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Abstract

Samples of U_6Fe were prepared by arc melting U and enriched ^{57}Fe . The samples display superconducting transitions which are sensitive to long-term exposure to air. Room temperature spectra of U_6Fe typically display a majority site A (quadrupole splitting $\Delta = 0.749(3)$ mm/s, isomer shift $\delta = -0.482(6)$ mm/s relative to Cu) and a minority site B ($\Delta = 0.55(3)$ mm/s, $\sigma = -0.12(3)$ mm/s) with the site intensity ratio (I_B/I_A) typically 0.05 to 0.10. The I_B/I_A intensity ratio increases upon air exposure of the samples. We have studied Mössbauer spectra as a function of temperature T in the range $15 \text{ K} \leq T \leq 310 \text{ K}$ paying particular attention to the T-variation of the isomer-shift and recoil-free-fraction of the majority site A. The results indicate a consistent softening of lattice vibrations of U_6Fe at $T \lesssim 170 \text{ K}$.

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1. INTRODUCTION

Superconductivity in compounds of Uranium with the transition metals (Mn, Fe, Co, Ni) was discovered⁽¹⁾ by Chandrasekhar and Huhl nearly 3 decades ago. In recent years, the low temperature physical properties of these superconductors have been the focus of intense experimental and theoretical scrutiny. This is largely the case because the origin of superconductivity in U materials may not always be of the usual kind where strong electron-phonon effects dominate. Results of recent low temperature specific heat, paramagnetic susceptibility, resistivity and upper critical field (H_{c2}) experiments taken together suggest that the origin of superconductivity in several U-compounds (particularly UBe_{13} and UPt_3) can be traced to a strongly interacting Fermi-liquid⁽²⁾ in which the superconducting electrons possess a large effective mass $m^* \approx 200$ times the free electron mass m_e . Specifically, DeLong and coworkers^(3,4) have shown that U_6Fe can be characterized as a moderately heavy ($m_e^* \approx 20 m_e$) fermion superconductor which also displays strong paramagnetism.

^{57}Fe Mössbauer spectroscopy provides a useful chemical probe of the transition metal site symmetry in U_6Fe . It also serves as a low-temperature probe of phonon spectral densities through T-dependent measurements of Debye-Waller factor (f-factor) and isomer-shift (δ). At low temperatures, these observables (F, δ) provide a measure of the -1 moment and the +1 moment of the phonon spectral density. We have performed⁽⁵⁾ such measurements on several samples of U_6Fe in the range $12 K < T < 300 K$ and report results of these experiments herein. We observe evidence of a consistent softening of the phonon spectral density over a broad temperature range $12 K < T < 170 K$. In this temperature range the Mössbauer Debye temperature of U_6Fe is found to be 332 K--i.e., 18 K lower than its value of 350 K found at higher temperatures ($170 K < T < 300 K$). Neither the

isomer shift nor the quadrupole splitting displays evidence of a first order anomaly in the temperature range $12 \text{ K} < T < 170 \text{ K}$. Recently, Kimball⁽⁶⁾ and co-workers have also reported T-dependent Mössbauer measurements of U_6Fe . There are certain similarities and differences between our findings and those of Kimball et al. on which we comment below.

2. EXPERIMENTAL

A closed cycle refrigerator (Air Products Model Displex 202) was used to cool U_6Fe absorbers to low temperatures. The absorber temperature was regulated using a Si-diode thermometer and a Lake Shore Cryotronics temperature controller model DRC-80C. The long term (24 hours) temperature stability of the system was typically $\pm 1/2 \text{ K}$. ^{57}Co in Cu metal was used as a source of 14.4 keV γ rays in the experiments. The source was held at room temperature.

Samples of U_6Fe were prepared by arc melting elemental Uranium and isotopically enriched (90%) ^{57}Fe meal, followed by a low temperature annealing as discussed elsewhere⁽⁷⁾. A total of four absorbers were studied, each from an independent arc melting preparation. Because of space limitations, we present detailed T-dependent results on only one of the absorbers, although these results are representative of the other samples. The absorber in question was prepared as follows. An ingot of U_6Fe stoichiometry was crushed to a fine powder in an Argon-atmosphere glove bag. The powdered sample was thereafter sealed in an evacuated fused silica ampoule and annealed at 200°C for about 120 hours to relieve strains incurred when the material was powdered. The annealed sample was mounted on a Be foil with General Electric Varnish 7014 and cured overnight at room temperature in an Argon glove bag before transferring the absorber into the vacuum shroud of a closed-cycle refrigerator.

The spectra were found in general to be characterized by a slightly asymmetric doublet (Fig. 1). We found it necessary to model the lineshape by considering the presence of two Fe sites giving rise to 2 quadrupole doublets (Site A: majority site; Site B: minority site), as shown in Fig. 1a. Note that a one-site fit to the same spectrum leads to systematic misfits near the locations denoted by arrows in Fig. 1a.

The special handling of the U_6Fe samples in an inert gas environment was necessitated on account of air sensitivity⁽⁵⁾ of the samples. Figure 1b shows a room temperature Mössbauer spectrum of the first U_6Fe sample studied, both in its virgin state and after approximately 1 month exposure to an ambient environment. The pronounced growth of the B-site spectrum upon air exposure clearly suggests that this particular site is related to an oxidation product, leading to the inevitable conclusion that site A is intrinsic to U_6Fe . It is worth noting that even the spectrum of the virgin U_6Fe sample (Fig. 1b) also displays traces of the B site. This is best revealed by a slight intensity asymmetry of the doublet and a concomitant misfit of the doublet spectrum near $v = +0.4$ mm/s in Fig. 1b. Spectra of each of the four U_6Fe samples that we investigated in our laboratory always displayed a slight intensity asymmetry. To account for the observed lineshape, we therefore felt compelled to analyze the spectra in terms of two sites. Figure 2 reproduces spectra obtained at selected temperatures. The site A parameters deduced from spectral analysis are summarized in Fig. 3.

3. DISCUSSION

The nuclear hyperfine structure parameters (isomer shift δ , quadrupole splitting Δ) of the majority site (A) and minority site (B) deduced from our spectra of U_6Fe are compared to those of UFe_2 ⁽⁸⁾ and previous results⁽⁹⁾ on U_6Fe

in Table I. We believe that site A is intrinsic to U_6Fe while the site B is characteristic of an oxide phase, whose nature is less certain at this time. The parameters of site A are in reasonable agreement to those reported recently by Kimball et al. and previously by Blow et al.

The T-dependence of the site A parameters (δ and Δ) shown in Fig. 3 exhibit a smooth variation with temperature. The $\delta(T)$ parameter can be well fit to a second order Doppler shift characteristic of a Debye temperature $\theta_D = 350$ K. The $\Delta(T)$ parameter, on the other hand, appears to decrease linearly with temperature (continuous line) although we could not rule out the possibility that the slope $d\Delta/dT$ changes slightly at or near $T = 150$ K (broken line), as shown in Fig. 3. The change in slope near $T \approx 150$ K is more obvious in a T-dependent measurement carried out on a $U_{5.9}Fe$ sample.

The T-dependence of the integrated line intensity derives from that of the Fe site Debye-Waller factor $f(T)$. The variation can be fit reasonably well to a Debye temperature $\theta_D = 350$ K as shown in Fig. 3. We note, however, that at $T < 170$ K there is a general reduction in Debye temperature and a value of $\theta_D = 332$ K is more appropriate at lower temperatures. This result is suggestive of a red shift in the phonon spectral density of U_6Fe and could be the result of a potential charge density wave state in this material^(6,10).

The present Mössbauer results on U_6Fe , particularly the T-variation observed by us at lower temperatures differs from that of Kimball et al.⁽⁶⁾ in the following respects. We do not observe a step-like discontinuity in the $\Delta(T)$, $\delta(T)$, and $f(T)$ parameters near $T = 90$ K. Interestingly, T-variation of the tetragonal cell length of U_6Fe established by neutron diffraction measurements⁽⁶⁾ reveals a smooth variation in the 'a' and 'c' lattice parameters. These findings do not support evidence of a structural phase transition near 90 K. The neutron

diffraction results on U_6Fe are clearly in harmony with the present Mössbauer results.

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References

1. B. S. Chandrasekhar and J. K. Hulm, *J. Phys. Chem. Solids* 7, 259 (1958).
2. G. R. Stewart, *Rev. Mod. Phys.* 56, 755 (1984).
3. L. E. DeLong, J. G. Huber, K. N. Yang, and M. B. Maple, *Phys. Rev. Lett.* 51, 312 (1983).
4. L. E. DeLong, R. P. Guertin, S. Hasanain, and T. Fariss, *Phys. Rev. B* 31, 7059 (1985).
5. G. Lemon, P. Boolchand, M. Stevens, M. Marcuso, L. E. DeLong, and J. G. Huber, *Bull. Am. Phys. Soc.* 29, 405 (1984).
6. C. W. Kimball, P. P. Vaishnava, A. E. Dwight, J. D. Jorgensen, and F. Y. Fradin, *Phys. Rev.* (to be published); also see *Bull. Am. Phys. Soc.* 29, 405 (1984).
7. J. J. Engelhardt, *J. Phys. Chem. Solids* 36, 123 (1975).
8. T. K. McGuire and R. H. Herber, *Solid State Commun.* 48, 393 (1983).
9. S. Blow, *J. Phys. and Chem. of Solids* 30, 1549 (1969); also see *J. Phys. C* 3, 845 (1970).
10. L. E. DeLong, G. W. Crabtree, L. N. Hall, H. Kierstead, H. Aoki, S. K. Dhar, K. A. Gschneidner, Jr., and A. Junod, *Physica* 135B, 81 (1985).

TABLE I

Host	T	δ^* (mm/s)	Δ (mm/s)	Ref.
UFe ₂	300 K	-0.46(3)	0.46(3)	McGuire & Herber
	300 K	-0.36(3)	0.47(1)	Blow et al.
U ₆ Fe	A 260 K	-0.482(6)	0.749(2)	Present work
	B	0.01(2)	0.56(3)	Present work
U ₆ Fe	250 K	-0.45(3)	0.72	Kimball et al.
U ₆ Fe	300 K	-0.59(3)	0.69(3)	Blow et al.

* Shifts relative to Cu metal at 300 K.

Figure Captions

Fig. 1 a) Gamma ray transmission vs source velocity for U_6Fe at room temperature. The top curve illustrates a model spectrum in which only one Fe site is assumed. The second curve demonstrates the systematic disagreement between the single-site model and the experimental data, particularly in regions emphasized by the arrows. The third curve illustrates a model spectrum composed of absorption contributions from two types ("A" and "B") of Fe site. The lowest curve demonstrates the excellent agreement between the two-site model and the experimental data.

b) Gamma ray transmission vs source velocity for U_6Fe at room temperature. The top two curves illustrate a single-site model fit of data for a freshly powdered sample. Only a small asymmetry of the doublet is observed, and the single-site model yields a reasonable fit of the data. The lower two curves demonstrate that a two-site model is necessary to explain the marked asymmetry of the spectrum of the same powder absorber after it was exposed to air for approximately one month.

Fig. 2. Gamma ray transmission of a U_6Fe absorber held at each of the three different temperatures given. The curves are model fits to the data assuming that two distinct Fe sites ("A" and "B") are present, as shown in Fig. 1. The parameterizations of these fits are illustrated in Fig. 3 and Table 1.

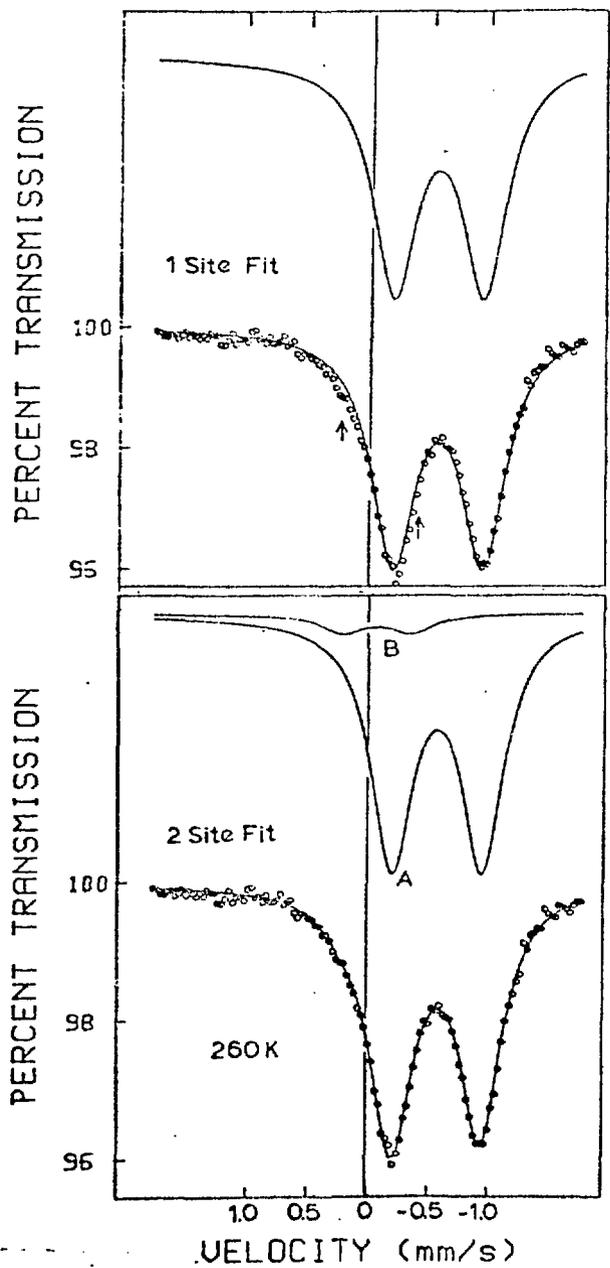
Fig. 3. Temperature dependence of the model fit parameters relevant to the A-site of U_6Fe .

Upper plot: Data for the temperature variation of $-\ln A$ (A is the integrated Mössbauer line intensity), which is proportional to the mean-square Fe thermal displacement. The curves give predicted temperature dependences of $-\ln A$ for several values of Fe-site Debye temperature θ_D . The fit for $\theta_D = 350$ K describes the data from room temperature to ~ 170 K, below which a softening of the lattice appears to occur, whereupon the data are in better agreement with a curve for $\theta_D = 332$ K.

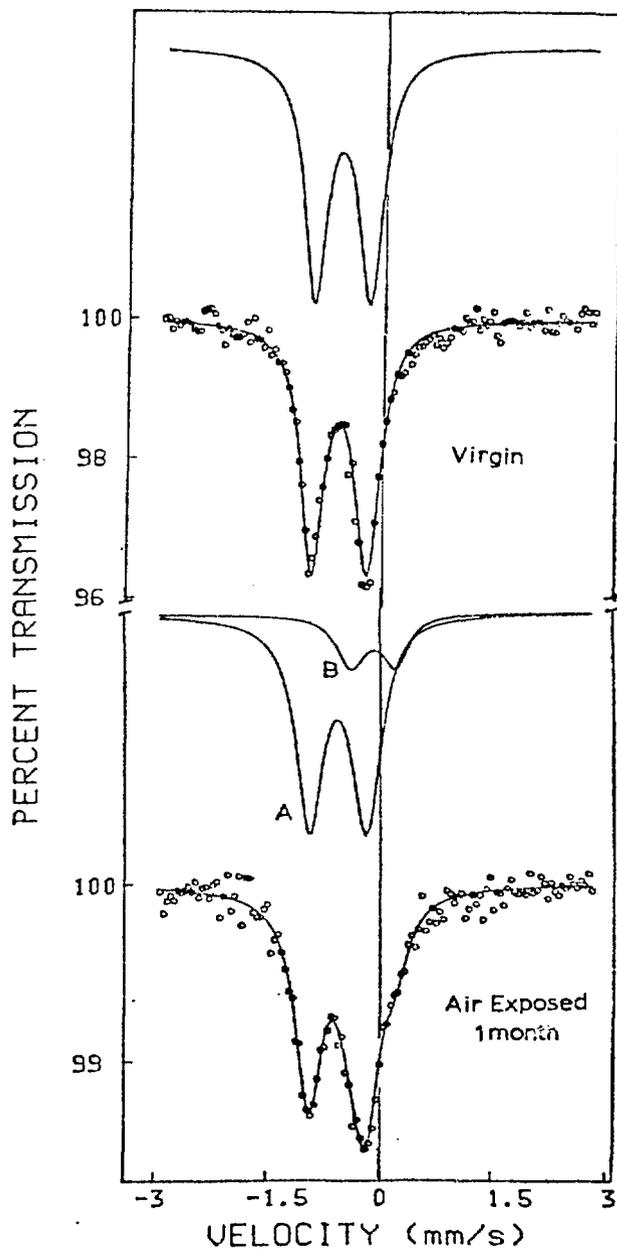
Middle plot: Temperature dependence of the Mössbauer quadrupole splitting Δ . The data appear to follow a smooth variation, within experimental error, as indicated by the solid guide line. The broken curve illustrates a possible change in slope $d\Delta/dT$ at $T \approx 150$ K, also consistent with the data. These results show no clear evidence for a structural phase transition in U_6Fe .

Bottom plot: Temperature dependence of the isomer shift δ . The data can be fitted with reasonable accuracy by the curve which gives the temperature dependence expected for an Fe-site $\theta_D = 350$ K.

FIGURE 1



(a)



(b)

FIGURE 2

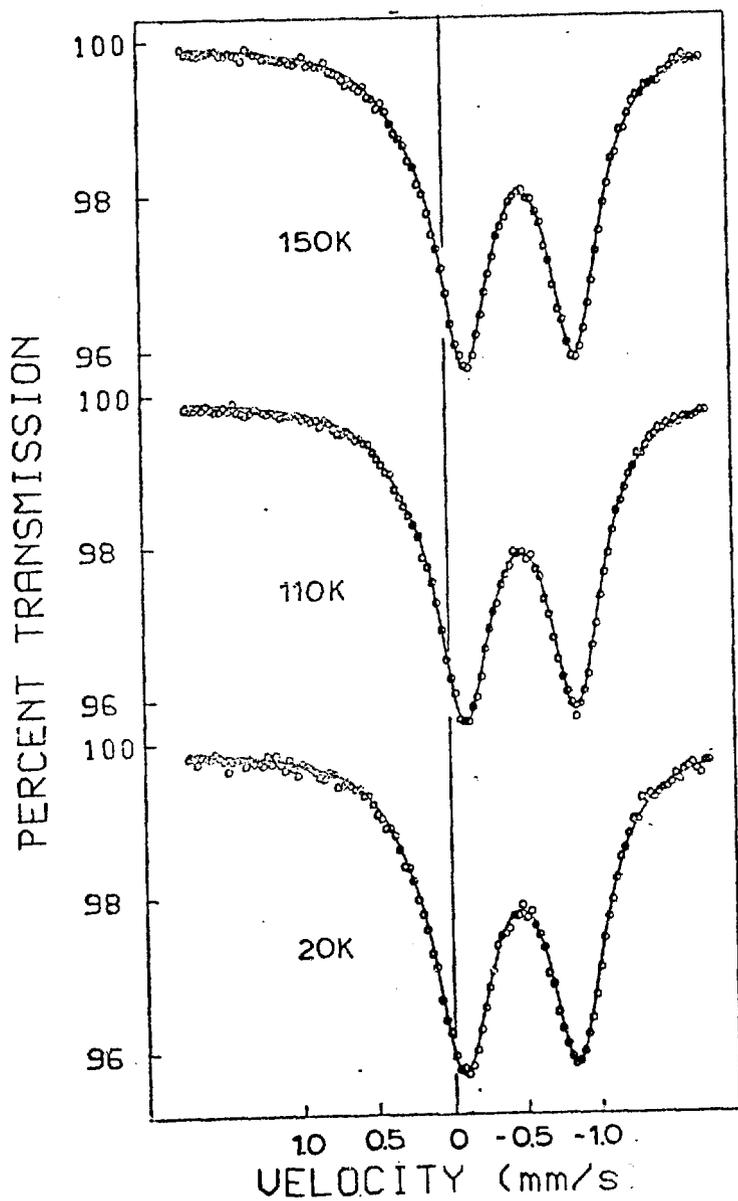


FIGURE 3

