Giant volume magnetostriction in the FeRh alloy

M. R. Ibarra and P. A. Algarabel
Departamento de Fisica de la Materia Condensada and Instituto de Ciencia de Materiales de Aragon, Universidad de Zaragoza, Consejo Superior de Investigaciones Científicas, Facultad de Ciencias, 50009 Zaragoza, Spain
(Received 8 March 1994)

In a search for high-magnetostrictive materials we have discovered in FeRh a large induced volume magnetostriction ($\approx 0.82\%$) at and above room temperature. Thermal-expansion measurements performed on the ordered CsCl crystallographic structure of FeRh in the temperature range 250–800 K reveal Invar-like behavior at $T_c = 680$ K associated with a paramagnetic-ferromagnetic second-order phase transition. At $T_{\text{F-AF}} = 405$ K, a large contraction of the lattice within the ferromagnetic (F) phase takes place through a first-order transformation resulting in a low-volume, low-temperature antiferromagnetic phase (AF) (anti-invar-like behavior). At moderate fields above room temperature and within the AF phase, we have found a giant value for the volume magnetostriction of $\omega = 8.2 \times 10^{-3}$. These results constitute evidence for the existence of the theoretically predicted metastable F phase (high-volume state) within the AF phase which can be reached by an applied magnetic field. The present experiments offer additional perspectives on an old problem in magnetism and suggest potential applications of this alloy as a high-magnetostrictive material.

INTRODUCTION

Since the pioneering work of Fallot and Hocart,[1] it has been known that in the ordered CsCl crystallographic structure of $Fe_{0.5}Rh_{0.5}$ a paramagnetic-ferromagnetic phase transition occurs at $T_c \approx 650$ K. Within the ferromagnetic (F) phase a peculiar ferromagnetic-antiferromagnetic (AF) phase transition takes place at a temperature $T_{\text{F-AF}} \approx 350$ K. Simultaneously, at this transition a 0.9% volume contraction occurs without change in the crystallographic structure. This singular transition is strongly concentration dependent and is only present in a very narrow concentration range of 5 at.% around $x = 0.5$ in the binary $Fe_{1-x}Rh_x$ phase diagram.[2] Both transition temperatures T_c and $T_{\text{F-AF}}$ are very sensitive to small concentration changes, an increase of only 1 at.% in Rh concentration giving rise to an increase of about 10% in the transition temperatures. At $T_{\text{F-AF}}$ a large drop in the electrical resistivity was observed.[3] Neutron diffraction experiments[4] performed at low temperatures in the AF phase showed that only the iron atoms carry a relatively large local magnetic moment, $\mu_{\text{Fe}} \approx 3.2\mu_B$, with no magnetic moment on the rhodium sites. At temperatures above $T_{\text{F-AF}}$, μ_{Fe} continues to have the same value. However, a local magnetic moment appears on the rodium sites, $\mu_{\text{Rh}} \approx 0.9\mu_B$. Recent first-principles total-energy band-structure calculations performed by Moruzzi and Marcus[5] predicted an equilibrium type-II AF magnetic ordering [antiferromagnetic coupling between successive layers of (111) iron layers] with no magnetic moment on the Rh atoms. A metastable F state is also predicted to exist with a unit cell larger than in the AF ground state. This F state is very close in energy to the low-volume AF ground state and can be reached either thermally or by applying a magnetic field. In fact, magnetization measurements[6] showed metamagnetic transitions within the AF phase.

The present work originated in the search for high-magnetostrictive materials. The largest magnetostriction at room temperature reported previously was observed in the rare-earth intermetallic $Tb_{0.27}Dy_{0.73}Fe_2$ (Terfenol)[7] ($\lambda_t = \lambda_{\parallel} - \lambda_{\perp} \approx 2 \times 10^{-3}$, giving $\omega = \lambda_{\parallel} + 2\lambda_{\perp} \approx 0$ at room temperature and in applied fields up to $H = 2.5$ T). We recently observed a giant volume magnetostriction in $TbMn_2$ of $\omega = -17 \times 10^{-3}$ at *low temperatures* and high applied magnetic fields.[8] These temperatures and field requirements for such a huge magnetostriction reduce the possibility of technical applications for such an alloy. Nevertheless, from these previous findings it was established that a mechanism different from the single-ion magnetoelastic coupling (as in Terfenol) can cause large magnetostrictions. In the case of $TbMn_2$, the large volume magnetostriction is a consequence of a field-induced transition from the expanded low-temperature state in which the Mn atoms carry a local magnetic moment of $\mu_{\text{Mn}} = 2.7\mu_B$, to a non-expanded phase, in which Mn atoms have no local magnetic moment. We have suggested from experiments on RMn_2 (R = rare earth) that research on magnetostrictive materials should be focused on compounds in which magnetic transitions occur with large magnetovolume effects.[9] With this idea in mind, we selected the unusual Fe-Rh system in the hope of finding a large magnetostriction. No evidence of large magnetostriction was previously reported in this compound to our knowledge. Early work by Melville *et al.*[10] gave magnetostriction constants $\lambda_{\perp} \approx 0.4 \times 10^{-3}$ and $\lambda_{\parallel} \approx 0$ at low temperature in FeRh. Nevertheless, our preliminary thermal-expansion result pointed out a difference in volume of 0.82% between F and AF phases. As a consequence, and based on the former RMn_2 results, we might expect a volume magnetostriction corresponding to a similar volume increase if the underlying mechanism is similar, i.e., a field-induced local moment.

0163-1829/94/50(6)/4196(4)/$06.00

EXPERIMENTAL DETAILS

The FeRh alloy was prepared from high-purity starting elements (99.99%) by arc melting in argon atmosphere. The final composition was tested by microprobe analysis. Heat treatment was performed under high vacuum (5×10^{-6} torr) at 1000 °C for 36 h and then the samples were slowly cooled down at an approximate rate of 10 °C/min. Powder from the sample can only be obtained by filing the sample but the stress induced during this process originates a transition from the bcc to the fcc structure. The powdered sample recovers the bcc structure after thermal annealing but it is uncertain if the annealed powdered sample has the same characteristics as the original bulk sample. In order to avoid this uncertainty, we performed x-ray analysis on the bulk sample using a D-MAX Rigaku diffractometer at the extended x-ray-absorption fine-structure (EXAFS) Spanish National Facility (Zaragoza). The results clearly showed a CsCl structure with a lattice parameter $a=3.000$ Å, with the presence of some traces of the fcc phase ($a=3.752$ Å), which is predominant in the x-ray diffraction pattern obtained on the powdered sample. The thermal expansion was measured in the temperature range 250–800 K using a commercial fully automatized dilatometer, based on the "push rod" and differential transformer method. The magnetostriction measurements were carried out using the strain-gauge technique under high pulsed magnetic field up to 14.5 T with a pulse width of 50 msec.

RESULTS AND DISCUSSION

A. Thermal expansion

The results from the thermal-expansion experiments are represented in Fig. 1. Three temperature regions are distinctly observed. The anharmonic Grüneisen behavior is strongly affected by the magnetic contribution. At temperatures below $T_c=680$ K an extra positive magnetic contribution appears as a consequence of the ferromagnetic ordering which significantly reduces the linear thermal expansion (LTE) coefficient α [$\equiv 1/L(\partial L/\partial T)$] by about 50% (see inset of Fig. 1 and Table I). Within the local-magnetic-moment approach (Heisenberg model), this extra contribution to the LTE coefficient arises from the thermal dependence of the two spin correlation functions and from the dependence of the exchange integral with distance.[11] On the other hand, within the itinerant-electron picture (Stoner model), a variation in the d-band polarization will produce a volume change. Within this latter scheme, Shiga[12] proposed that this contribution should be proportional to the square of the local magnetic moment rather than of the magnetization, as predicted by the extended Stoner model. For such an approach Shiga made use of a "local" band model, previously introduced by Korenman, Murray, and Prange,[13] where longitudinal spin fluctuations (Stoner excitations) and transverse spin fluctuations (spin-wave excitations) are responsible for the extra contribution to the LTE, usually call the "Invar" contribution. The magnitude of the α change observed at T_c in FeRh (Fig. 1, inset) suggests that the transverse spin fluctuations of magnetic moments with local character are responsible. In fact, a significant change of the local band polarization (Stoner scheme) through the transition would produce a magnetovolume effect orders of magnitude higher than the change observed in this compound at T_c.

TABLE I. Summary of the main magnetic and magnetoelastic properties of the FeRh alloy ($T_{F\text{-}AF}=405$ K, $T_C=680$ K). μ is the magnetic moment, α the linear thermal expansion coefficient, λ_t the anisotropic magnetostriction, and ω the volume magnetostriction.

FeRh (50 at. % Rh)	$T<T_{F\text{-}AF}$ (AF phase)	$T_{F\text{-}AF}<T<T_c$ (F phase)	
μ_{Fe} (μ_B)	3.2	3.2	Ref. 4
μ_{Rh} (μ_B)	0	0.9	Ref. 4
α (10^{-6} K^{-1})	9.5	6	This work
$10^6\lambda_t$	<10	<10	This work
$10^6\omega$	8200	<10	This work

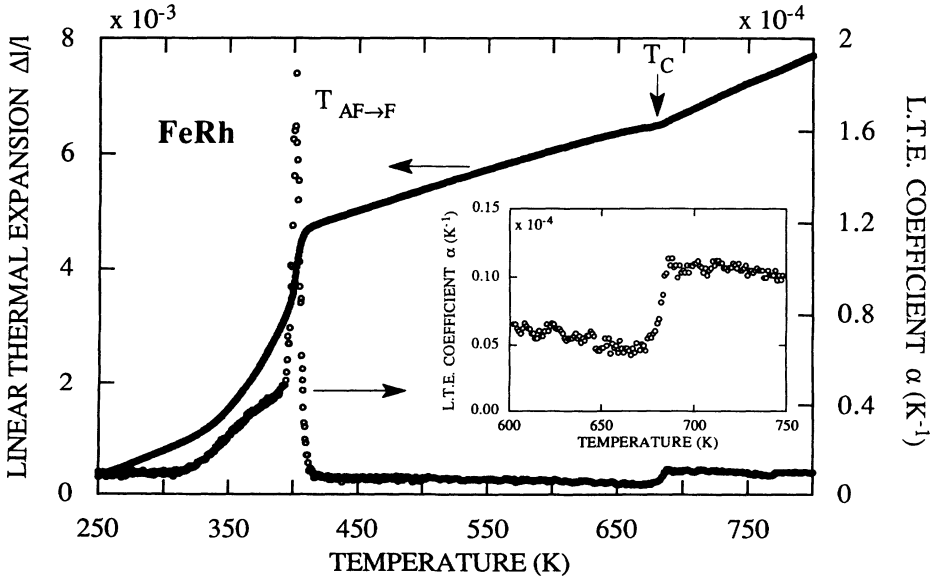

FIG. 1. Linear thermal expansion (LTE) and LTE coefficient α for FeRh. The inset shows the LTE coefficient around T_c.

In the temperature range between $T_{F\text{-}AF}=405$ K and T_c the ferromagnetic order is characterized by the existence of a large local magnetic moment at the Fe sites, $\mu_{Fe}=3.2\mu_B$, together with a local moment at the Rh sites, $\mu_{Rh}=0.9\mu_B$. At $T_{F\text{-}AF}$ the F-AF phase transition is accompanied by a very large and sharp drop of the LTE (Fig. 1), and the observed volume change amounts to 0.82%. The AF phase is characterized by type-II AF ordering in which μ_{Fe} keeps the same moment of $3.2\mu_B$ but there is no local magnetic moment at the Rh sites ($\mu_{Rh}=0$). At this transition, transverse spin fluctuations should not have any role, because the transition starts in the F phase and therefore the large observed contraction should be ascribed to a large spontaneous volume magnetostriction produced by the collapse of the Rh local magnetic moment within the AF phase. Consequently, such behavior can be accounted for within the framework of the above-mentioned Shiga local band model.

The observed behavior is quite peculiar, since, in general, thermal excitations of longitudinal spin fluctuations tend to collapse the local moments of the Rh atoms, as happens in Invar alloys[12] and also in the RMn_2 intermetallics.[14] A recent first-principles total-energy band calculation, based on the augmented-spherical-wave method, performed by Moruzzi and Marcus[5] predicted the existence of a low-volume AF ground state in FeRh and a high-volume F state, which lies as a metastable state above the AF state at low temperatures, separated by an energy barrier. Such a F state can be attainable either by thermal overbarrier excitations or under an applied magnetic field. This would reduce both the energy barrier and the F energy level below the AF energy level, giving rise to the transition. According to this theoretical prediction the thermal-expansion results look completely understandable, being the opposite of the Invar effect and thus called anti-Invar.[15]

B. Magnetostriction

We have performed high-pulsed-magnetic-field magnetostriction measurements above room temperature and up to 14.5 T. The measurements were carried out along the parallel ($\lambda_\parallel$) and perpendicular ($\lambda_\perp$) directions to the applied magnetic field. Both magnetostriction values were found to be independent of the field direction ($\lambda_\parallel=\lambda_\perp$), and consequently the anisotropic magnetostriction $\lambda_t=\lambda_\parallel-\lambda_\perp$ is negligible and the volume isotropic magnetostriction $\omega=\lambda_\parallel+2\lambda_\perp$ reaches a hugh value. In Fig. 2 we display the volume magnetostriction isotherms of FeRh obtained above room temperature. As may be observed, a large value of the magnetostriction [$\omega=(8.2\pm0.2)\times10^{-3}$] is reached above certain critical field values. The magnetostriction values above these critical fields are constant. In Fig. 3 we represent the thermal dependence of the maximum magnetostriction. An almost constant value at temperatures well below $T_{F\text{-}AF}$ is observed. The magnetostriction rapidly vanishes as we approach $T_{F\text{-}AF}$. In fact, in the F phase the volume magnetostriction is negligible ($\omega<10^{-6}$). A first attempt to explain this large volume magnetostriction might be based on the hypothesis of a metamagnetic transition in

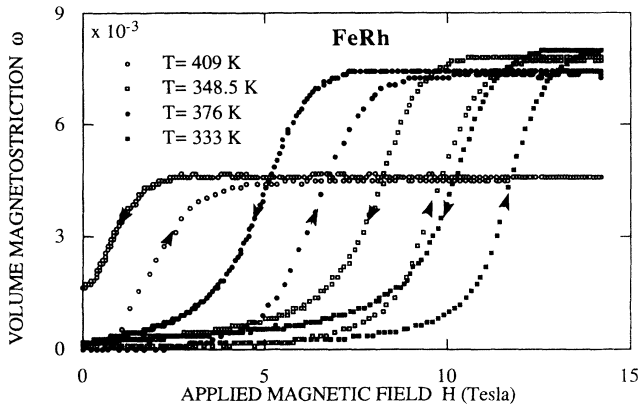

FIG. 2. Isotherms of the volume magnetostriction ω for FeRh vs applied magnetic field (the arrows show the direction of the field variation).

which the antiferromagnetic ordering will be destroyed by the applied magnetic field. This process would encompass a rotation of the magnetic moments (spin-flip or spin-flop processes) to reach the F state, where the magnetic moments are well aligned. If such is the mechanism, we should also observe a large volume magnetostriction in the F phase at low fields when the polycrystalline sample reaches the saturation magnetization. This is not the case, and as a consequence we discard such a hypothesis. We should take into consideration that the value observed for the field-induced volume magnetostriction is of the same order as the spontaneous volume change up to T_c observed in the thermal-expansion results. This fact constitutes clear evidence that the effect of the field is to induce a transition from the low-volume AF phase to the high-volume F phase through a first-order magnetic phase transition at a determined critical field H_{cr} (see Fig. 2). This critical field is temperature dependent and its thermal dependence is displayed in Fig. 4. The values of H_{cr} were obtained at the maximum slope of the isotherm curves and display a linear dependence with temperature in the range of our available magnetic fields. A large hysteresis of about 2 T is also observed at the first-order field-induced transition, as expected.

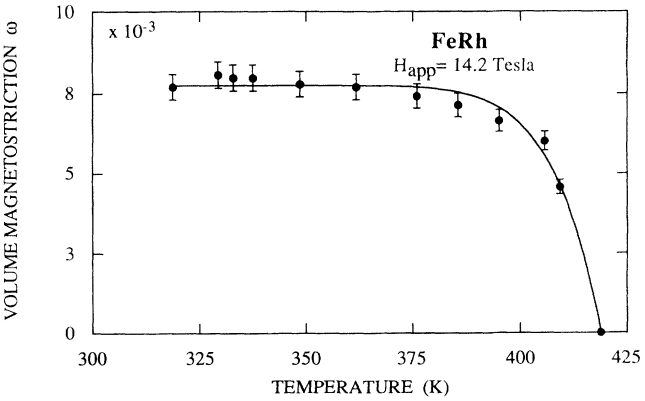

FIG. 3. Thermal dependence of the volume magnetostriction ω at 14.2 T for FeRh (the line is a visual guide).

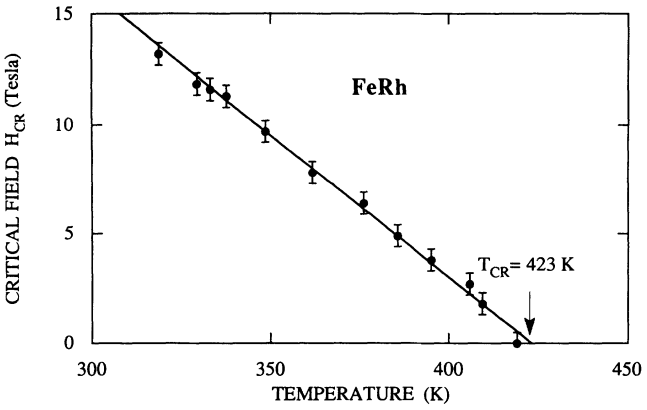

FIG. 4. Thermal dependence of the critical field H_{cr} obtained from the magnetostriction isotherms for increasing field.

CONCLUSIONS

Thermal-expansion results reveal that the FeRh alloy is an interesting system in which both Invar and anti-Invar effects are present in different range of temperatures. The Invar-like behavior in FeRh is observed at and below T_c and it is mainly attributed to transverse fluctuation of the local magnetic moments, which remain practically constant through and below the transition within the F phase. The anti-Invar behavior is observed at $T_{F\text{-}AF}$ and it is attributed to the collapse of the local μ_{Rh}, as a consequence of the longitudinal spin fluctuations at low temperatures.

We have observed in this alloy a very large field-induced magnetostriction above room temperature. This huge volume magnetostriction gives experimental support to the theoretically predicted existence of a metastable ferromagnetic high-volume state in which the Rh has a local magnetic moment. This underlying mechanism for the huge magnetostriction in FeRh can be related to that observed in $TbMn_2$ which shows a large volume magnetostriction at low temperatures. However the existence of such a magnetostriction in FeRh at and above room temperature makes this alloy very attractive as a candidate for application as a magnetostrictive transducer.

ACKNOWLEDGMENTS

The authors acknowledge Professor A. del Moral for a critical reading of the paper. We also acknowledge Dr. J. García and Dr. J. Blasco for the x-ray analysis and the financial support of the Spanish CICYT under Grant No. PB92-0095.

[1]M. Fallot and R. Hocart, Rev. Sci. **77**, 498 (1939).
[2]G. Shirane, C. W. Chen, and P. A. Flinn, Phys. Rev. **131**, 183 (1963).
[3]J. S. Kouvel and C. C. Hartelius, J. Appl. Phys. **33**, 1343 (1962).
[4]G. Shirane, C. W. Chen, P. A. Flinn, and R. Nathans, J. Appl. Phys. Suppl. **33**, 1044 (1963).
[5]V. L. Moruzzi and P. M. Marcus, Phys. Rev. B **46**, 2864 (1992).
[6]J. B. McKinnon, D. Melville, and E. W. Lee, J. Phys. C **1**, S46 (1962).
[7]A. E. Clark, in *Ferromagnetic Materials,* edited by E. P. Wohlfarth (North-Holland, Amsterdam, 1980), Vol. 1, p. 531.
[8]M. R. Ibarra, C. Marquina, L. Garcia-Orza, and A. del Moral, Solid State Commun. **87**, 695 (1993).
[9]M. R. Ibarra, C. Marquina, L. García-Orza, Z. Arnold, and A. del Moral, J. Appl. Phys. (to be published).
[10]D. Melville, A. del Moral, J. A. Ricodeau, and E. W. Lee, in *Proceedings of the XXth International Conference on Magnetism, Moscow* (Nauka, Moscow, 1974), Vol. 1, p. 174.
[11]E. Callen and H. B. Callen, Phys. Rev. A **139**, 455 (1965).
[12]M. Shiga, J. Phys. Soc. Jpn. **50**, 2573 (1981).
[13]V. Koreman, J. L. Murray, and R. E. Prange, Phys. Rev. B **16**, 4032 (1977).
[14]M. Shiga, Physica B **149**, 293 (1988).
[15]V. L. Moruzzi, Phys. Rev. B **41**, 6939 (1990).