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Magnetic properties of Fe_xCu_{100-x} solid solutions

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In the equilibrium states, the solid solubility between Fe and Cu is negligibly small. Using vapor deposition, however, we produced Fe_xCu_{100-x} solid solutions over the entire composition range. All the samples were crystalline: bcc structure at the Fe-rich side and fcc structure at the Cu-rich side. The transition from bcc to fcc occurred at around $x=70$, where the two phases were found to coexist. The fcc alloys exhibit a magnetic dilution leading to a magnetic percolation threshold at $x_c \simeq 18$, rarely seen in binary Fe alloys. Below x_c, only spin-glass-like ordering is observed. Across the structure transition from fcc to bcc, there is a large discontinuity in T_C, and a very slight change in the atomic volume. Surprisingly, there are no noticeable discontinuities in the magnetic moment, hyperfine field, and isomer shift. The electronic structure of these alloys is discussed based upon x-ray photoemission spectroscopy measurement.

The alloying effect on magnetism of transition metals has been a subject of long-standing interest. In particular, the behavior of Fe-based alloys has been extensively studied, since it is more complex than that of other metals. For instance, while the alloying effect of Co- and Ni-based alloys can be understood, in most cases, within the framework of Friedel's theory,[1] the magnetic moment in Fe-based alloys does not follow a simple rule. This is generally considered to be a consequence of the magnetic weakness of Fe, in which the majority spin band is not filled, so that the system has a high susceptibility to external or internal perturbation.[2] In many cases, the magnetic moment of the Fe atom is quickly reduced by alloying, and the alloy system becomes nonmagnetic substantially before the percolation limit for dilution is reached. In this paper, we report the observation of an exception to this general rule: in the Fe-Cu solid solution, the magnetic moment of the Fe atom remains nearly constant up to very high concentrations of Cu.

In the equilibrium state, Fe and Cu have very small mutual solid solubility and form no intermetallic compounds, even though their atomic radii are quite similar. This behavior is in accordance with the positive value of the calculated heat of mixing between Fe and Cu.[3] However, by using vapor-quenching methods such as sputtering, which bypass the liquid phase, the solid solubility can be extended, and a Cu-Fe solid solution can be formed over the entire range of composition.[4,5]

Samples of Fe_xCu_{100-x} alloys were produced by a magnetically assisted high-rate sputtering device operated in the dc mode. Samples typically 8–15 μm thick were deposited on various substrates, i.e., Kapton, sapphire, copper, etc., and cooled to liquid-nitrogen temperature. In some cases, thicker substrate-free samples were obtained. The atomic structure of the films on Kapton substrates were studied by x-ray diffraction, both by the conventional powder method using Cu $K\alpha$ radiation,and by energy-dispersive x-ray diffraction using a white x-ray source and energy-sensitive solid-state (intrinsic Ge) detector.[6]

It was found that the Fe-rich samples with $x > 75$ are in the bcc structure, while the samples with $x < 60$ are in the fcc structure. The samples with the intermediate compositions contain both bcc and fcc phases. The width

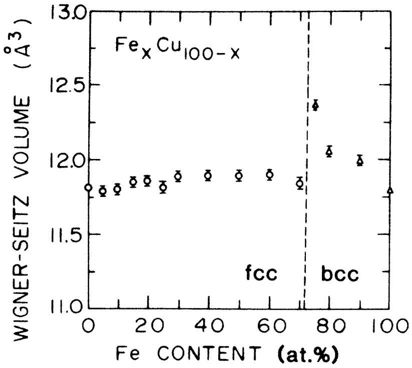

FIG. 1. Composition dependence of the Wigner-Seitz cell volume in Fe_xCu_{100-x}, calculated from the results of the energy dispersive x-ray diffraction. The results are consistent with those obtained by the standard diffraction measurement using Cu $K\alpha$ radiation.

of the diffraction lines indicates that the grain size in the single-phase region is much larger than 300 Å, but in the two-phase samples it was much shorter and was of the order of 40 Å for $x=75$. With the exception of the samples near the pure elemental limits, the solid solution was metastable and irreversible phase separation occurred upon heating, generally above 500 K. This result differs from the earlier report by Kneller[4] which stated that the phase change occurs between $x=10$ and $x=50$. The atomic volume in terms of the Wigner-Seitz cell volume is shown in Fig. 1. It is observed that alloying Fe into Cu hardly changes the lattice constant, but alloying Cu into bcc Fe induces a slight initial expansion of the lattice. The atomic volume at $x=75$ is anomalously large, indicating the tendency to instability of the bcc phase. Furthermore, the atomic volume changes only very slightly ($\sim 1.5\%$) through the phase transition from bcc to fcc. These results are consistent with the general knowledge[7] that the interatomic potential for Cu has a stronger core-core repulsion due to the filled d-electron shell, while the interatomic distance at which the potential is minimum is similar for Fe and Cu; note that in the bcc lattice, the potential minimum lies between the first- and second-nearest neighbors.[8]

The measurements of the magnetic ordering temperatures (T_C) of the samples have been made by Mössbauer spectroscopy and, in some cases, by bulk magnetic measurements. For the samples with $x<50$, the values of T_C are all lower than 450 K and can be safely determined without causing irreversible changes of the samples. These values, expressed by solid circles, are shown in Fig. 2 as a function of x. For the samples with $x>60$, the T_C's are much higher. Partial or complete phase transformation of the samples occurred after the T_C measurements were made even under high heating and cooling rates to avoid prolonged heating of the samples. These values are expressed by open circles in Fig. 2. For some of these intermediate compositions, Fig. 2 displays more than one determined value of T_C. In the case of $Fe_{60}Cu_{40}$, the values determined from fast heating and cooling circles are different due perhaps to inaccuracy or structural relaxation. In the case of $Fe_{70}Cu_{30}$, however, the data clearly display two distinct values of T_C differing by about 300 K.

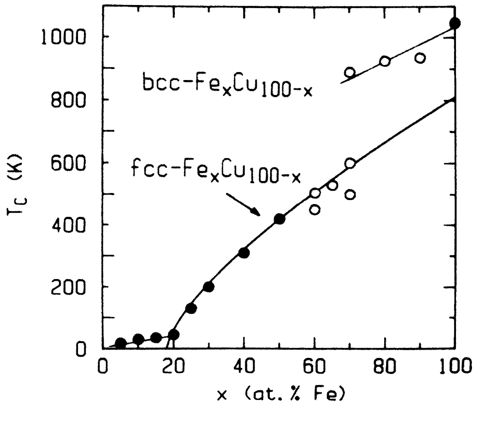

FIG. 2. Magnetic ordering temperatures of Fe-Cu alloys.

The magnetic ordering temperatures of all the Fe-Cu alloy samples as shown in Fig. 2 clearly illustrate that the values of T_C are higher for the bcc phase than for the fcc phases. A double T_C observed in $Fe_{70}Cu_{30}$ is a result of a mixture of both phases. More importantly, the fcc Fe-Cu alloys exhibit characteristics of simple magnetic dilution, which has not been realized in any binary Fe—transition-metal alloy systems, crystalline or amorphous. The magnetic dilution leads to a percolation behavior with a threshold of about $x_c=18$, which is in good agreement with the theoretical predictions for the fcc structure.[9] The values of T_C for the fcc alloys of $x>20$ can be well described by the equation $T_C(x)=37\ (x-18)^{0.7}$ which is the solid curve in Fig. 2.

The magnetic ordering temperatures of samples with

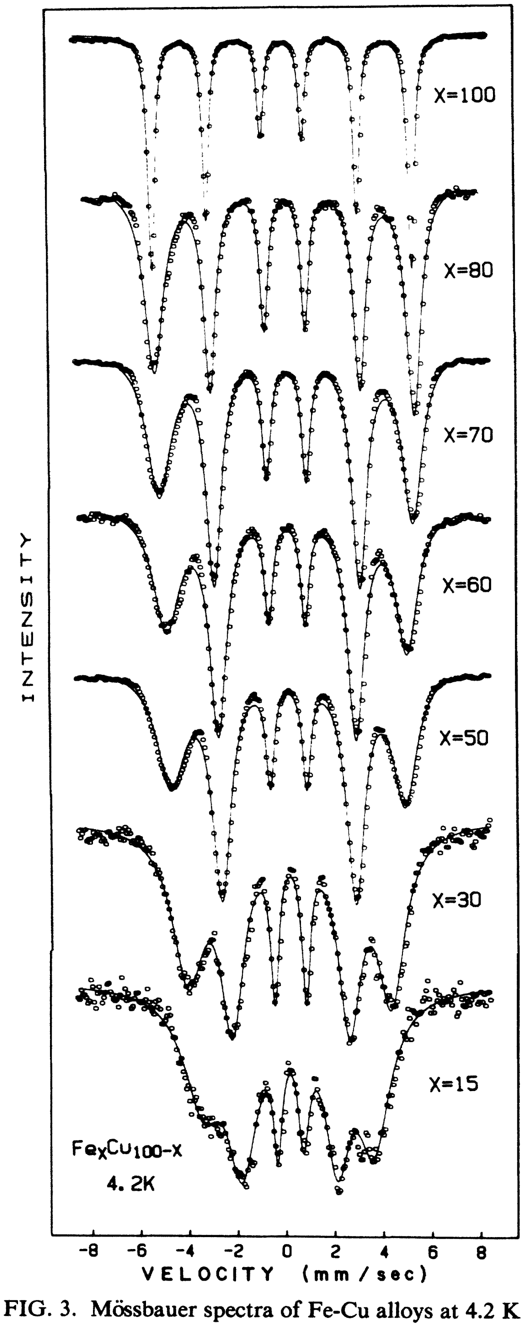

FIG. 3. Mössbauer spectra of Fe-Cu alloys at 4.2 K.

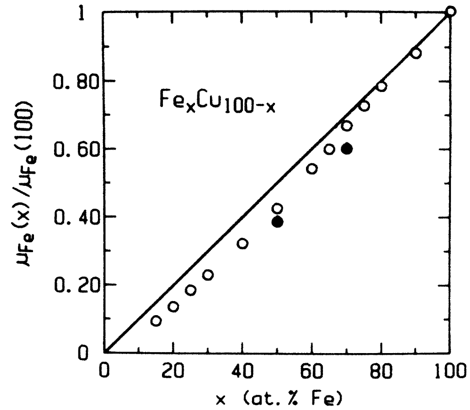

FIG. 4. Normalized hyperfine fields $H_{eff}(x)/H_{eff}(100)$ (open circles) and moments $\mu_{Fe}(x)/\mu_{Fe}(100)$ (solid circles) per transition-metal atom versus Fe concentration. The straight line is the result for a simple magnetic dilution.

still lower Fe content lie on a different curve as shown in Fig. 2. This curve is similar to those of crystalline Fe-Au (Ref. 10) and amorphous (Fe-Ni)—metalloid alloys,[11] and the ordering is spin-glass-like. This magnetic phase diagram suggests, although we have not yet examined it closely, the possibility of double magnetic transitions, paramagnetic—ferromagnetic—spin-glass or more complex ones, just above the percolation threshold.

Mössbauer spectra of the Fe-Cu samples at 4.2 K are shown in Fig. 3. Since nonenriched Fe was used, the low-Fe-content samples show a much smaller effect, reflected by the poorer statistics of the spectra. Several features are apparent from those spectra. With the exception of the $x=15$ sample where the magnetic ordering temperature is rather low, these spectra are essentially the same as those at 0 K. Other than that of pure α-Fe, all spectra exhibit broader linewidths, the result of multiple inequivalent Fe sites, as expected for disordered crystalline alloys. However, the broadenings are considerably smaller than those found in amorphous solids.[12] The effective hyperfine field (H_{eff}) and isomer shifts used are the most probable values determined by the spectral peak positions. The saturation effective hyperfine field H_{eff} decreases slightly with decreasing Fe content, but it is *finite* for *all* compositions. From the empirical but well-established approximation of the proportionality between the Fe hyperfine and magnetic moment, it is clear that the Fe moment never vanishes. This should be contrasted with the behavior of a very large number of binary alloys of Fe and a nonmagnetic element (B, V, Ti, Zr, Hf, Nb...), crystalline or amorphous, where the Fe moment and hyperfine field vanish at a finite Fe concentration x_c which varies from 40 to 60 at.%.[12] It is also noted that near the structural transition range ($60 \leq x \leq 75$) from bcc to fcc, there is *no* discontinuity in H_{eff} at all. There is at best a slight increase in the linewidths of the spectra in the transition range.

In Fig. 4 we plot the normalized hyperfine field $H_{eff}(x)/H_{eff}(100)$ (open circles) or $\mu_{Fe}(x)/\mu_{Fe}(100)$ (solid circles) *per transition-metal atom* as a function of x, the Fe concentration. The data of fcc Fe-Cu nearly coincide with the 45° straight line shown, which would be the results for a simple magnetic dilution. The values for bcc Fe-Cu alloys are also found to be close to the straight line. One also notes that although there are few magnetic-moment data points shown in Fig. 4, the agreement with the hyperfine-field results is clear. The results in Fig. 5 are replotted as the magnetic moment per atom versus the d-electron concentration, by normalizing the $H_{eff}(100)$ to the magnetic moment of pure Fe. The slope is about $-0.7\mu_B$ per electron, which is less steep than those found for Fe-Co-Ni alloys. The moment corresponding to $n_d=10$ is close to the moment in pure Ni, but the moment corresponding to $n_d=9$ is substantially less than that of Co.

The isomer-shift results are shown in Fig. 6. Alloying with Cu causes the Fe isomer shift to increase. Just as in the case of the hyperfine field described earlier, there is no anomaly in the isomer shift across the structural transition region. Extrapolating the measured isomer shifts, one obtains a value of ~0.18 mm/sec, relative to α-Fe, for dilute Fe in Cu. This is comparable to the value of 0.225 mm/sec observed in dilute Fe*Cu* alloys.[13] We have also carried out an x-ray photoemission spectroscopy (XPS) study using Al $K\alpha$ excitation. The vacuum level was about 2×10^{-10} Torr, and the surface of the sample was cleaned by Ne sputtering. The results shown in Fig. 7

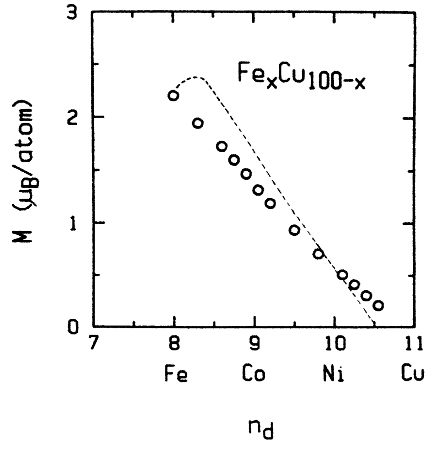

FIG. 5. Magnetic moment per atom versus d-electron concentration for Fe-Cu alloys. The dashed curve represents data of other Fe- and Ni-based alloy systems.

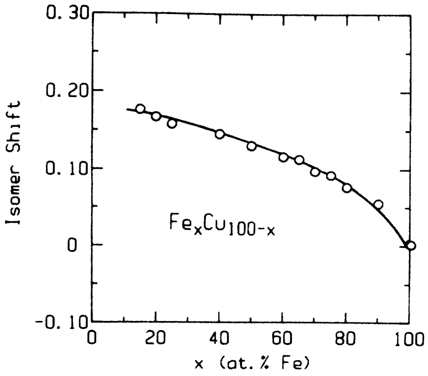

FIG. 6. Isomer shift (relative to α-Fe) of Fe-Cu alloys as a function of Fe content.

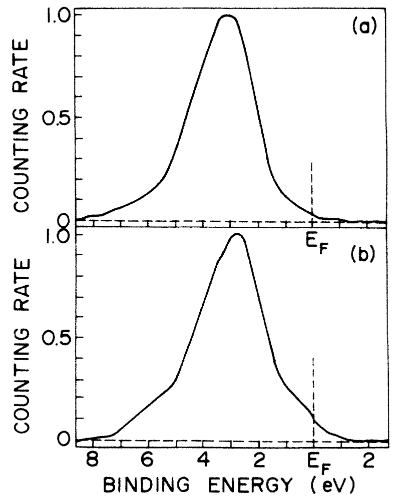

FIG. 7. Valence-band XPS of (a) Cu and (b) $Fe_{50}Cu_{50}$, using Al $K\alpha$ (1.4866 keV) radiation. The counting rate is normalized to the peak height.

indicate that the Fe *d* states are formed above the Cu *d* states. Note that the cross section of the Fe *d* states is much less than that of the Cu *d* states; thus, the Fe *d* band is seen only as a shoulder on the Cu *d* band.

Across the structural transition, there is a large difference in the magnetic ordering temperature (T_C) as shown in Fig. 2. Most intriguingly, there are no observable discontinuities in the magnetic moment, hyperfine field, or isomer shift, as shown in Figs. 4 and 6. To be sure, these quantities all contain distributions due to the disordered nature of the metastable crystalline alloys. But surprisingly, the discontinuities, if any, are less than the distribution widths thereby escaping detection.

The observed magnetic behavior of Fe-Cu alloys can be reasonably well understood by considering their electronic structure. In pure metals the position of the Cu *d* band relative to the Fermi level is lower than that of the Fe *d* band by about 2 eV.[14] Upon alloying, therefore, the Cu *d* band would mainly affect only the lower half or $\frac{2}{3}$ of the Fe *d* band and would not influence strongly the electronic structure near the Fermi surface. Therefore, the alloying of Cu would not significantly disturb the magnetism of Fe, as the light transition metals do. On the other hand, the slight expansion of the lattice and the possible narrowing of the Fe *d* band, since the *d* states of Fe and Cu do not resonate well, would promote the Fe atoms from the weak ferromagnetism in pure Fe, in the sense that the Fermi surface exists in both majority and minority spin bands, to the strong ferromagnetism, which is defined by the filled majority-spin band. Thus, even the transition to the fcc phase did not weaken the magnetism of Fe, and unlike Fe-Ni the Invar-like loss of magnetism was not observed. Somewhat similar to the case of Ni alloying, the Cu alloying does not completely drive the system to strong ferromagnetism, but at high Cu concentrations the alloy gradually approaches strong ferromagnetism. This is in contrast to the cases of Fe-Co and Fe-Au, in which a relatively small addition of Co or Au promotes strong magnetism, and therefore the magnetic moment is increased upon alloying.[15]

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[1] J. Friedel, Nuovo Cimento Suppl. **7**, 287 (1958).

[2] R. M. Bozorth, *Ferromagnetism* (Van Nostrand, London, 1951).

[3] A. R. Miedema, Z. Metallkd. **70**, 345 (1979).

[4] E. F. Kneller, J. Appl. Phys. **35**, 2210 (1964).

[5] K. Sumiyama and Y. Nakamura, J. Magn. Magn. Mater. **35**, 219 (1983).

[6] T. Egami, J. Mater. Sci. **13**, 2589 (1978).

[7] V. Vitek and Y. Minonishi, Surf. Sci. **144**, 196 (1984).

[8] R. A. Johnson, Phys. Rev. **134A**, 1329 (1964).

[9] See, e.g., J. W. Essam, Rep. Prog. Phys. **43**, 833 (1980).

[10] U. Gonser, R. W. Grant, C. J. Meechan, A. H. Muir, Jr., and H. Wiedersich, J. Appl. Phys. **36**, 2124 (1965).

[11] M. L. Spano and S. M. Bhagat, J. Magn. Magn. Mater. **24**, 143 (1981).

[12] See, e.g., K. M. Unruh and C. L. Chien, Phys. Rev. B **30**, 4968 (1984).

[13] *Isomer Shifts*, edited by G. K. Shenoy and F. E. Wagner (North-Holland, New York, 1978), p. 903.

[14] V. L. Moruzzi, J. F. Janak, and A. R. Williams, *Calculated Electronic Properties of Metals* (Pergamon, New York, 1978).

[15] A. P. Malozemoff, A. R. Williams, and V. L. Moruzzi, Phys. Rev. B **29**, 1620 (1984).