

Polymorphism of amorphous pure iron

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We investigate the state of amorphous pure Fe by utilizing various Fe-based amorphous alloy systems having stable amorphous phases up to very high Fe concentrations and extrapolating the properties toward those of amorphous pure Fe. Concentration dependence of hyperfine interaction parameters of Fe-early transition metal (Ti, Zr, Hf, Nb, Ta, and Mo) and Fe-metalloid (B, Sb, Si, and Ge) reveals the polymorphism of amorphous Fe.

I. INTRODUCTION

Amorphous pure Fe is a very appealing entity, not only for the fundamental understanding, but also for the fabrication of new Fe-based amorphous alloys of practical interest. Unfortunately, the extreme instability has prevented the successful fabrication of amorphous pure Fe. An attractive alternative is to utilize various amorphous systems having a stable amorphous phase up to very high Fe concentrations and extrapolate the properties toward amorphous Fe. Based on the magnetic properties, it has been suggested¹ that more than one kind of amorphous Fe could exist. However the polymorphism of amorphous Fe remains controversial, any definite conclusions require further experimental results in various aspects.

Taking the advantage of the vapor-quench method in making binary amorphous alloys over a wide concentration range, we have studied two important classes of Fe-based amorphous alloys, i.e., Fe-early transition metal (ET) (ET = Ti, Zr, Hf, Nb, Ta, and Mo) and Fe-metalloid (M) (M = B, Sb). The purpose of this work is to give a systematic study of the concentration dependencies of magnetic characteristics and hyperfine interactions, namely, magnetic hyperfine field, isomer shift (IS), and electric quadrupole splitting (QS), which probes into the problem of amorphous pure Fe.

II. EXPERIMENT

All the samples studied in this work were prepared by a magnetron sputtering system. The vacuum before the sputtering was in the 10^{-8} – 10^{-7} Torr range. The films were deposited onto liquid-nitrogen-cooled substrates of copper and Kapton with 4-mTorr Ar as the sputtering gas. Typical sputtering rate was in the range of 500–1000 Å/min and the sample thicknesses are about 5–15 μm. Detailed sample fabrication has been described in Ref. 2.

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 ⁵⁷Co in Rh source.

III. RESULTS AND DISCUSSION

A common feature shared by all Fe-ET 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 dependent on the alloy system). In Fig. 1, the concentration dependencies of the effective magnetic hyperfine field (H_{eff}) at 4.2 K of four Fe-ET sys-

tems are displayed, where H_{eff} is proportional to the average magnetic moment of Fe atoms. All the crystalline samples obtained with the same sputtering method have bcc structures, and can be regarded as extensions of bcc α -Fe. Extrapolating the H_{eff} of the amorphous phase to pure Fe, we find that the H_{eff} of amorphous Fe is much lower than that of bcc-Fe. The magnetic ordering temperatures of *all* the binary amorphous Fe-ET 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-ET, in Fe-M systems such as Fe-B, Sb, Si (Ref. 3), and Sn (Ref. 4), *no* discontinuity is observed in magnetic moment at the phase boundary, and the magnetic moment continuously approaches the moment of bcc-Fe by extrapolation. Figure 1 also shows the concentration dependence of H_{eff} of two typical Fe-M sys-

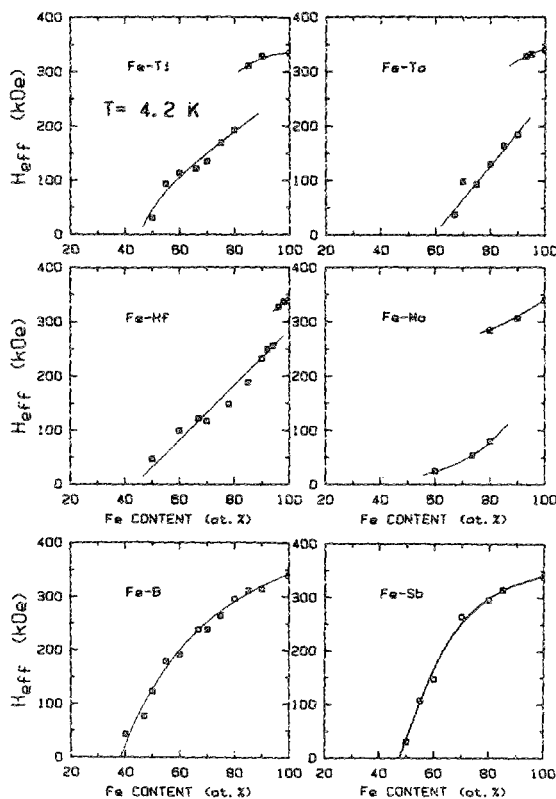


FIG. 1. Concentration dependencies of effective magnetic hyperfine field at 4.2 K of Fe-early transition metal and Fe-metalloid amorphous systems.

tems, Fe-B and Fe-Sb, in which a smooth curve connecting the H_{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-ET alloys is very different from that in Fe-M alloys and the structural topology of amorphous pure Fe is not unique.

The possibility of different short-range orders in amorphous pure Fe is further supported by isomer shift (IS) and quadrupole splitting (QS) data. The two hyperfine interaction parameters of IS and QS, readily available from the Mössbauer spectrum, are related to the local atomic environment. IS measures the s -electron density at the nucleus, giving valuable information about charge transfer and electron distribution, whereas QS is sensitive to the local atomic symmetry and short-range order. If the short-range order of amorphous Fe is indeed nonunique, we should expect the extrapolated IS and QS to be different too.

Figure 2 shows the concentration dependence of isomer shift at 300 K with respect to bcc α -Fe for several Fe-M and Fe-ET systems. In all the Fe-M and Fe-ET systems studied here and those studied by other groups, we find that the following observation is always true, that is, the sign of IS in Fe-M systems are exclusively positive, and in Fe-ET systems negative. This has been studied previously^{5,6} and can be explained by the relative importance of interatomic charge transfer and intra-atomic s - d electron conversion. What is more intriguing in Fig. 2 is that the extrapolated IS value of amorphous Fe from Fe-M systems (~ 0.04 mm/s) is very different from that obtained from Fe-ET systems (~ -0.06 mm/s). It is well known that the IS of Fe depends sensitively on its structure.⁷ 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/s, i.e. $IS_{\gamma\text{-Fe}} = -0.08$ mm/s, a value close to that of amorphous Fe extrapolated from Fe-ET alloys.

Another useful parameter is the electric quadrupole splitting (QS) which is zero for crystalline α - or γ -Fe because of the cubic symmetry. In amorphous solids, the atomic site symmetry is lower than cubic, therefore QS value is

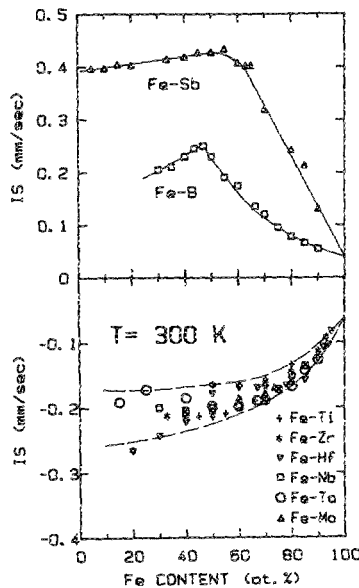


FIG. 2. Concentration dependencies of isomer shift with respect to bcc α -Fe at 300 K of Fe-ET and Fe-M amorphous systems.

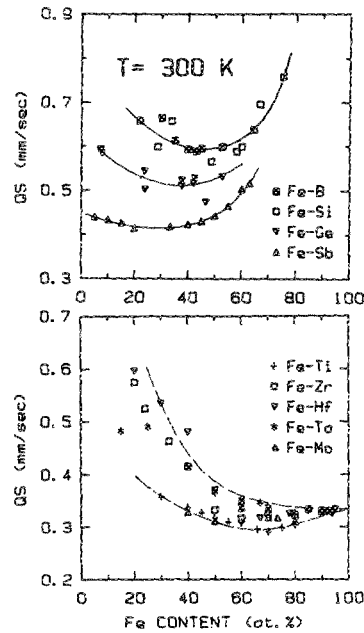


FIG. 3. Concentration dependencies of electric quadrupole splitting at 300 K of Fe-ET and Fe-M amorphous systems. The data on Fe-Si and Fe-Ge systems are from Refs. 8 and 9.

never zero. Figure 3 shows the concentration dependence of QS at 300 K for Fe-M and Fe-ET systems. A point of special interest is that the QS of amorphous Fe obtained from Fe-ET system is about 0.33 mm/s. In the Fe-M systems, QS at the Fe-rich side cannot be directly obtained, because the samples are magnetic above 300 K, 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,⁸ Ge,⁹ and Sb share similar behaviors. As the Fe concentration increases above 40 at. % of Fe, QS also increases. Although a definite QS value for amorphous Fe can not be directly obtained, it should, according to the trend, be much larger than the QS value of amorphous Fe obtained from Fe-ET systems (0.33 mm/s). It is therefore conclusive that the short-range order as revealed from the QS data are not unique in amorphous Fe.

It is not necessary to insist on an unique form of amorphous Fe. Under different conditions such as alloying and high pressure, the portion of different local units may adjust themselves and physical properties will vary accordingly. In its crystalline form, Fe exhibits weak ferromagnetism. Its magnetic properties sensitively depend on the structure and nearest-neighbor distance.¹⁰⁻¹² Amorphous Fe may consist of a group of structural units similar to those of bcc, fcc, and hcp. The different morphology could be a result of different portions of these units and nearest-neighbor distances with similar free energies. Diffraction study on high Fe concentration Fe-based amorphous alloys is promising in determining the atomic structure of amorphous pure Fe.

IV. CONCLUSIONS

Concentration dependence of magnetic hyperfine field, isomer shift and electric quadrupole splitting of Fe-ET and Fe-M amorphous systems indicate clearly that amorphous pure Fe is polymorphic. The amorphous pure Fe obtained from Fe-M systems has larger IS, QS and magnetic moment than those from Fe-ET systems.

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