Iron d-band occupancy in amorphous Fe$_x$Ge$_{1-x}$

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Fe L_{III} and L_{II} electron-energy-loss spectra of amorphous alloys Fe$_x$Ge$_{1-x}$ ($0.2 \leq x \leq 0.6$) have shown that there is no charge transfer between germanium and the iron d band, and a charge-transfer mechanism cannot be responsible for the decrease of the iron magnetic moment on alloying with germanium. The results do show substantial hybridization manifested as an intraband or intra-atomic redistribution of electrons within the d band.

Amorphous binary alloys of the form $M_x A_{1-x}$, where A is a metalloid (B, Si, Ge, Sn) and M is a magnetic $3d$ transition metal (Fe, Co, Ni), exhibit complex and unusual magnetic properties.[1] Since these alloys are amorphous and can be prepared over a broad range of composition, it is possible to study magnetic, structural, and transport properties of single phase systems without the chemically imposed restrictions of stoichiometric composition.

A particularly striking aspect of the $M_x A_{1-x}$ alloys is the decreasing magnetic moment per magnetic atom with increasing A content.[2] Since the alloys are amorphous, the mechanism for the fall off of the magnetic moment and the resultant changes in the electronic structure of the magnetic atom must be explained in terms of short-range effects only. Two models, or theories, may be invoked to explain the loss of magnetic moment, the first being an electron transfer from A atoms to the d band of the magnetic atom,[3] and the second being a broadening of the d band through hybridization with the orbitals of the A atoms.[2,4,5]

The charge-transfer explanation, which relies strongly on a rigid band model, is attractive in its simplicity but for reasons cited in Ref. 2 may only have fortuitous predictive abilities. Resistivity,[6,7] magnetoresistance, magnetic and magnetooptical properties,[2,8,9] high-field measurements,[5] x-ray photoemission spectroscopy (XPS),[4] and Mössbauer effect[4,10] experiments have been performed on the Fe$_x$Ge$_{1-x}$ amorphous system in an effort to understand the effects of alloying on magnetic and d-band structures. These studies infer but do not confirm unambiguously that no electron transfer into the iron d band takes place.

We have used electron-energy-loss spectroscopy (EELS) in an attempt to resolve this question in the amorphous alloy Fe$_x$Ge$_{1-x}$. By probing the Fe L_{III} and L_{II} edges via this technique, we can directly probe changes in the number of d holes in the iron band due to alloying with germanium.

When an incident beam of monoenergetic electrons impinges on a sufficiently thin material, some electrons will be transmitted suffering no energy loss, some will be elastically scattered, some inelastically scattered, and some

will be transmitted after suffering an energy loss.[11] One important energy-loss mechanism is the excitation of a core-level electron into high-lying bound states or into the continuum. Phenomenologically, these processes are similar to those giving rise to XANES (x-ray-absorption near-edge structure) and EXAFS (extended x-ray-absorption fine structure) in x-ray-absorption experiments.[12–16]

EELS or x-ray-absorption experiments in the range of 400—1200 eV can measure the L_{III} and L_{II} edges of the first-row transition metals. L-edge electron-energy loss and XANES spectra manifest themselves as Lorentzian-shaped peaks on a steplike background. In x-ray absorption spectroscopy it has been established that the sum of the L_{III} and L_{II} x-ray edge peak amplitudes is proportional to the total number of d holes in the conduction or valence band of a metal, since the overwhelming contributions to the L_{III} and L_{II} edge spectra are transitions from the $|2p^{3/2}\rangle$ and $|2p^{1/2}\rangle$ initial states to the $|nd^{5/2}\rangle$ and $|nd^{3/2}\rangle$ final states.[17] In the main, however, L-edge experiments have been limited to elements in which hard x rays ($h\nu > 6$ keV) can be used. To probe these transitions in the first-row transition metals, it is an equivalent and experimentally simpler procedure to measure the energy-loss function using an EELS spectrometer on a transmission electron microscope (TEM). We are thus provided with a convenient and extremely sensitive tool for the problem at hand, namely to determine the changes in occupation of the d band of iron responsible for the change of magnetic moment.

EXPERIMENTAL

Samples were prepared by simultaneous electron-beam evaporation onto air-cleaved NaCl(001) crystals. The ultrahigh vacuum (UHV) system base pressure was between 2×10^{-10} and 1×10^{-9} Torr ($\sim 10^{-8}$ Pa) and was kept below 1×10^{-7} Torr during evaporation. Deposition rates were maintained at a total of about 3 Å/sec by use of separate quartz crystal monitors. Automatic control of deposition rates by the monitors was about ± 0.2 Å/sec over short times. Alloy compositions were determined

from the total Fe and Ge thicknesses, which were measured to better than 3 Å overall out of $\simeq 300$ Å. Substrates and crystal monitors were maintained below 20 C by water cooling. The EELS samples were floated off the NaCl in H_2O onto suitable TEM holders. Elemental analysis of the products by means of the electron-induced x-ray fluorescence in the TEM yielded good agreement with those determined from the calculated thicknesses.[18]

The electron-energy-loss spectra were obtained from a Phillips EM 400T electron microscope operating at 120 kV with 2–3 eV resolution. The spectrometer used was a Gatan model 607 energy-loss spectrometer, and the data were recorded and stored on an EDAX 9100/70 MCA. (Data processing was performed on an external mainframe computer.) The 300 Å samples were sufficiently thin to ensure that no plural scattering events were recorded, and the 3.5 mrad acceptance angle ensured that the dipole approximation for the energy-loss spectra was still valid. All samples were inspected for uniformity and homogeneity, and *in situ* electron diffraction confirmed their amorphicity. Following the energy-loss experiment, each sample was visually inspected in the microscope to see that no radiation damage had occurred.

ANALYSIS

The L_{III} and L_{II} EELS and XANES spectra can be analyzed to give information about the d-state occupancy. In order to proceed, a pre-L_{III} edge background of the form $I(E) = AE^{-R}$ is removed.[11] This leaves only energy-loss or photon-absorption contributions arising from the $2p \rightarrow nd$ transitions in the element of interest. Following background subtraction, the Lorentzian peaks arising from core-to-bound state transitions can be deconvoluted from the core-to-continuum state transition by approximating the latter by

$$\sigma_i(E) = \int_0^\infty \frac{\sigma_i(E_0)\gamma_i/2\pi}{(E-E_0)_i^2 + (\gamma_i^2/4)} dE$$

$$= \sigma_i(E_0)\left[\frac{1}{2} + \frac{1}{\pi}\arctan[(E-E_0)_i/\gamma_i/2]\right] , \quad (1)$$

where $\sigma_i(E_0)$ is the constant continuum background, E_0 is the continuum onset energy, and γ_i is the lifetime broadening.[17] The peaks arising from transitions to bound states in the d band can then be described by Lorentzians superimposed on the backgrounds described above, and the superposition of the functions can be fit via a Levenberg-Marquardt algorithm to the observed spectra. It was assumed that $\sigma_{L_{II}}(E_0) = \frac{1}{2}\sigma_{L_{III}}(E_0)$ and $\gamma_{L_{II}} = \gamma_{L_{III}}$ to reduce the number of free variable parameters in the calculation.

The EELS spectra of the Fe_xGe_{1-x} alloys and the best fits to the spectra are shown in Fig. 1; the spectrum of a pure crystalline iron film is included for the sake of comparison. The relevant information returned from these
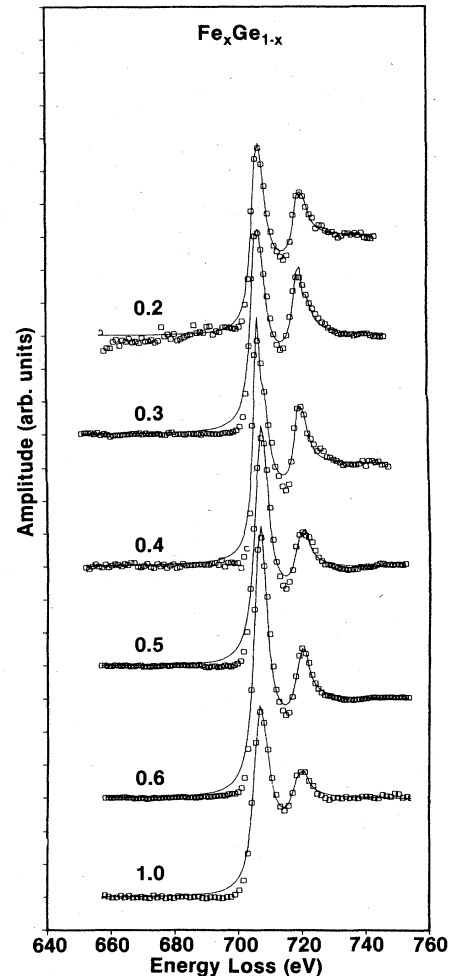

FIG. 1. L_{III} and L_{II} edges for Fe_xGe_{1-x} normalized to total number of iron atoms. Open squares are data; solid line is best fit to data.

fits are the amplitudes of the L_{III} and L_{II} bound-state transitions as a function of composition, since this information can describe the total number of holes in the d band as well as the ratio of the holes in the $d^{5/2}$ and $d^{3/2}$ final states.[19]

The probability of a transition from an initial state to a final state can be related to experimentally observable spectral features via Fermi's Golden Rule as follows:

$$I(\omega) = \int \mu(E)dE = |\langle i|\hat{H}|f\rangle|^2 \rho(E) , \quad (2)$$

where $I(\omega)$ is an intensity defined as the integral of the absorption or energy-loss spectrum $\mu(E)$, $\langle i|$ and $|f\rangle$ are the initial and final states of the system, $\hat{H}$ is the dipole Hamiltonian, and $\rho(E)$ is the density of states. Mattheiss and Dietz,[20] have shown that for L_{III} and L_{II}-edge events with initial states $\langle n'l'j'|$ and final states $|lj\rangle$ the right-hand side of Eq. (2) can be written

$$\frac{2}{2j'+1}I_{L_i}(\omega) = \frac{2}{2j'+1}\int \mu_{L_i}(E)dE = \frac{2\pi^2 N_0}{mc}\frac{2mh\omega_{L_i}}{2h^2}(2j'+1)\sum_{l,j}A_{lj}^{n'l'j'}(E)N_{lj}(E) , \quad (3)$$

where $h\omega_{L_i}$ is the energy of the transition, N_0 is the number of atoms in the excited volume, and the prefactor $2/(2j'+1)$ accounts for initial state multiplicities. In Eq. (3), $N_{lj}(E)$ is an energy-dependent density of states such that

$$h_j = \int_0^\infty N_{lj}(E)dE \tag{4}$$

is the total number of holes of j symmetry.

The summation term in Eq. (3) contains the statistical weighting of channels from $\langle n'l'j'|$ to $|lj\rangle$ where

$$2(j'+1)\sum_{l,j}A_{lj}^{n'l'j'}(E)N_{lj}(E) = \begin{cases} \left[\dfrac{6h_{5/2}+h_{3/2}}{15}\right][R_d^{2p^{3/2}}(E)]^2 \,, & L_{III} \text{ edge} \tag{5a} \\[3mm] \left[\dfrac{h_{3/2}}{3}\right][R_d^{2p^{1/2}}(E)]^2 \,, & L_{II} \text{ edge} \tag{5b} \end{cases}$$

and where

$$[R_{lj}^{n'l'j'}(E)] = \int_0^R r^3 R_{n'l'j'}(r)R_{lj}(r,E)dr \tag{6}$$

is the radial dipole matrix element connecting the core state $|n'l'j'\rangle$ and the final states $|lj\rangle$.

The above expressions allow us to relate the experimentally observed intensities with the number of holes in the $d^{5/2}$ and $d^{3/2}$ bands. It can be assumed[18,19] that the radial matrix elements $R_{lj}^{n'l'j'}(E)$ are the same for the $j=\frac{3}{2}$ and $j=\frac{5}{2}$ final states, and we can relate the number of $d_{5/2}$ holes ($h_{5/2}$) to the total number of holes in the d band h_{tot} by first considering

$$\frac{\frac{1}{2}I_{L_{III}}}{I_{L_{II}}} = \frac{\frac{1}{2}\int\mu_{L_{III}}(E)dE}{\int\mu_{L_{II}}(E)dE}$$

$$= \frac{\omega_{L_{III}}}{\omega_{L_{II}}}\frac{(6h_{5/2}+h_{3/2})/15}{h_{3/2}/3} \tag{7}$$

and

$$h_{tot} = h_{5/2} + h_{3/2} \tag{8}$$

giving

$$\frac{\frac{5}{2}\dfrac{I_L}{I_{L_{II}}}\dfrac{\omega_L}{\omega_{L_{III}}}-1}{5+\dfrac{5}{2}\dfrac{I_{L_{III}}}{I_{L_{II}}}\dfrac{\omega_{L_{II}}}{\omega_{L_{III}}}}h_{tot} = h_{5/2}\,. \tag{9}$$

One can also easily derive an expression for the fractional change in the total number of holes, $(h_{tot})_1/(h_{tot})_2$, permitting comparisons between d occupancies of similar materials 1 and 2. If, in the two systems being considered, the radial matrix elements $R_{lj}^{n'l'j'}(E)$ do not change appreciably due to hybridization, we can write

$$\frac{(h_{tot})_1}{(h_{tot})_2} = \frac{(h_{5/2}+h_{3/2})_1}{(h_{5/2}+h_{3/2})_2}$$

$$= \frac{[(\frac{21}{12})I_{L_{II}}/\omega_{L_{II}}+(\frac{15}{12})I_{L_{III}}/\omega_{L_{III}}]_1}{[(\frac{21}{12})I_{L_{II}}/\omega_{L_{II}}+(\frac{15}{12})I_{L_{III}}/\omega_{L_{III}}]_2}\,. \tag{10}$$

In the particular Fe_xGe_{1-x} system being studied, it is reasonable to assume that the radial matrix elements for the L-edge transitions will not change dramatically with composition. If we expand the expression for $R_{lj}^{n'l'j'}$ as

$$\int_0^\infty r^3 R_{n'l'j'}(r)R_{lj}(r,E)dr = \int_0^\infty r^3 R_{n'l'j'}(r)R_{Fe}(r)dr + x\cdot\int_0^\infty r^3 R_{n'l'j'}(r)R_{Fe(nn)}(r+g(r-r')dr$$

$$+(1-x)\cdot\int_0^\infty r^3 R_{n'l'j'}(r)R_{Ge(nn)}(r+g(r-r'))dr+\ldots\,, \tag{11}$$

where the first term on the right-hand side is a local or atomic contribution from the absorbing iron atom itself, the second term is a contribution from iron nearest neighbors distributed around the absorbing Fe by $g(r-r')$, the third term of Ge near neighbors distributed by $g(r-r')$, and so on. Changes in $R_{l,j}^{n'l'j'}(r)$ will be small variations in a second-order effect since differences in higher terms effect only the small differences in overlap coupling of the initial (core) state with similar near neighbors.

Finally, it is also possible to determine the ratio of the holes in the $j=\frac{5}{2}$ and $j=\frac{3}{2}$ states by

$$\frac{h_{5/2}}{h_{3/2}} = \frac{1}{6}\left[\frac{5I_{L_{III}}\omega_{L_{II}}}{2I_{L_{II}}\omega_{L_{III}}}-1\right]\,. \tag{12}$$

Equations (8), (9), (10), and (12) give us the means to measure directly changes in the d-band occupancy of a system given the intensities and frequencies of the L_{III} and L_{II} transitions.

RESULTS

Figure 1 shows the EELS L-edge spectra of the $Fe_x Ge_{1-x}$ alloys studied, along with the EELS spectrum of pure crystalline iron for the sake of comparison. The open squares are the experimental data, and the solid lines are the best fits to the spectra using Lorentzians for the L_{III} and L_{II} peaks on the backgrounds described by Eq. (1). All spectra were normalized to N_0, the total number of iron atoms in the excited volume, by dividing by $\sigma(E_o)$.

If the loss in the magnetic moment of $Fe_x Ge_{1-x}$ alloys with increasing Ge concentration were due to electron transfer from the germanium atoms to the iron d band, the amplitudes of the peaks should decrease. According to the rigid band model, the iron band structure would not change significantly on alloying but rather the empty density of states above E_F for the metal would fill with electrons transferred from Ge. Spin-polarized d-band calculations by Tawil and Callaway[21] for crystalline Fe show that nearly all the d-band holes are spin minority holes; only a few percent of the total density of states above E_F is due to spin majority states. Consequently, if the rigid-band-change-transfer model were valid we would expect the number of d holes to map directly onto the iron moment as a function of germanium concentration since spin minority holes carry the Fe moment.

Figure 2 shows that this is not the case. In Fig. 2, the solid line is the reduced iron moment $\mu = \mu_x/\mu_{Fe}$ and the open circles are the ratio of the number of d holes in the amorphous alloys to the number of holes in the iron sample derived from Eq. (10). The normalized number of holes does not map onto the moment but stays nearly constant across the composition range. These results demonstrate that charge transfer to the d band does not occur and the simple hole filling model is not adequate.

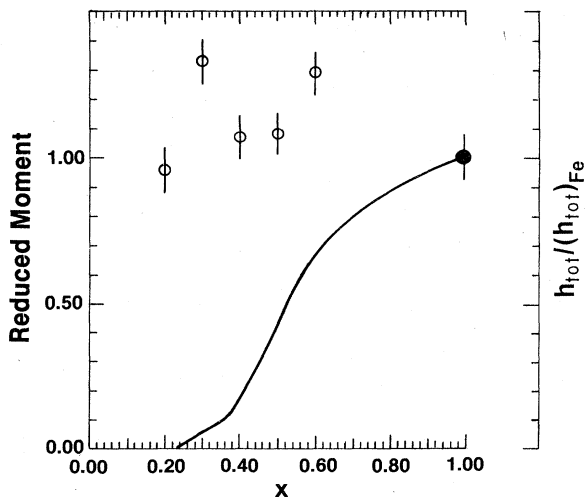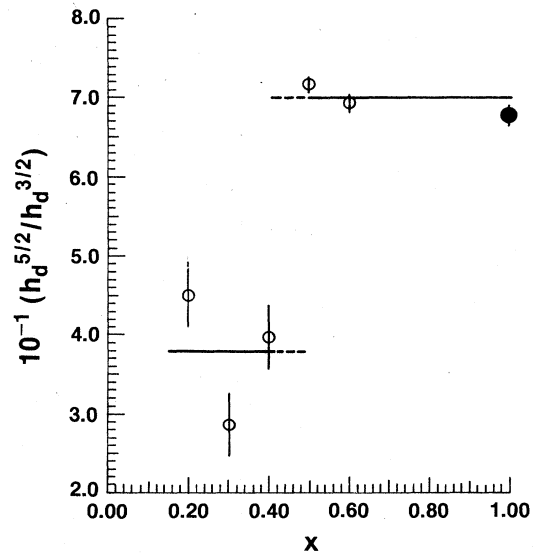While the total number of holes within the d band of

FIG. 3. Ratio of $d_{5/2}$ to $d_{3/2}$ holes. (Solid circle is data from crystalline iron.)

iron does not seem to change with alloying, there is a significant change within the d band. The ratio of the amplitudes of the L_{III} and L_{II} peaks does change dramatically with composition, as can be seen by inspection of Fig. 1. In Fig. 3 we show the ratio of $d_{5/2}/d_{3/2}$ holes as a function of composition based on Eq. (11). The decrease in the $h_{5/2}/h_{3/2}$ ratio occurs at about the same composition as the maximum rate of decrease in the moment, and it is reasonable to assume that the redistribution of the d holes is due to hybridization resulting in increased spin pairing, thus reducing the moment.

Our results strongly support the idea that the decrease in the moment of iron on alloying with a metalloid is not due to charge transfer but rather to band hybridization. These results are correct and conclusive as long as the ratio $[R_{ij}^{n'l'j'}(E)]^2_{alloy}/[R_{ij}^{n'l'j'}(E)]^2_{Fe}$ does not change significantly on alloying. In a subsequent study, we will present calculations of these matrix elements based on structural studies to address this point and evaluate the extent this ratio may deviate from unity.

The changes in the ratio of $d_{5/2}/d_{3/2}$ holes with composition is conclusive since the radial matrix elements cancel when this ratio is calculated by Eq. (12). From the change in the ratios of the empty d states we can see that a hybridization must take place and that any model of the magnetic behavior of the metal-metalloid alloy must be explained in terms of an intra-atomic or intraband redistribution of the d-band electrons.

FIG. 2. Reduced iron moment μ_x/μ_{Fe} (from Ref. 2) (solid line) and reduced total d-band holes h_{tot}/h_{Fe} (circles) (solid circle at $x = 1$ is data from crystalline iron).

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