Magnetic double transition in Au-Fe: Observation of spin canting in zero magnetic field

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We report on new analytical techniques applied to the ^{57}Fe Mössbauer spectra of the alloy Au-16.8 at.% Fe showing a magnetic double transition. With analysis of the effect of the electric-quadrupole hyperfine interaction on the spectra, it can be shown even from spectra in zero external magnetic field that the transition at $\tilde{T}_f$ is a spin-canting transition.

Many magnetic alloys which are typical spin-glasses at low concentrations become ferromagnetic above some critical concentration. In such systems near this concentration, magnetization and susceptibility properties indicate that the ferromagnetic (FM) phase is reentrant: below the FM transition at T_c, a second transition at $\tilde{T}_f$ to a new spin-glass-like state occurs (for a recent review, see Ref. 1). The nature of this second transition has been the subject of much recent controversy, especially for the *Au*Fe system,[2–14] which is the subject of this Brief Report. Lauer and Keune (LK)[7] and Varret, Hamsić, and Campbell[8] have shown from Mössbauer effect measurements in a magnetic field that below $\tilde{T}_F$, the magnetic state is no longer collinear: the average $\langle \sin^2\theta \rangle$ increases from zero below $\tilde{T}_f$, where θ is the angle between the magnetic Fe moment and the external field $H_{\rm ext}$. It is also observed that the average hyperfine field $B_{\rm HF}(T)$ increases below $\tilde{T}_f$ faster than in the (collinear) FM phase. This is related to an increase in the average magnetic moment $\bar{S}$ in the low-temperature state.[8,13] These two results are summarized in the canting model. In the FM phase, all moments are parallel to the spontaneous magnetization $\vec{M}_s$. Spin components transverse to $\vec{M}_s$ are free to rotate and do not contribute to the moment S (thermally averaged spin). At $\tilde{T}_f$, these components freeze out, canting the moment out of the direction of $\vec{M}_s$, and increasing its magnitude.

Spin canting similar to the observed $\tilde{T}_f$ transition has been predicted by Gabay and Toulouse (GT)[15] in the infinite-range model with Heisenberg spins. The GT transition from collinear to canted FM is described by the transverse order parameter: $q_t = \langle S_t^2 \rangle_J$. S_t is the transverse component of the thermally averaged spin and $\langle\ \rangle_J$, the average over the disorder (a recent review is given in Ref. 16). The interest in Mössbauer measurements for double transition studies stems from the possibility of determining the related parameter:[13] $\langle \sin^2\theta \rangle = \langle (S_t/S)^2 \rangle$ from relative line intensities. Thus, it is important to know if such results, from experiments in the presence of magnetic field, can be compared to zero-field results. This is the purpose of the present study.

The canting model applied to *Au*Fe has led to some controversy due to the known[17] chemical short-range order (SRO) in these quenched metastable alloys. Violet and Borg (VB)[10] have argued that SRO leads to phase segregation into Fe-rich platelets and remaining solid solution. These then determine the magnetic transitions. Their conclusions have been questioned by Brand and Keune[18] and by Monod and Campbell,[19] and they have modified their conclusions somewhat,[20] retaining, however, the idea that the magnetic state is determined by chemical SRO. Beck[11] has argued from susceptibility and magnetization measurements that no long-range FM order exists at any temperature in the double transition region. He proposed that the 4.2 K spectra (as fitted with two sextets) can be explained by platelets of differing thickness (two and three atomic layers). In his view, the effects seen in these alloys are due to short-range order and dynamic relaxation of such Fe clusters. It is difficult to reconcile this with the known agreement between ac and dc susceptibility[2,3,5] and with neutron diffraction results.[4] Whittle and co-workers[21] have argued from similar fits that the two subspectra represent spin-glass and cluster glass, or cluster glass and FM phases, depending on the Fe concentration. This ignores the temperature dependence of the spectra[18] and the systematic trends in the paramagnetic and magnetic spectra with Fe concentration,[22–24] which demonstrate the infuence of *local* environments on the spectra.

The purpose of this Brief Report is to show by new analytical methods applied to the *Au*-^{57}Fe spectra that in the double transition region, despite clear evidence for chemical SRO, the magnetic behavior is homogeneous. Both low-field (LF) and high-field (HF) portions of the spectra show the same $\tilde{T}_f$. This we do by treating the spectra as two overlapping hyperfine field distributions:

$$P(B_{\rm HF}) = P^{(\rm LF)}(B_{\rm HF}) + P^{(\rm HF)}(B_{\rm HF}) \ .$$

We can show further that the transition at $\tilde{T}_f$ is characterized by the spontaneous canting of the moments, and we show this from spectra taken in *zero magnetic field.* This result is possible because the electric quadrupole (EQ) hyperfine interaction defines locally an axis [principal axis of the electric field gradient (EFG) tensor, denoted as the z axis]. The nature of the orientation of the magnetic moments with respect to this (local) axis influences the spectrum line positions and profile. This forms the basis of a method for distinguishing the canted and the collinear states from measurements in zero magnetic field.

The addition of the EQ interaction to the magnetic hyperfine Hamiltonian leads in first order to a line shift 2ϵ given by ($\frac{3}{2} \rightarrow \frac{1}{2}$ transition, asymmetry parameter $\eta = 0$)

$$2\epsilon = \frac{e^2 Q q_{zz}}{2}\left[\frac{3\cos^2\Phi - 1}{2}\right] \qquad (1)$$

in the usual notation. q_{zz} is the largest EFG tensor component, defining the z axis, and Φ is the angle which B_{HF} makes with this axis. In a cubic environment, all EFG components are zero, but in random alloy systems this is no longer true and one must consider each possible neighboring configuration. Defining a local structure factor $S(p)$ as the sum over p impurity (Fe) neighbors at angles Φ_i: $S(p)=\sum_i[3\cos^2(\Phi_i)-1]$, the local line shift can be written as $2\epsilon(p)=Q_pS(p)$. The parameter $2Q_p=e^2Qq_{zz}/2$ is to be found from fitting the spectra. The resulting Lorentzian sextet $L_6[\Gamma, 2\epsilon(p), B_{HF}]$ must be averaged over the allowed values of $S(p)$ and p (Γ is the linewidth). Assuming no correlation between the EFG z axis and B_{HF}, this leads to an effective sextet $L_6(\Gamma, \langle 2\epsilon\rangle, B_{HF})$, with no net EQ line shift: $\langle 2\epsilon\rangle = 0$. In this case, however, it is necessary to consider the magnetic dipole interaction from neighboring Fe atoms as well.[25,26] This is locally correlated with the EQ interaction because of the identical angular dependence. The effective hyperfine field $B_{eff}(p)$ for the configuration p is then given by $B_{eff}(p)=B_{HF}+h_{2p}S(p)$, where h_{2p} is the dipole field coefficient. Brand, Lauer, and Herlach[27] have shown that for small asymmetry, averaging $L_6[\Gamma, 2\epsilon(p), B_{HF}(p)]$ over p leads to an effective spectrum $L_6[\Gamma_i, \langle 2\epsilon\rangle, B_{HF}]$ again with $\langle 2\epsilon\rangle = 0$, but an *asymmetric line profile*: differing effective linewidths Γ_i for equivalent line pairs. In addition, they have extended this model to cases where B_{HF} is also site dependent, yielding the distribution $P(B_{HF})$. The present work follows this approach, improving on the accuracy of the calculation of the line profile to include larger asymmetrical effects (thus, the sum over neighbors p must be explicitly calculated), and including the possibility to treat separately two overlapping distributions. In the presence of overlap, the solution for the fit program must be stabilized by imposing the (physically reasonable) condition that $P^{(j)}(B_{HF})=0$ at the upper and lower limits of each subdistribution $j=$ LF, HF. A more detailed discussion will be published later.

This analysis has been applied to spectra from the solid-solution quenched Au-16.8 at.% Fe sample studied previously by LK. Several characteristic spectra (measured in zero external field) and resulting $P(B_{HF})$ are shown in Fig. 1. For the low-temperature spectra it was necessary to separate $P(B_{HF})$ into distinct but overlapping LF and HF distributions. This improves on the simple two-sextet fits used by others,[10,21] and allows us to treat the 2ϵ line shift and Q_p-h_{2p} line profile terms separately, improving on the procedure used by LK. The resulting values of the average hyperfine field $\bar{B}_{HF}(T)$ are shown in Fig. 2(a), where a sharp change in slope is observed in both LF and HF values, at a temperature $\tilde{T}_f \simeq 40$ K (essentially confirming the 45 K given by LK). Above $\tilde{T}_f$, the two distributions overlap, and no effort has been made to separate them [as seen in the spectrum for 39.5 K, Fig. 1: the small bump in $P(B_{HF})$ is an artifact[28]].

Below $\tilde{T}_f$, a *line shift* 2ϵ is found separately for the LF and HF peaks, similar to those found by others,[7,10,21] with $2\epsilon(\text{LF})>0$ and $2\epsilon(\text{HF})<0$. We see, however, in Fig. 2(b) that both decrease in magnitude as $T\rightarrow\tilde{T}_f$. At low temperatures, little or no asymmetry is found in the LF and

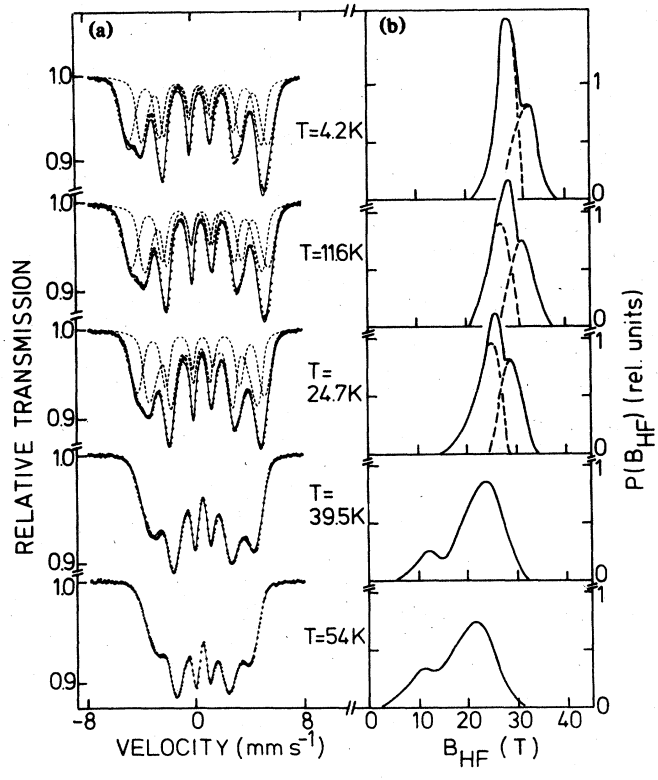

FIG. 1. (a) Zero-field Mössbauer spectra for Au-16.8 at.% Fe (quenched) for several characteristic temperatures below and above $\tilde{T}_f$. (b) Resulting distribution $P(B_{HF})$ showing the separation into LF and HF parts at low temperatures (see text).

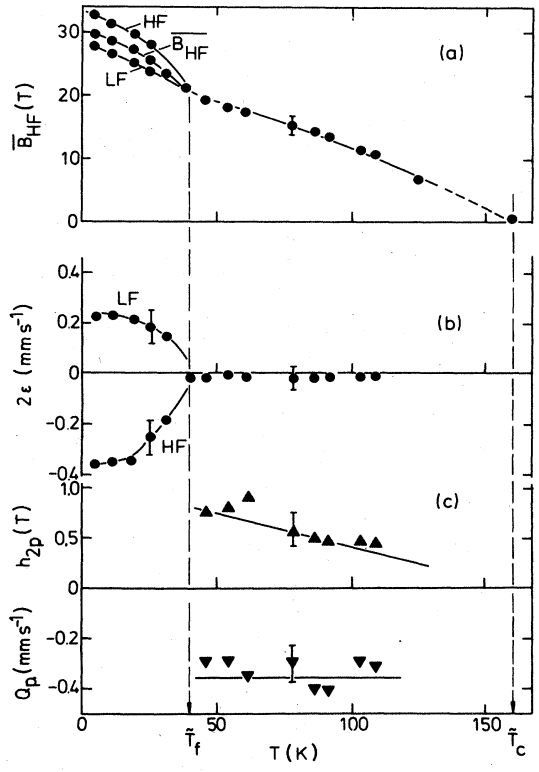

FIG. 2. (a) Average hyperfine field $\bar{B}_{HF}$ separated into LF and HF parts. (b) EQ line shift 2ϵ for LF and HF parts of $P(B_{HF})$. (c) Q_p and h_{2p} as calculated from the spectral asymmetry (see text).

HF distributions.[29]

For $T \geq \tilde{T}_f$, 2ϵ is essentially zero: there is no EQ line shift found in the collinear FM phase. However, above $\tilde{T}_f$, the spectra (Fig. 1) show a distinct asymmetric line profile characteristic of the $Q_p - h_{2p}$ correlation. The values found for these parameters are shown in Fig. 2(c), where we remark that only the relative sign between Q_p and h_{2p} is relevant. h_{2p} is found to vary with temperature, and scale with $\bar{B}_{\rm HF}(T)$. Since h_{2p} is assumed to be due to the dipole field of the Fe neighbors, this is a reasonable result. It is also found that Q_p is constant above $\tilde{T}_f$, and to a good approximation the absolute value of $2Q_p$ is equal to the average EQ interaction due to single neighbor, as found by Window.[24] Our result of $|2Q_p| \simeq 0.72 \pm 0.06$ mm/s should be compared to his $Q_0 = 12Q_1/29$ mm/s, which for 16.8 at.% Fe (Fig. 2 of Ref. 23) is equal to 0.74 mm/s.

Our results can be summarized as follows. For temperatures far below $\tilde{T}_f$ it is found that there are locally preferred directions for the moments (directions of $B_{\rm HF}$) with respect to the local EFG z axis, resulting in nonzero 2ϵ(LF) and 2ϵ(HF). As $T \rightarrow \tilde{T}_f$ from below, the moments rotate out of these directions into a common direction given by $\vec{M}_s$. This changes the spin structure with respect to $\vec{M}_s$ from canted below $\tilde{T}_f$ to collinear above. In this change, $S(p)$ changes from a constant value below $\tilde{T}_f$ [within the LF and HF parts, yielding 2ϵ(LF) and 2ϵ(HF)], to a distribution of values above (yielding the parameters Q_p and h_{2p}). This produces the described change in spectrum profile.

We conclude that despite SRO, the quenched *Au*Fe alloy studied here shows homogeneous magnetic behavior with a FM transition at T_c and a canting transition at $\tilde{T}_f$ in zero external field. The transition at $\tilde{T}_f$ is similar to the GT transition as predicted theoretically. Other evidence[4] suggests that below $\tilde{T}_f$ the spontaneous magnetization $\vec{M}_s$ is nonzero, which is also in agreement with GT and consistent with our results.

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