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Nature of the magnetic ground state in Fe-Ni Invar alloys

M. M. Abd-Elmeguid, U. Hobuss, and H. Micklitz
Institut für Experimentalphysik IV, Ruhr-Universität Bochum, D-4630 Bochum, Federal Republic of Germany

B. Huck and J. Hesse
Institut für Metallphysik and Nukleare Festkörperphysik der Technischen Universität Braunschweig,
Mendelssohnstrasse 3, D-3300 Braunschweig, Federal Republic of Germany

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Systematic low-temperature ^{57}Fe Mössbauer effect (ME) and ac susceptibility (χ) studies in the temperature range 70–1.7 K on the classical ferromagnetic (FM) $Fe_{65}Ni_{35}$ Invar alloy are reported. We unexpectedly observe a relative decrease in the average effective hyperfine (hf) field, $\bar{B}_{\rm eff}$ of about 6% on lowering the temperature from 30 to 4.2 K. The analysis of the experimental results (ME and χ) denies the existence of a reentrant spin-glass ground state as recently suggested. It is concluded that the observed low-temperature hf field anomaly is caused by a few percent of inhomogeneously distributed spin-flipped Fe atoms which exhibit FM order above 30 K.

INTRODUCTION

The unusual magnetic properties of ferromagnetic (FM) fcc $Fe_{1-x}Ni_x$ $(30 \leq x \leq 45)$ Invar alloys have been extensively studied over many years.[1] A central issue connected with the magnetic anomalies of these alloys is the nature of their magnetic ground state. Several experimental techniques applied to these FM alloys revealed an inhomogeneous magnetic ground state at low temperature: magnetic susceptibility,[2] rotational hysteresis torque,[3] optical studies,[4] and neutron diffraction.[5] The Mössbauer effect (ME), one of the most suitable tools for such studies, has been frequently used to investigate the average hyperfine (hf) field $\bar{B}_{\rm eff}$, at the ^{57}Fe nucleus and its distribution, $P(B_{\rm eff})$, in Fe-Ni Invar alloys in order to obtain a physical picture for the magnetic ground state in these systems, e.g., see Refs. 6–11. From recent ME studies on the classical $Fe_{65}Ni_{35}$ Invar alloy, it has been shown that most of the Fe atoms ($\simeq 90\%$) are in the FM state,[9,10,12,13] while the residual fraction of Fe atoms is supposed to exhibit either antiferromagnetic[10,13] (AF) or frustrated and AF moments.[12]

Quite contrary to this physical picture of the magnetic ground state in this system, another physical aspect has been brought up by Miyazaki *et al.*:[14] the authors concluded from ac susceptibility measurements on Fe_xNi_{1-x} $(30 \leq x \leq 45)$ Invar alloys a reentrant spin-glass (SG) transition below $T \simeq 30$ K, thus putting the above picture of the magnetic ground state into question. It is puzzling that below $T \simeq 30$ K a low-temperature anomalous behavior also was observed many years ago by other macroscopic experimental methods: differential magnetic susceptibility,[2] velocity of sound,[15] ultrasonic absorption,[16] and thermal expansion.[17]

To clarify these low-temperature anomalies we have performed systematic low-temperature ^{57}Fe ME measurements on a classical $Fe_{65}Ni_{35}$ Invar alloy with and without external magnetic field ($B_{\rm ex}$). The basic idea of our experiments is to check whether these low-temperature anomalies below 30 K are reflected in the temperature dependence of both $\bar{B}_{\rm eff}$ and $P(B_{\rm eff})$. If this is true, the influence of $B_{\rm ex}$ should give additional information on the nature of the magnetic state at low temperatures. To our knowledge such systematic ME studies have not been performed before and will be reported here for the first time.

EXPERIMENTAL

A commercial FM $Fe_{65}Ni_{35}$ ($T_c \simeq 500$ K) Invar alloy (foil of 20 μm thickness) was purchased from Goodfellow Metals Ltd. Low-temperature x-ray diffraction measurements showed the purity as well as the stability of the fcc structure down to 4.2 K (no martensitic, fcc→bcc, transition). The ME spectra of the sample were collected using a ^{57}Co: Rh source at temperatures between 70 and 4.2 K in $B_{\rm ex}$ of 0 and 2 T. We also have performed ac susceptibility measurements in the same temperature range on the same sample before and after annealing.

RESULTS

Figure 1 shows some typical ^{57}Fe ME spectra of $Fe_{65}Ni_{35}$ at different temperatures and at $B_{\rm ex} = 0$ T. All ME spectra were fitted by a modified histogram method, taking into account a correlation between quadrupolar effects and hf fields.[18] As shown in Fig. 1, all ME spectra look very similar. However, by a careful comparison of the shape of the spectra relative to the base line, we find an unusual behavior: the *sagging* of the ME spectrum relative to the base line begins to increase gradually on lowering the temperature below $T = 30$ K, whereas the positions of the resonance lines remain almost unchanged. This effect is best seen in Fig. 2(a), where the ME spectra at $T = 30$ and 4.2 K are plotted with a common base line. As a result of this anomalous behavior, the shape of the hf field distribution, $P(B_{\rm eff})$, reveals a gradual change on decreasing the temperature below 30 K down to 4.2 K [Fig. 2(b)]: we observe an increase of the shoulder in $P(B_{\rm eff})$

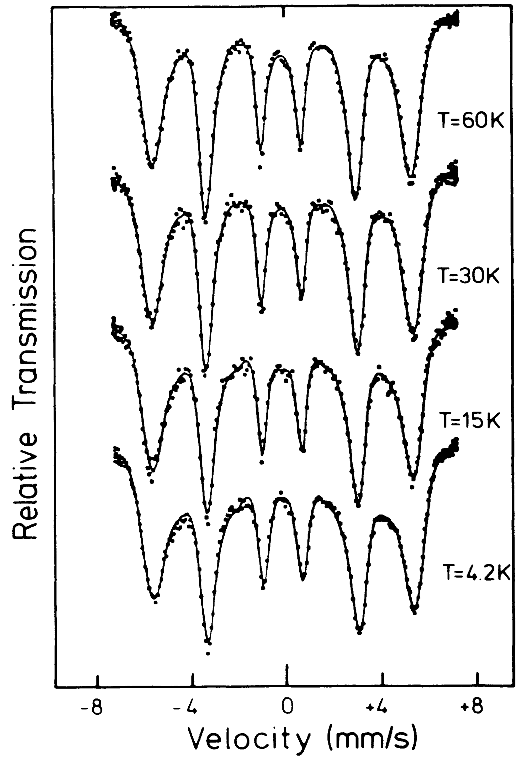

FIG. 1. Typical ME spectra of $Fe_{65}Ni_{35}$ at various temperatures and at $B_{ex}=0$ T.

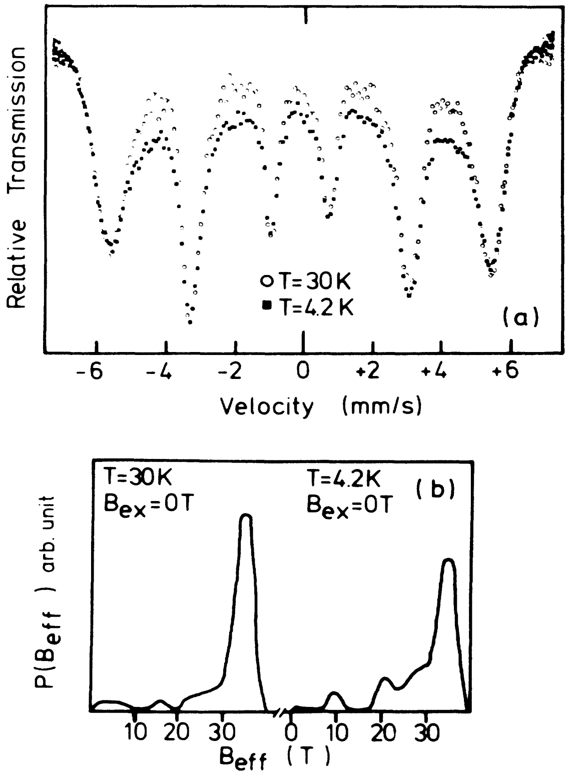

FIG. 2. (a) ME spectra of $Fe_{65}Ni_{35}$ collected at $T=30$ and 4.2 K and $B_{ex}=0$ T plotted with a common base line. Note the difference of the *sagging* of the two spectra relative to the base line; (b) hyperfine field distribution $P(B_{eff})$ as obtained from the analysis of the $Fe_{65}Ni_{35}$ ME spectra at $T=30$ and 4.2 K.

centered around 30 T by about 15% at the expense of the amount of the main peak centered at about 35 T.

To obtain further information about the source of this anomalous behavior below 30 K, we have collected ME spectra in the same temperature range but in an external magnetic field, $B_{ex}=2$ T. This is the method usually used to account for a possible FM→SG reentrant transition in some metallic alloys [e.g., Au–16.8 at. % Fe (Ref. 19) and $Fe_5Ni_{73}Si_9B_{13}$ (Ref. 20)], where this field strength did not destroy the reentrant behavior. Figures 3(a) and 3(b) show the ME spectra collected at 48 and 4.2 K in $B_{ex}=2$ T (parallel to γ-ray direction) and their hf distributions, respectively. In this case the relative intensity of lines 2 and 5 ($\Delta m=0$ transitions) is zero [Fig. 3(a)], indicating that B_{ex} (perpendicular to the sample surface) is large enough to saturate the FM state of the system. On decreasing the temperature from 48 to 4.2 K we find no change in the relative intensity of lines 2 and 5 as would be expected from a possible FM→SG reentrant behavior.[19,20] This finding is supported by the temperature dependence of the ac susceptibility performed on the same sample without B_{ex}, Fig. 4 (curve *a*), which is temperature independent. The shape of $P(B_{eff})$ in $B_{ex}=2$ T does not change with temperature [see Fig. 3(b)]. However, we find a remarkable difference in the shape of $P(B_{eff})$ at 4.2 K with and without external magnetic field [compare Figs. 2(b) and 3(b)]: the shoulder centered around 30 T disappears in $B_{ex}=2$ T and the intensity of the main peak at 35 T increases by the same amount ($\simeq 15\%$).

DISCUSSION

The temperature dependence of $\bar{B}_{eff}$ as obtained from the analysis of the ME spectra in $B_{ex}=0$ and 2 T is plotted in Fig. 5. The anomalous behavior of $\bar{B}_{eff}$ below 30 K with $B_{ex}=0$ T is clearly seen, and the disappearance of this anomaly in $B_{ex}=2$ T is evident. The relative decrease at $T=0$ K in $\bar{B}_{eff}(0)$, $\Delta\bar{B}_{eff}(0)/\bar{B}_{eff}(0)$, is estimated to be about 6% [$\Delta\bar{B}_{eff}(0)$ is the difference between the value for $\bar{B}_{eff}(0)$ extrapolated from the high-temperature data, assuming a $T^{3/2}$ law, and the observed value for $\bar{B}_{eff}$ at $T=0$ K]. As shown before, this effect is clearly reflected in the change of the shape of $P(B_{eff})$ with decreasing temperature. On the other hand, no change in the ac susceptibility is observed in the same temperature range.

In the following we discuss the low-temperature hf field anomaly on the basis of a local magnetic model proposed by Müller and Hesse.[9] It will be shown that such an anomaly is connected with changes in the spin structure of the alloy as a function of temperature. As is well known, B_{eff} in magnetic alloys can be described by two main contributions:[9,12,13]

$$B_{eff}=B_c+nB_{thf}\ , \tag{1}$$

where B_c is the contribution due to the polarization of the

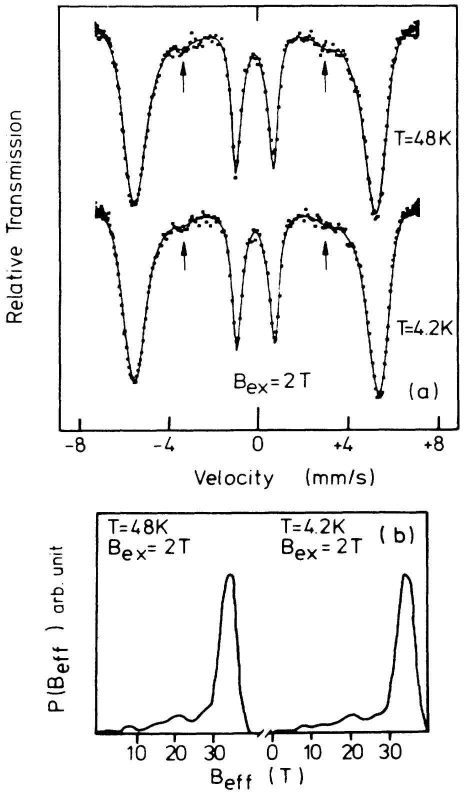

FIG. 3. (a) ME spectra collected at $T=48$ and 4.2 K in $B_{\rm ex}=2$ T. Arrows mark the position of lines 2 and 5 (see text); (b) hyperfine field distribution $P(B_{\rm eff})$ as obtained from the analysis of the ME spectra at $T=48$ and 4.2 K in $B_{\rm ex}=2$ T.

core and the conduction electrons by the local magnetic moment, and $B_{\rm thf}$ denotes the conduction-electron polarization by the magnetic moment of the n nearest-neighbor (NN) atoms (transferred hf field). If all NN Fe atoms ($\bar{n}=7.8$ in $Fe_{65}Ni_{35}$) are ferromagnetically ordered, Eq. (1) represents a pure FM state, resulting in a hf field distribution $P(B_{\rm eff})$ with one main peak centered around 35 T.

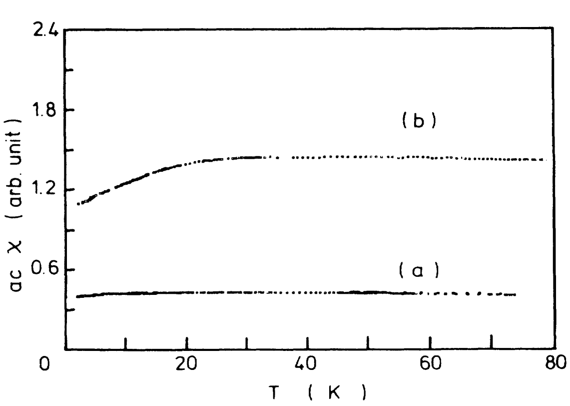

FIG. 4. ac susceptibility χ as a function of temperature of $Fe_{65}Ni_{35}$: (a) without heat treatment; (b) after annealing (see text).

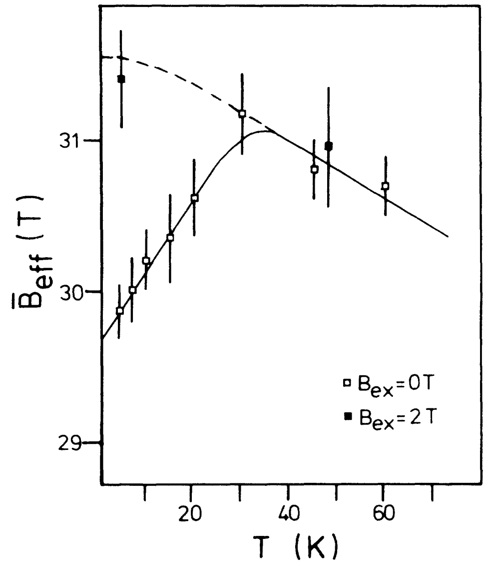

FIG. 5. Variation of the average effective magnetic hf field, $\bar{B}_{\rm eff}$, with temperature for $Fe_{65}Ni_{35}$ in $B_{\rm ex}=0$ T(□), solid curve, and $B_{\rm ex}=2$ T (■). Dashed line is the extrapolation of the high-temperature data points assuming a $T^{3/2}$ law for the T dependence of $\bar{B}_{\rm eff}$.

According to model calculations,[9,12] this mean peak is related to five, six, seven, eight, and nine Fe atoms in the NN shell occurring with binomial probabilities and having FM coupled (parallel) spins. For $n \geq 10$ frustrated and AF coupled (antiparallel) spins are suggested, resulting in a contribution to $P(B_{\rm eff})$ at low hf fields ($\lesssim 10$ T). However, as mentioned before, we observe at 4.2 K a relative increase ($\simeq 15\%$) of a shoulder in $P(B_{\rm eff})$ centered at 30 T. The fact that this value is shifted only by about 5 T from the FM peak suggests that this shoulder originates from a disturbed FM local environment. We consider, for the sake of simplicity, that this disturbance of the FM spin structure is due to the flipping of some Fe spins in the NN shell. The contribution of Ni atoms to $B_{\rm eff}$ is neglected as usually assumed.[10] In such a case $B_{\rm eff}$ is given by

$$B_{\rm eff}=-B_c+nB_{\rm thf} \qquad (2)$$

for a spin-flipped atom, having its spin antiparallel with respect to the NN spins, and

$$B_{\rm eff}=+B_c+(n-2n')B_{\rm thf} \qquad (3)$$

for a non-spin-flipped atom with n' spin-flipped atoms in its NN shell.

In the following we first discuss the behavior of $\bar{B}_{\rm eff}$ ($T=0$ K) and then the shoulder in $P(B_{\rm eff})$. Equations (2) and (3) can be used to account for different values for $B_{\rm eff}$ related to different spin configurations in the NN shell.[9] The observed relative decrease of $\bar{B}_{\rm eff}$ at $T=0$ K, $\Delta\bar{B}_{\rm eff}(0)/\bar{B}_{\rm eff}(0)=6\%$, on the other hand, can be used for a rough estimation of the amount of the spin-flipped atoms in the FM matrix: assuming a statistical distribution of the spin-flipped atoms, this decrease in $\bar{B}_{\rm eff}$ corresponds to an amount of 3% spin-flipped atoms. This amount would be slightly increased for the case where the spin-flipped atoms are inhomogeneously distributed, but not to more than 6% (in the extreme case where AF clusters [$B_{\text{eff}}=2.7$ T (Ref. 21)] appear in the FM matrix).

Next, we focus on the dominant effect, namely the relative increase ($\simeq 15\%$) of the shoulder in $P(B_{\text{eff}})$ which is centered at 30 T and extended to lower fields down to about 20 T. It is important to emphasize that the observation of a 15% increase in $P(B_{\text{eff}})$ at $B_{\text{eff}}=30$ T does not correspond to a fraction of 15% spin-flipped atoms: one spin-flipped Fe atom causes a change in B_{eff} for all its NN Fe atoms. Because each Fe atom has 7.8 NN Fe in the mean, such "spin flip" is enhanced by the factor 7.8. Thus, the observed change of 15% in $P(B_{\text{eff}})$ is caused by a change in the spin direction of only about 2% of the Fe atoms.

To account for the origin of the shoulder at 30 T we have used Eq. (3) together with the well-known values for B_c and B_{thf}.[9,10] From this it follows that two to three NN Fe atoms have to be spin flipped in order to obtain a value of $B_{\text{eff}}=30$ T. A value $\bar{n}'=2.5$, however, would mean that about 30% of the NN Fe atoms are spin flipped. This is in clear contradiction to the former estimate of $\simeq 3\%$ of statistically distributed spin-flipped Fe atoms as obtained from the observed 6% relative decrease in B_{eff}. It clearly indicates that the distribution of the spin-flipped Fe atoms occurs inhomogeneously and not in a statistical way[22] in a statistical alloy with randomly distributed Fe and Ni atoms. This conclusion is further supported by the fact that such a large fraction (one-third) of spin-flipped Fe atoms would result in a drastic change of the magnetic ground state of the system. However, the ac susceptibility does not display any discontinuity in the temperature range from 60 to 1.7 K [see Fig. 4(b)]. From the above analysis we therefore suggest that small regions (only a few percent of the total volume) with a large number of spin-flipped Fe atoms are segregated from the FM matrix. The shoulder in $P(B_{\text{eff}})$, centered at 30 T, is extended down to about 20 T. Such a hf field (20 T) corresponds to four spin-flipped Fe atoms in the NN shell. Local regions with four spin-flipped Fe atoms in the NN shell represent a state with about half of the NN Fe spins aligned in an antiparallel direction, leading to $B_{\text{thf}}=0$.

Finally, we want to comment on the low-temperature anomalous behavior of the ac susceptibility of $\text{Fe}_{1-x}\text{Ni}_x$ ($30 \leq x \leq 45$) reported by Miyazaki *et al.*[14] In our measurements we observe a remarkable decrease in the ac susceptibility below 30 K after vacuum annealing of our sample at 1300 K for 100 h and fast quenching [see Fig. 4(b)]. However, by performing again careful ME measurements on the annealed sample we do not find any effect due to the annealing on the local magnetic behavior of the sample: we observe the same relative decrease in $\bar{B}_{\text{eff}}$ below 30 K as observed before annealing. These results show that the low-temperature behavior of the ac susceptibility of the annealed sample does not originate from *any* changes in the magnetic ground state of the sample. This conclusion is strongly supported by very recent observations of a similar behavior of the ac susceptibility below 20 K in FM systems [e.g., $\text{Fe}_{80-x}\text{B}_x$ and $(\text{Fe}_{80-x}\text{Ni}_x)_{85}\text{B}_{15})$], without displaying a reentrant SG transition.[23] Here, this effect is suggested to be connected with a thermal activation of Bloch wall movements. Furthermore, additional experimental results against a SG ground state in $\text{Fe}_{65}\text{Ni}_{35}$ are reported by Shiga *et al.*[24] and very recently by Huck and Hesse:[25] the effect of Mn substitution, $\text{Fe}_{65}(\text{Ni}_{1-x}\text{Mn}_x)_{35}$, on the magnetic behavior of $\text{Fe}_{65}\text{Ni}_{35}$ has been investigated, $0.05 \leq x \leq 0.4$, by measuring the ac susceptibility[24,25] and dc magnetization.[25] From the proposed magnetic phase diagram a reentrant SG region was observed for $x \leq 0.2$;[24] however, a purely FM ground state in $\text{Fe}_{65}\text{Ni}_{35}$ was obtained by extrapolating to $x=0$.

CONCLUSION

The above discussion shows that the FM ground state of $\text{Fe}_{65}\text{Ni}_{35}$ contains a few percent of locally inhomogeneous spin-flipped regions. These regions exhibit, on the average, 30% of spins with opposite alignment to the FM matrix. Furthermore, our results (ME and ac susceptibility) deny the occurrence of a SG reentrant transition as suggested recently by Miyazaki *et al.*[14]

On the basis of our ME results we also can understand the low-temperature anomalous behavior, mentioned before, observed by differential susceptibility, ultrasonic absorption, and sound-velocity measurements in these alloys on the basis of our ME results. Here, we draw the same conclusion as given in Refs. 2, 15, and 16 about the nature of the magnetic ground state of $\text{Fe}_{65}\text{Ni}_{35}$, namely the existence of flipped (AF) spins in the FM matrix at 4.2 K. However, we have shown from the analysis of our ME results that the low-temperature anomaly is caused by spin-flipped Fe atoms which exhibit FM order above $T=30$ K, i.e., which are not in a paramagnetic state above 30 K as has been previously suggested.[2,15,16,26]

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