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Magnetic properties and hyperfine interactions in concentrated Fe-Ag alloys

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Fe and Ag, mutually insoluble in both the liquid state and the solid state, are two elements with no previously known alloys and compounds. Using a vapor-quench technique, we have fabricated, for the first time, noncrystalline, *concentrated* Fe-Ag alloys. The first measurements of the magnetic properties and hyperfine interactions of Fe-Ag in the solid state are reported. The successful fabrication of these alloys suggests that the vapor-quench method can be used to form other previously inaccessible alloys based on mutually insoluble components.

I. INTRODUCTION

Problems related to the formation of metallic alloys and compounds are of great interest from both practical and fundamental standpoints. One aspect of this problem is to understand why many combinations of metallic elements readily form alloys or compounds while some are essentially insoluble.[1] In this respect the Fe-Ag system is one of the most extreme, the solubility in *both* the liquid and solid states being well below 1%.[2] Consequently, no concentrated Fe-Ag alloys or compounds have previously been reported. Successful attempts to study Fe-Ag alloys have been restricted to compositions near the dilute elemental limits. All studies, for example, of the Fe hyperfine interactions have been limited to source experiments (by diffusion of ppm quantity of ^{57}Co into Ag)[3,4] or ion implantation experiments (Fe into Ag).[5] In the latter case, analysis of the resulting samples revealed that most of the Fe-containing phases are not Fe-Ag alloys, further confirming the near insolubility of Fe in Ag. It is not surprising that these samples, containing such small amounts of Fe, are nonmagnetic.

Since the solubility of Fe and Ag as liquid is very small, the usual metallurgical procedures would not yield even metastable Fe-Ag alloys. If, however, the liquid state could be by passed and a sufficiently high effective quenching rate achieved the possibility remains for preserving some *single-phase, metastable,* and *concentrated* Fe-Ag alloy. As described in detail in the remainder of this paper, this expectation has been realized.

In this work we report the successful fabrication of new, concentrated Fe-Ag alloys made by a vapor-quenching process. The first measurements of the magnetic properties and hyperfine interactions are also reported. The existence of such alloys raises interesting questions concerning the solubility of the elements and it suggests that other insoluble metallic systems may also be fabricated into solid alloys.

II. EXPERIMENTAL

There are several well-established rapid-quenching processes, with the two most common being the liquid-quench and vapor-quench methods.[6-8] As mentioned earlier, owing to the phase separation of Fe and Ag as liquids, one would not expect any method of cooling from the melt, rapid or otherwise, to form single-phase alloys of Fe and Ag. For this reason we have used the vapor-quench method, relying on its higher effective quenching rate and the avoidance of the liquid state altogether. In this respect one notes that this method has successfully been applied in recent years in making a number of amorphous solids.[8,9] Its high effective quenching rate is demonstrated by the fact that many vapor-quenched amorphous solids cannot be obtained by liquid quenching.[10]

Compositions near $Fe_{50}Ag_{50}$ were chosen for study based on the following considerations. These compositions, far from the pure elemental limits, would represent a concentrated Fe-Ag alloy. In addition, recent experience with a variety of amorphous Fe-*X* (*X* = B, C, Zr, Nb, etc.) alloys indicates that samples in this concentration range usually exhibit greater stability than those containing much greater amounts of metallic constituents.[9-11] From the standpoint of their magnetic properties, samples with high Fe concentrations often have Curie temperatures near, or even above, their crystallization temperatures, making T_c determinations difficult or impossible. On the other hand, Fe-*X* systems with low Fe concentrations are nonmagnetic. Thus Fe-Ag samples near the equiatomic compositions offer the best prospects for being magnetic, having conveniently low values of T_c, and being reasonably stable at room temperature.

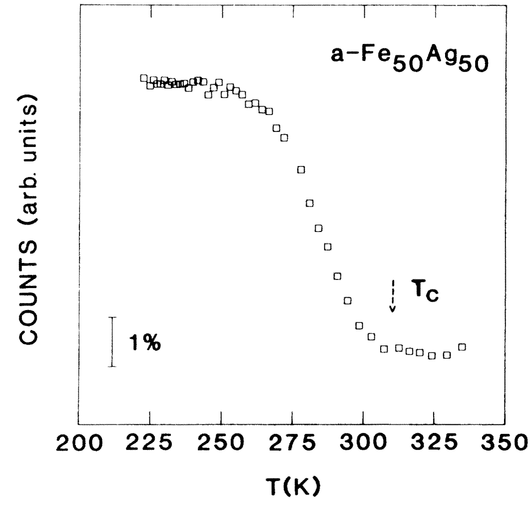

FIG. 1. Determination of the magnetic ordering temperature (indicated by the arrow) of $Fe_{50}Ag_{50}$ from the onset of the magnetic hyperfine interaction by the thermal scan method.

All the samples have been prepared by a high-rate sputtering device. Owing to the insolubility of Fe and Ag as liquids it is impossible to prepare homogeneous arc-melted sputtering targets. Instead, pressed targets made from appropriate amounts of well-mixed Fe (99.9% pure) and Ag (99.99%) powder have been used. Films from 5 to 10 μm in thickness have been deposited at rates of about 0.03 μm/min onto liquid-nitrogen-cooled copper or Kapton substrates. Water-cooled substrates were also tried but with poorer results due to the low crystallization temperatures of the samples. In those runs where single-phase Fe-Ag alloys failed to appear, the sample contained large amounts of crystalline α-Fe as expected.

The film composition and the absence of occluded gases (e.g., oxygen) in some of the samples have been confirmed by Auger analyses. In some cases the film surfaces show evidence of discoloring after exposure to the atmosphere for several weeks. This is probably due to surface oxidation although no change in the transmission Mössbauer spectrum has been found. For this reason, additional samples have been made with a 1-μm-thick Al overcoat. There are no observable differences in the bulk properties between the Al-coated samples and the bare samples.

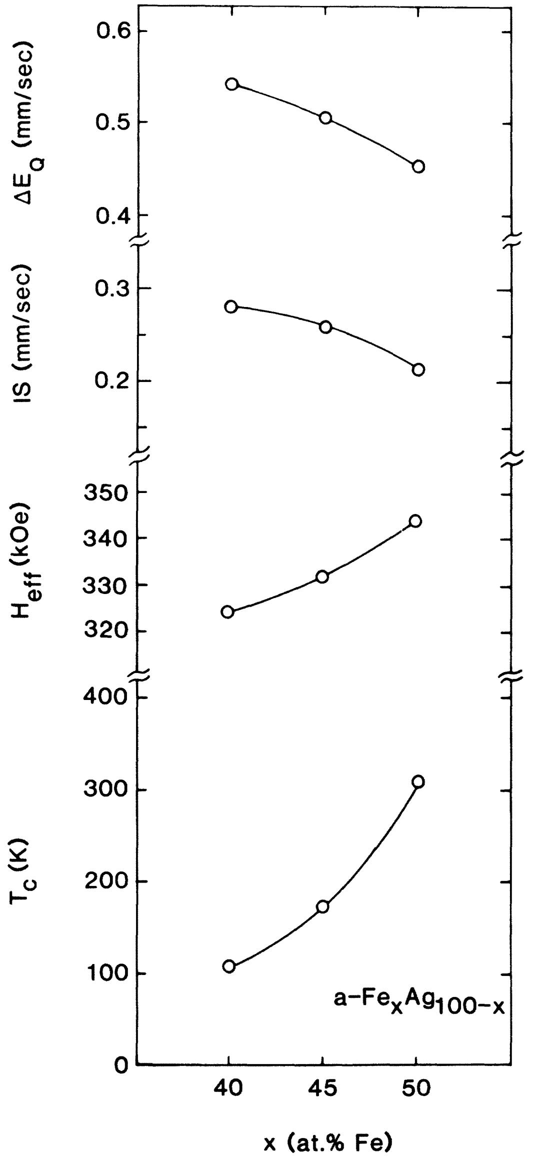

FIG. 2. Magnetic ordering temperature (T_c), effective hyperfine field ($H_{\rm eff}$) at 4.2 K, isomer shifts (IS) relative to α-Fe at room temperature, and quadrupole splitting (ΔE_Q) at room temperature of vapor-quenched Fe$_x$Ag$_{100-x}$ alloys.

Of considerable interest is the structure of the Fe-Ag alloys. If the vapor-quenched Fe-Ag alloys were crystalline, one would expect their structure to be either bcc (in the case of pure Fe) or fcc (in the case of pure Ag). However, x-ray diffraction measurements reveal that these samples are *noncrystalline* with no sharp lines indicative of any crystalline phases.[12] Considering the insolubility of Fe and Ag, this is perhaps not surprising. The noncrystalline nature of the samples is further confirmed by the crystallization process observed at elevated temperatures. Nevertheless, like x-ray characterization of all noncrystalline solids, one cannot rule out with absolute certainty the possibility of microcrystallites which may escape detection due to their extremely small sizes.[13]

Conventional ^{57}Fe Mössbauer spectroscopy has been used to study the hyperfine interactions and magnetic properties of these samples. A thermal scan method has been used to determine the values of the magnetic ordering temperatures as well as the crystallization temperatures. ac susceptibility measurements have also been used to determine the magnetic ordering temperatures. The details of the susceptibility measurements will be reported elsewhere.

III. RESULTS AND DISCUSSIONS

Owing to the nearly complete insolubility of Fe and Ag, crystalline α-Fe appears if a single-phase Fe-Ag alloy fails to materialize. The absence of α-Fe is, therefore, a necessary condition for the existence of an Fe-Ag alloy. Crystalline α-Fe is ferromagnetic below the Curie temperature of 1043 K. The hyperfine properties are well known with a distinct isomer shift, no quadrupole splitting due to the cubic site symmetry, and a saturation hyperfine field of 342 kOe.[14] These signatures of α-Fe are readily identifiable by Mössbauer spectroscopy, even if the α-Fe is only one of several phases present in a sample. No evidence indicating the presence of α-Fe has been found in the spectra of the sputtered Fe-Ag alloys. In fact, the magnetic properties and hyperfine interactions of the Fe$_x$Ag$_{100-x}$ ($40 \leq x \leq 50$ at. % Fe) are completely different from those of crystalline α-Fe.

The magnetic ordering temperatures (T_c) of the samples have been determined from the onset of the magnetic hyperfine interaction as shown in Fig. 1 in the case of Fe$_{50}$Ag$_{50}$. The value of T_c increases sharply from 110 K for Fe$_{40}$Ag$_{60}$ to 310 K for Fe$_{50}$Ag$_{50}$ as shown in Fig. 2. These values have also been independently confirmed by ac susceptibility measurements to within the experimental uncertainty of a few degrees.

The crystallization temperature of the samples turns out to be quite low (see below). The sharply rising values of T_c suggest that for high-Fe-content samples (e.g., $x \gtrsim 60$ at. % Fe), the values of T_c are likely to be near or above the crystallization temperature and therefore beyond direct experimental determination.

Mössbauer spectra of the Fe-Ag alloys in the paramag-

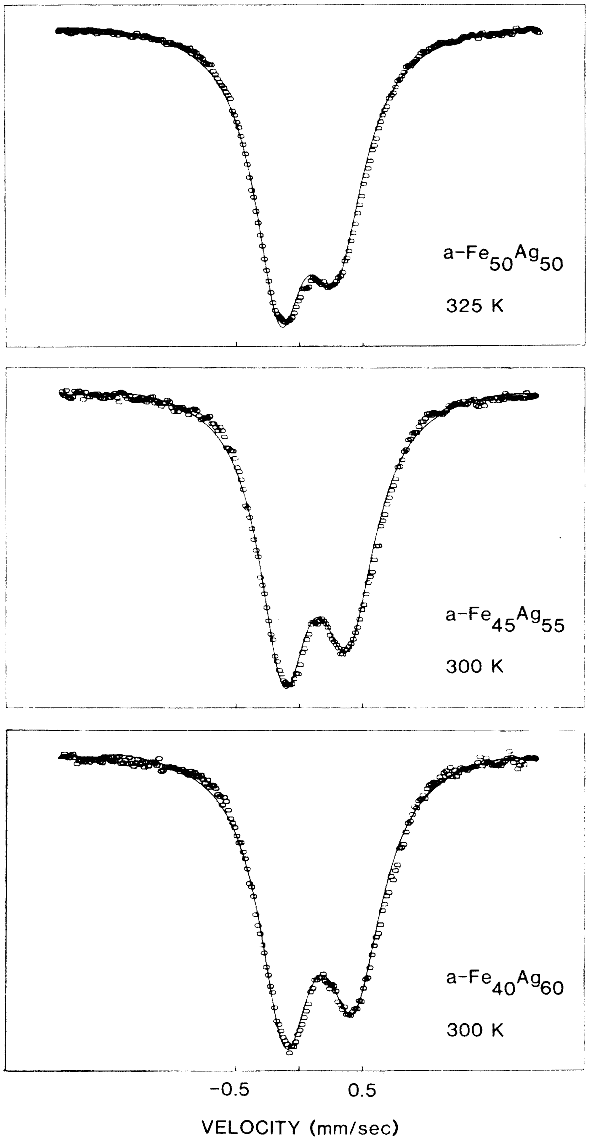

FIG. 3. Quadrupole spectra of Fe_xAg_{100-x} near room temperature.

netic state ($T > T_c$) are shown in Fig. 3. These spectra are quadrupole-split doublets with no magnetic hyperfine interaction. The spectrum of $Fe_{50}Ag_{50}$ is taken at 325 K instead of 300 K, as in the other cases, because its Curie temperature ($T_c = 310$ K) is slightly above room temperature. The slight asymmetry of the two peaks, as very often observed in many amorphous solids, is most likely caused by a correlation of the isomer shift and quadrupole splitting.[15] The quadrupole splitting varies from about 0.55 mm/sec for $Fe_{40}Ag_{60}$ to 0.45 mm/sec for $Fe_{50}Ag_{50}$ as shown in Fig. 2. The observed large quadrupole splitting provides direct evidence that the Fe site symmetry is generally *noncubic*. This feature, although generally observed in all amorphous solids, should be contrasted with crystalline α-Fe, for which the quadrupole splitting is zero. Furthermore, at room temperature, the spectrum of α-Fe is a six-line pattern (similar to that shown in the top of Fig. 4), which is completely different from those shown in Fig. 3.

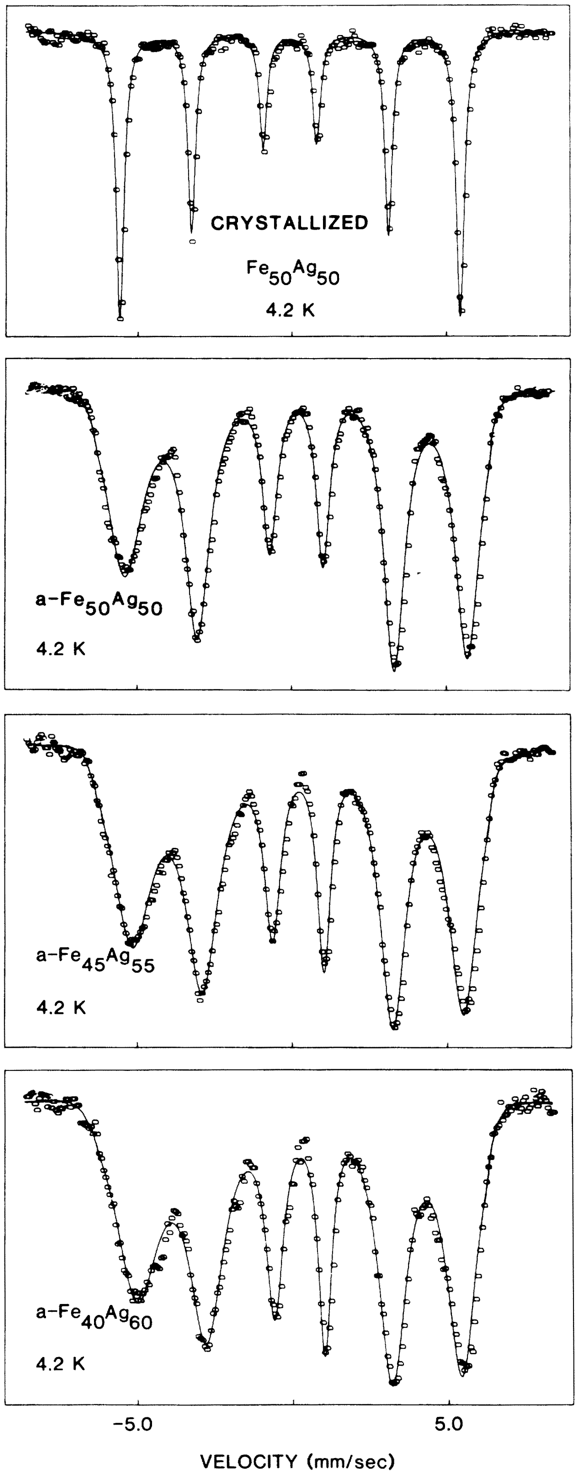

FIG. 4. Mössbauer spectra of crystallized $Fe_{50}Ag_{50}$ (top) and noncrystalline Fe_xAg_{100-x} at 4.2 K.

Below T_c, magnetic hyperfine spectra are observed as shown by the bottom three spectra in Fig. 4. The spectral linewidths, although large compared with those of crystalline solids, are noticeably smaller than those of many well-known amorphous solids.[9,10] This indicates that the hyperfine field distributions are relatively narrow. The asymmetry in the line intensities can be accounted for by a

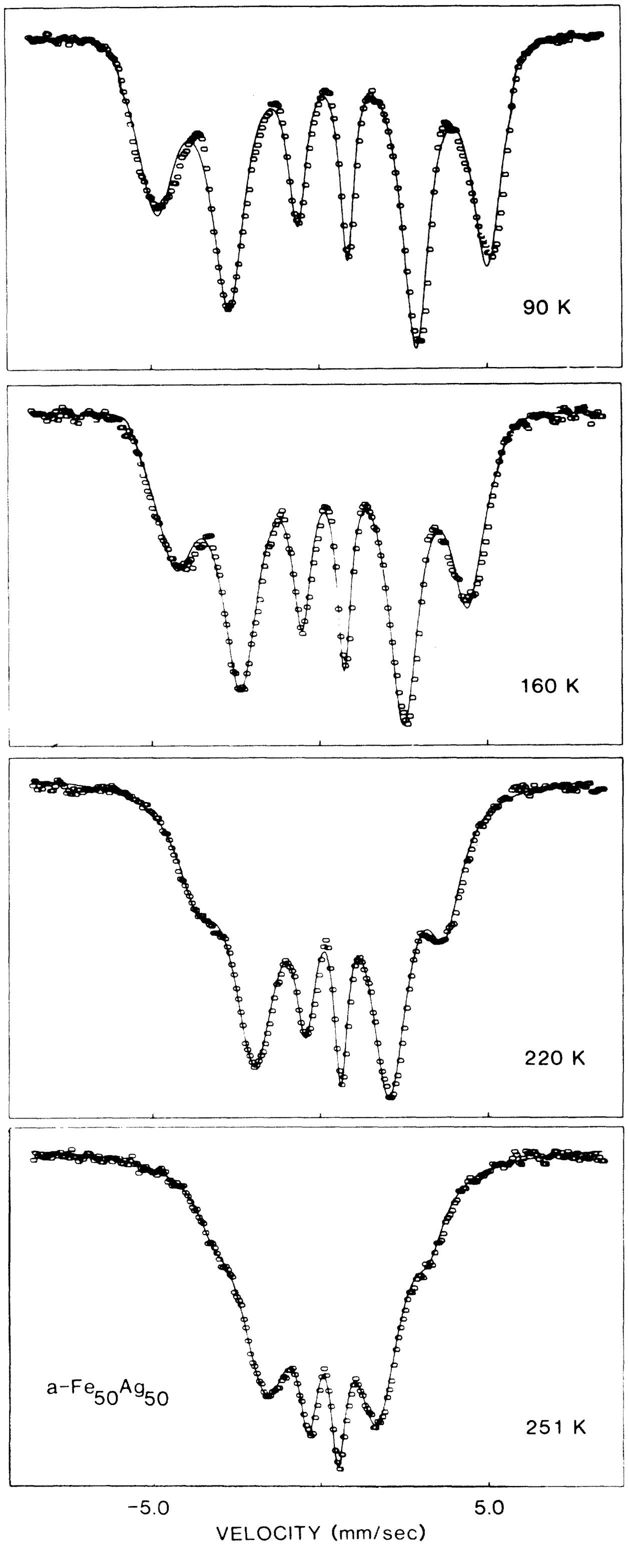

FIG. 5. Mössbauer spectra of $Fe_{50}Ag_{50}$ at various temperatures.

correlation between the isomer shift and the hyperfine field.[16] On the other hand, since the six spectral lines are rather well resolved, the spectra can be well described by six independent spectral lines, the positions of which define an effective hyperfine field (H_{eff}). The effective hyperfine field at 4.2 K (essentially that at $T=0$ K) varies from 325 to 345 kOe for the Fe-Ag alloys as shown in Fig. 2. It is worth noting that, despite as much as 60% dilution, the Fe hyperfine field and therefore the Fe moment are only slightly diminished. This should be contrasted with many amorphous Fe-*X* systems in which a drastic reduction of the hyperfine field and moment occurs with decreasing Fe content.[9–11] The magnetic properties of Fe-Ag suggest that the strong chemical effects (e.g., charge transfer,[17] bond model,[18] etc.) which are dominant in other metallic glasses, are less important. In this respect, the magnetic behavior is more characteristic of simple dilution. From this standpoint, the Fe-Ag system may turn out to be magnetically simpler, and therefore more desirable, for the study of magnetic properties than the more common metallic glasses.

At increasing temperatures, the magnetic hyperfine splitting decreases as shown in Fig. 5. The resulting effective hyperfine fields, as a function of temperature, are shown in Fig. 6 and are consistent with the behavior expected for a homogeneous magnetic solid.[14] It should be mentioned that these spectra are distinctively different from the superparamagnetic spectra observed in small magnetic particles, a possibility one might consider.[19] Furthermore, the fact that ac susceptibility and Mössbauer spectroscopy measurements yield the same T_c, despite their vastly different effective measuring times, also rules out the possibility of superparamagnetism in small magnetic particles. The measured values of T_c therefore indicate genuine magnetic transitions of bulk homogeneous solids.

The metastable nature of these noncrystalline solids is demonstrated by the crystallization process. The crystallization behavior of the samples has also been followed by the thermal scan method. An abrupt change in the counting rate occurs at the onset of crystallization. For the present samples, this occurs in the temperature range of 525–575 K. One such example is shown in Fig. 7 for $Fe_{50}Ag_{50}$. Mössbauer spectra of the crystallized samples reveal only *one* Fe-containing phase which exhibits all the

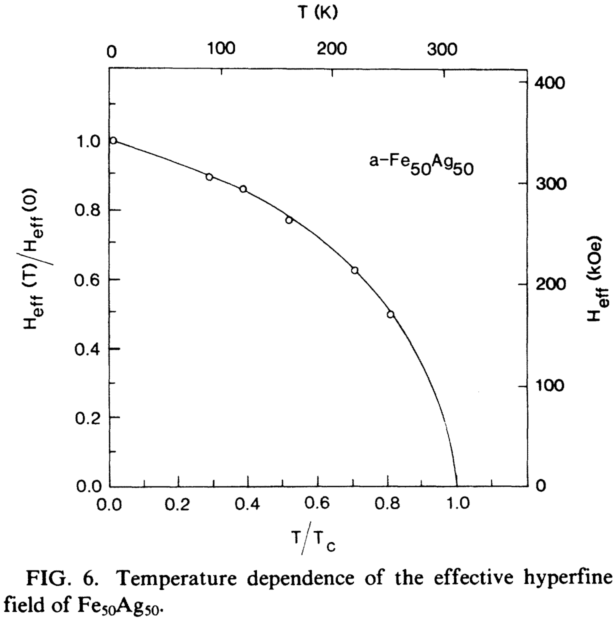

FIG. 6. Temperature dependence of the effective hyperfine field of $Fe_{50}Ag_{50}$.

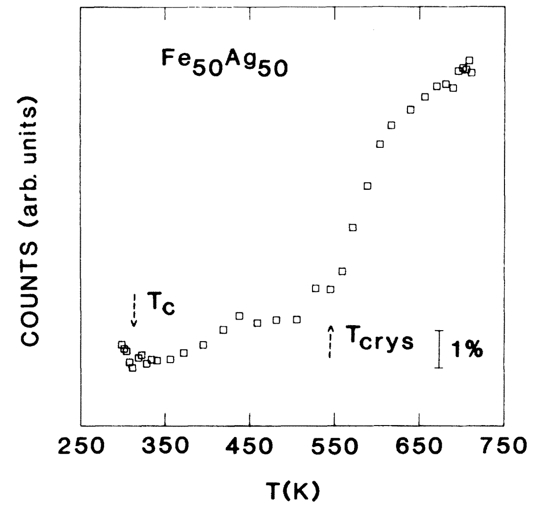

FIG. 7. Crystallization of $Fe_{50}Ag_{50}$ as observed by the thermal scan method. The arrows indicate T_c of the noncrystalline state and the approximate onset of crystallization (T_{crys}).

characteristics of crystalline α-Fe as shown at the top of Fig. 4. These results demonstrate the metastability of the Fe-Ag alloys, reconfirm the insolubility of Fe and Ag in the crystalline state, and show that α-Fe is the only stable Fe-containing solid in the Fe-Ag system.

Solid solubility, or lack thereof, is usually defined under equilibrium conditions. Extensions (i.e., nonequilibrium) of solid solubility limits, however, can sometimes be obtained by rapid quenching from the melt, as first demonstrated by Duwez and co-workers,[6] or by vapor-deposition techniques. In the present case of Fe-Ag we have shown that drastic extensions of the equilibrium solubility limits can be achieved even in an alloy system for which there is negligible solubility in both the solid and liquid states. The existence of alloys of this kind raises a number of interesting questions concerning the atomic structure, the cohesive energy, heats of solution, and the factors determining alloy stability.[1] Furthermore, the fact that these Fe-Ag alloys are noncrystalline illustrates that the formation of a noncrystalline state does not depend on the existence of crystalline alloys or compounds.

Finally, the successful fabrication of these Fe-Ag alloys indicates that other immiscible metallic systems, hitherto not accessible to experimental investigation, may also be made into single-phase solids. Our preliminary results on Fe-Pb, another well-known immiscible system, show that this is indeed the case.[11]

ACKNOWLEDGMENTS

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[12] The noncrystallinity of the Fe-Ag sample was determined from films deposited on Kapton substrates. The x-ray diffraction patterns, similar to those of many other amorphous solids, show no evidence of sharp diffraction peaks. Because of a non-negligible contribution from the substrates, we have not attempted to obtain the radial distribution functions from the x-ray analyses. We are currently preparing suitable samples (e.g., substrate free) for such purposes.

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