphous pure Fe is not unique.

The possibility of different states in amorphous pure Fe is further supported by IS and QS data. The two hyperfine interaction parameters IS and QS, readily available from Mössbauer spectra, are related to the local atomic environment. IS measures the *s*-electron density at the nucleus, giving information about charge transfer and electron distribution, whereas QS, measuring the local electric field gradient, is sensitive to the local atomic symmetry and short-range order. If the short-range order of *a*-Fe is indeed nonunique, we should expect the extrapolated IS and QS to be different also.

Figure 2 show the concentration dependence of isomer shift at 300 K with respect to bcc α-Fe for several Fe-M and Fe-T_E systems. In all the Fe-M and Fe-T_E systems studied here and those studied by other groups, we find that the following observation is always true, that is, the sign of the IS in Fe-M systems is exclusively positive, and is negative in Fe-T_E systems. This has been studied previously[13,14] and can be explained by the relative importance of interatomic charge transfer and intra-atomic *s*-*d* electron conversion. What is most intriguing in Fig. 2 is that the extrapolated IS value of *a*-Fe from Fe-M systems ($\sim$0.04 mm/sec) is very different from that obtained from Fe-T_E systems (~ -0.06 mm/sec). It is well known that the IS of Fe depends sensitively on its structure.[15] In its crystalline form, Fe can have a few different structures such as bcc α-Fe and fcc γ-Fe. The IS of γ-Fe is smaller than that of α-Fe by 0.08 mm/sec, i.e., $\delta^{\rm IS}_{\gamma\text{-Fe}} = -0.08$ mm/sec, a value close to that of *a*-Fe extrapolated from Fe-T_E alloys.

Another useful parameter is the electric QS, which is zero for crystalline α-Fe or γ-Fe because of the cubic symmetry. In amorphous solids, the atomic site symmetry is lower than cubic, therefore the QS value is never zero. Figure 3 shows the concentration dependence of QS at 300 K for Fe-M and Fe-T_E systems. A point of special interest is that the QS of *a*-Fe obtained from these Fe-T_E systems is about 0.33 mm/sec. In the Fe-M systems, the QS at the Fe-rich side cannot be directly obtained, because the samples are magnetic above 300 K, where the quadrupole interaction is no longer the dominant hyperfine interaction. Consequently, the QS data at 300 K are available in a narrower concentration range. Nevertheless, it can be seen from Fig. 3 that the QS of Fe-B, Si (Ref. 16), Ge (Ref. 17), and Sb share a similar behavior: As the Fe concentration increases above 40 at.% of Fe, QS also increases. Although a definite QS value for amorphous Fe cannot be directly obtained, it should, according to the trend, be much larger than the QS value of amorphous Fe obtained from Fe-T_E systems (0.33 mm/sec). It is therefore conclusive that the short-range order, as revealed from the QS data, is not unique in *a*-Fe.

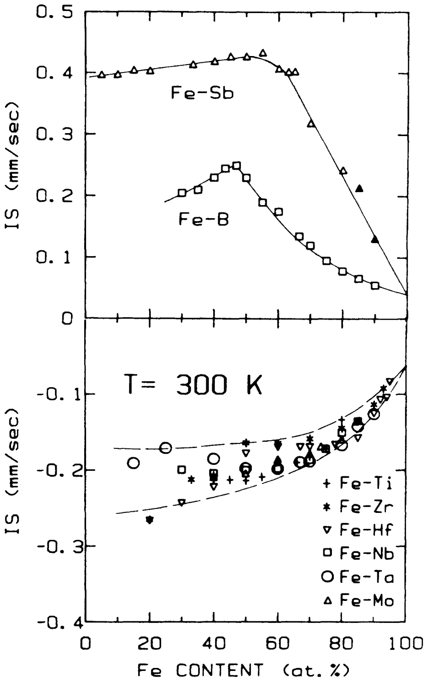

FIG. 2. Concentration dependence of isomer shift with respect to bcc α-Fe at 300 K of Fe-T_E and Fe-M amorphous systems.

It is not necessary to insist upon a unique form of *a*-Fe.[18] Under different conditions such as alloying and high pressure, a portion of different local units may adjust themselves and physical properties will vary accordingly. It is a reasonable conjecture that *a*-Fe may consist of a group of local structural units similar to those of bcc, fcc, and hcp. Therefore its magnetic properties should be related to those of bulk Fe in different structural forms, because an iron atom surrounded by one or, at most, two shells of neighbors generally exhibits bulk properties.[2] In its crystalline form, the magnetic properties of Fe depend sensitively on the structure and nearest-neighbor distance. The bcc α-Fe is the most stable phase of Fe, having a

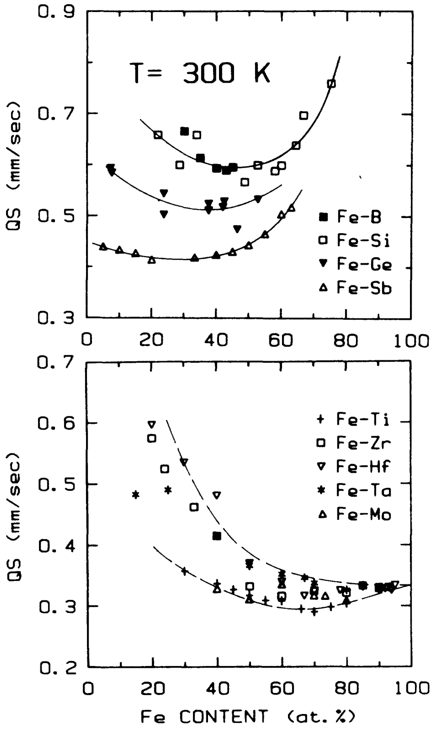

FIG. 3. Concentration dependence of electric quadrupole splitting at 300 K of Fe-T_E and Fe-M amorphous systems. The data for Fe-Si and Fe-Ge systems are from Refs. 16 and 17.

magnetic moment of $\mu_{\mathrm{Fe}}=2.21\mu_B$ and a T_c of 1044 K. As for the fcc γ-Fe, Tauer and Weiss[6] postulated the existence of two states. The γ_1 state was considered to be antiferromagnetic with a moment of about $0.5\mu_B$, while the γ_2 state was ferromagnetic with a moment of about $2.8\mu_B$. Recently, the two-state hypothesis of fcc Fe has attracted a great deal of attention. Modern *ab initio* band calculations performed independently by Kubler,[2] Bagayoko and Callaway,[3] Wang, Klein, and Krakauer,[4] and Pinski *et al.*[5] all confirmed the existence of a low-Fe-atomic volume, low moment ($<1\mu_B$), antiferromagnetically ordered fcc-Fe state, and a high-Fe-atomic volume, high moment ($>2\mu_B$), ferromagnetically ordered fcc-Fe state. The transition between these two states occurs at a nearest-neighbor distance of about $d_{\mathrm{NN}}=2.54$ Å (Kubler), 2.60 Å (Bagayoko *et al.*), 2.56 Å (Wang *et al.*), and 2.50 Å (Pinski *et al.*). On average, $d_{\mathrm{NN}}=2.55$ Å or $V_{\mathrm{Fe}}=11.7$ Å^3 can be chosen as the *critical* nearest-neighbor distance or Fe atomic volume.

Experimentally, the γ_1 state has been observed in Fe precipitates from supersaturated Fe-Cu solid solution,[19] and in thin epitaxial Fe films on Cu.[20] The high-moment γ_2 state has not been observed conclusively. However, recently metastable homogeneous fcc-Fe-Cu alloys have been made by vapor quenching over a very large concentration range.[21] The γ-Fe has an extrapolated atomic volume exceeding that of the critical value, with a T_C of 800 K and a magnetic moment of about $2\mu_B$. These characteristics are very close to those expected for the γ_2 state of Fe.

Structural studies of a number of transition-metal–metalloid and transition-metal–transition-metal amorphous alloys indicate that the structure of the transition metal resembles the dense-random-packing structure, with coordination number of about 12 and volume packing fraction approaching 74%, which is similar to the fcc structure.[1] Therefore, the different moment states of a-Fe from Fe-T_E and Fe-M (Fig. 1) naturally lead us to propose a connection with the γ_1 and γ_2 states of fcc Fe. In the a-Fe obtained from Fe-T_E, a certain portion of the local units are γ_1-Fe-like, and these are responsible for the Fe moment reduction and the emergence of antiferromagnetic interactions. In fact, many Fe-rich Fe-T_E alloys are asperomagnetic in nature and have small ordering temperatures (<300 K).[8-10,22] The large sudden change in magnetic moment at the amorphous-crystalline phase boundary is then a consequence of the structural change from γ_1-Fe-like to bcc-α-Fe-like local units. On the other hand, the fcc local units in a-Fe obtained from the Fe-M system are γ_2-Fe-like, being a high-moment state with a moment similar to that of bcc α-Fe. This relation was also suggested recently by Cowlam and Carr in a-Fe-B alloys.[23] The implication in the above discussion is that in Fe-T_E systems, a-Fe has a smaller nearest-neighbor distance or average Fe atomic volume than the a-Fe in Fe-M systems. Structural studies support this postulate. Values of the nearest-neighbor distance or the atomic Fe volume obtained from structural investigations are about $d_{\mathrm{NN(Fe)}}=2.60$ Å or $V_{\mathrm{Fe}}=12.3$ Å^3 as extrapolated from the Fe-B system.[24-26] Such values are above the critical value for the $\gamma_1-\gamma_2$ transition. However, in the Fe-T_E systems, the opposite was observed, for example, extended x-ray-absorption fine structure[27] and neutron diffraction[28] of $\mathrm{Fe_{90}Zr_{10}}$ indicated that $d_{\mathrm{NN(Fe)}}$ is about 2.415 and 2.45 Å. The density study[29] of the Fe-Zr system gave an average pure Fe atomic volume of $V_{\mathrm{Fe}}=10.71$ Å^3 (i.e., $d_{\mathrm{NN(Fe)}}=2.47$ Å). It should be mentioned that the value of the magnetic moment and the nature of the magnetic order in the Fe-rich region of the Fe-T_E alloys differ from those of γ_1-Fe. This infers that the Fe-T_E alloys also consist of local units which are ferromagnetic and have appreciable moments. The coexistence of local ferromagnetic and antiferromagnetic units makes the Fe-T_E alloys generally asperomagnetic in nature.

In conclusion, concentration dependence of magnetic hyperfine field, magnetic ordering temperature, isomer shift, and electric quadrupole splitting of a number of Fe-T_E and Fe-M amorphous systems indicate clearly that amorphous pure Fe has different states. It is suggested that the a-Fe obtained from Fe-T_E and Fe-M systems contains a certain portion of γ_1-fcc-Fe and γ_2-fcc-Fe local structural units, respectively, which is supported by structural studies of Fe-T_E and Fe-M amorphous systems.

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