PHYSICAL REVIEW B VOLUME 49, NUMBER 5 1 FEBRUARY 1994-I

Anomalous recoilless fraction of 30-Å-diameter FeOOH particles

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(Received 16 December 1992; revised manuscript received 19 October 1993)

Investigation of a 30-Å iron oxyhydroxide catalyst by Mössbauer spectroscopy revealed that the recoilless fraction decreased dramatically with increasing temperature, becoming effectively zero at 50 K. This effect is explained on the basis of a combined effect of the recoil of the particle and the particle motion due to thermal agitation. The mean-square amplitude of particle motion is derived as a function of temperature. Application of uniaxial pressure to the sample or freezing the sample in carnuba wax increased the recoilless fraction markedly by enhancing the interparticle contact forces.

I. INTRODUCTION

It is well known that the physical properties of small particles may differ substantially from their corresponding bulk properties. A number of studies have been done on the Mössbauer effect of ultrathin films and fine particles. Von Eynatten and Bommel[1] observed a dramatic size-and temperature-dependent lowering of the recoilless fraction for iron microcrystals ranging in size from 70 to 450 Å and proposed oscillation of microcrystals and the effect of surface phonons as two possible explanations for such behavior. Similar effects of smaller recoil-free fractions compared to the corresponding bulk materials have been observed for iron oxide phases[2,3] and for microcrystals of gold,[4,5] tin,[6] and tungsten.[7] Such behavior has been attributed to a cutoff frequency in both the lower- and higher-frequency limits of the phonon spectra in the Debye model. As discussed by Van Wieringen, the theory of cutoff frequency is adequate if the particle size is large enough to give a recoil-free absorption.[8] The Mössbauer effect seen in a number of studies on small particles is due to the fact the recoil is shared by a number of particles depending on the packing of the powder sample. Therefore the degree of packing plays an important role in determining the Mössbauer effect. However, the temperature-dependent behavior of the recoil-free fraction is independent of the degree of packing and has usually been attributed to the particle motion. Niemanstsverdriet *et al.*[9] found a 35% decrease in the recoilless fraction of 200 Å α-FeOOH between 150 and 400 K and attributed it to particle motion. Viegers and Trooster[5] suggested that the vibrations of the particle as a whole are responsible for the anomalous decrease of the recoilless fraction f with temperature in small particles of gold metal, and they proposed the expression

$$f(T)=f_l(T)f_p(T) , \qquad (1)$$

in which T is the temperature, f_l represents the influence of the lattice vibrations on the recoilless fraction, and f_p accounts for the motion of the particle. The validity of this approach was demonstrated by Hayashi *et al.*[10] for small iron particles. Here we present the Mössbauer results from a 30-Å Fe oxide catalyst which effectively showed a total loss of the recoil-free fraction between 10 and 50 K. The disappearance of the recoilless fraction at such a low temperature (~ 50 K) for ^{57}Fe is quite unusual. To our knowledge, such a drastic decrease with increasing temperature to an effectively zero recoilless fraction for iron in a solid material has never been previously observed below room temperature. The results are explained in terms of a combined effect of the particle motion due to thermal agitation and the recoil of the particle on absorption of the γ ray.

EXPERIMENTAL PROCEDURES

The ultrafine iron oxide catalyst (Nanocat) was provided by Mach I, Inc.[11] It was produced by the controlled oxidation of an organic iron compound, which is vaporized at a temperature below about 500 °C. The gaseous iron-containing compound is then diluted with an inert gas and oxidized in an oxygen-containing atmosphere to form small particles of iron oxide. The catalyst is a free-flowing powder of reddish brown color. Transmission electron microscopy (TEM) studies[12] show the particles to be approximately spherical with an average diameter of 32 Å. Both TEM (Ref. 12) and x-ray-absorption fine-structure (XAFS) studies[13] indicate that the structure of the catalyst is predominantly FeOOH.

Mössbauer experiments were carried out on this catalyst using a constant-acceleration spectrometer of standard design.[14–16] The radioactive source consisted of 50–100 mCi of ^{57}Co in a Pd matrix. The sample was in powder form and was mounted in a Plexiglas compression holder presenting a thin aspect to the γ-ray beam. Sample cooling to temperatures as low as 10 K was achieved using an Air Products displex cryogenic system. Intermediate temperatures between 10 K and room temperature were obtained using a temperature-controlled cartridge heater inserted in the copper sample block. Calibration spectra of metallic iron at room temperature were obtained simultaneously at the other end of the drive.

RESULTS AND DISCUSSION

Figure 1 shows the 45- and 10-K Mössbauer spectra of the as-received ultrafine 30-Å catalyst. It can clearly be seen that the recoilless fraction f, as measured by the ab-

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sorption area *A*, increases significantly on cooling from 45 to 10 K. The room-temperature spectrum exhibited no observable Mössbauer effect. Spectra obtained at a series of temperatures below room temperature established that no significant Mössbauer effect is observed down to about 50 K. The disappearance of the recoilless fraction for ^{57}Fe in a solid material at such a low temperature, as far as we know, has never been reported before. A similar set of experiments were performed on the same sample after pressing it in a hydraulic press at a pressure of 600 kg/cm^2. The sample was then crushed into a powder form, and spectra were obtained at several temperatures between 10 K and room temperature in the same low-temperature experimental setup. The room-temperature and 12-K spectra of the pressed sample are shown in Fig. 2. For this sample, which produced a significant Mössbauer absorption even at room temperature, the amount of sample required to obtain approximately the same absorption at 10 K was about one-fifth of that for the as-prepared sample. It is evident that the recoilless fraction is markedly increased by the application of pressure. However, the Mössbauer spectra of the pressed sample at 10 and 45 K are virtually identical to the spectra of the as-received sample at those temperatures, with the exception of the increased recoilless fraction (f) for the pressed sample, indicating that the particle size is not affected by pressing the sample. TEM results for the 30-Å raw and "pressed" catalysts (Fig. 3) confirmed that the sample submitted to hydrostatic pres-

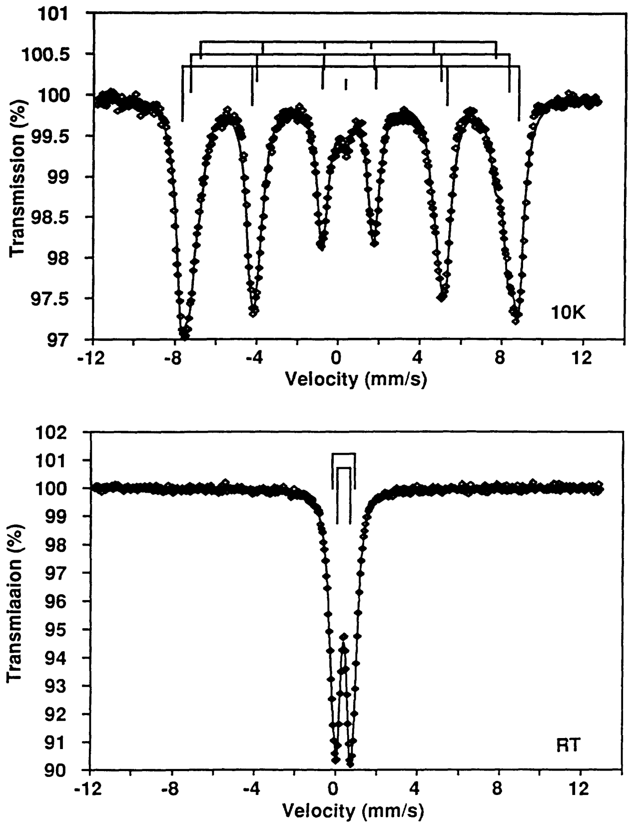

FIG. 2. Mössbauer spectra of 30-Å pressed sample at 10 K and room temperature.

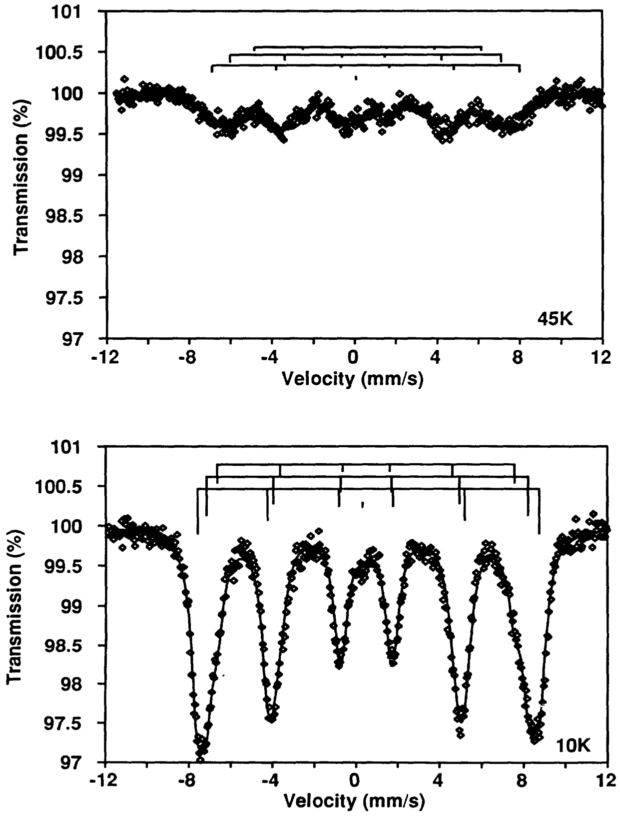

FIG. 1. Mössbauer spectra of 30-Å catalyst at 45 and 10 K.

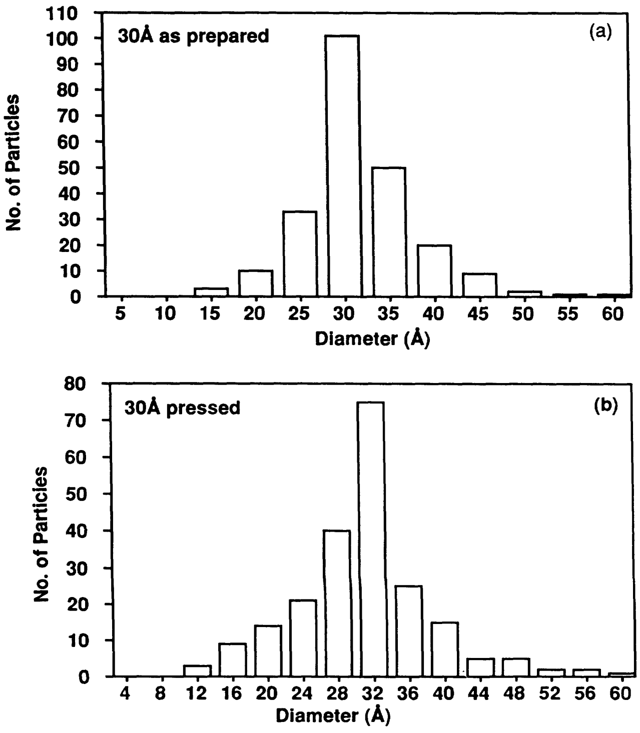

FIG. 3. Size distribution, as determined by TEM for (a) as-prepared catalyst, (b) pressed catalyst.

sure has essentially the same size distribution as the as-received sample.[12] Similar experiments were performed on the as-prepared sample frozen in carnuba wax, and the results were similar to those for the pressed sample. Mössbauer spectra were also obtained for a bulk α-FeOOH sample with surface area of 75 M^2/g, which exhibited strong absorption at all temperatures between 10 K and room temperature.

Mössbauer spectra of the as-received ultrafine 30-Å Fe-oxyhydroxide sample between 10 and 45 K consisted of six broadened lines, with a distribution of magnetic hyperfine fields. The spectra were least-squares analyzed by fitting the magnetic phase as three sets of six Lorentzian peaks. The Mössbauer spectra of the sample submitted to pressure and the sample frozen in carnuba wax exhibited a gradual collapse from a size-peak magnetic spectrum at 10 K to a quadrupole doublet at room temperature, indicating superparamagnetic behavior which is expected for particles of this size. This effect could not be observed in the as-received sample because the as-received sample exhibited zero recoil-free fractions at temperatures above 50 K. However, a gradual reduction of magnetic hyperfine field was observed for the as-prepared sample in going from 10 to 45 K. The Mössbauer parameters at different temperatures for the as-received sample, the sample submitted to pressure, and the sample frozen in carnuba wax are summarized in Table I. The bulk α-FeOOH sample showed a six-line magnetic pattern at all temperatures between 12 K and room temperature, with Mössbauer parameters consistent with published results.[17,18]

In order to calculate the value of the recoil-free fraction, the effective Mössbauer absorption thickness is determined by the least-squares fitting program by comparing the experimental peak with the theoretical expression[19,20]

$$A(x_{N,j}) = \frac{f_s \Gamma_0 \pi x_{N,j}}{2} \times e^{-x_{N,j}/2} \left[I_0 \left[\frac{x_{N,j}}{2} \right] + I_1 \left[\frac{x_{N,j}}{2} \right] \right] , \quad (2)$$

where $x_{N,j}$ is the effective thickness associated with peak

TABLE I. Mössbauer parameters for 30-Å Fe-oxyhydroxide catalyst. Hyperfine field (H) (kG), isomer shift (IS) (mm/s), quadrupole splitting (QS)(mm/s). The approximate percentage error in the reported values is 5%.

Sample	T (K)	H	IS	OS	% Fe
Fe-oxide catalyst	10	507	0.52	0.05	44
(as prepared)		477	0.50	0.02	38
		441	0.46	−0.02	18
			0.35		1
	25	497	0.52	0.05	42
		467	0.48	0.03	38
		429	0.48	−0.03	19
			0.35		1
	40	475	0.55	0.02	42
		422	0.44	0.06	36
		378	0.55	−0.09	20
			0.38		1
	45	461	0.54	0.02	37
		406	0.50	0.05	41
		341	0.68	−0.02	19
			0.20		3
Fe-oxide catalyst	10	513	0.53	0.04	48
(pressed)		485	0.50	0.02	34
		450	0.42	−0.01	16
			0.28		2
	50K	475	0.54	0.04	38
		432	0.51	0.03	40
		382	0.52	0.02	21
			0.30		1
	295		0.34	0.63	57
			0.34	1.08	43
Fe-oxide catalyst	10	507	0.50	0.06	40
(in carnuba wax)		476	0.52	00	39
		440	0.43	0.02	21
	295		0.34	0.63	58
			0.34	1.20	42

j of the phase N, I_0 and I_1 are the modified Bessel functions, f_s is the recoilless fraction of the source, and Γ_0 is the natural width (0.0968 mm/s) of the 14.4-keV level of Fe^{57}. For the current, single-phase sample, the total effective absorber thickness X is obtained by summing the effective thicknesses of all peaks, j, of all magnetic and quadrupole components k indicated in Table I:

$$X = \sum_{k,j} x_{k,j} \ . \tag{3}$$

The recoilless fraction of the absorber, f, is then given by

$$f = \frac{X}{\sigma_0 a_{57} n d} \ , \tag{4}$$

where σ_0 is the nuclear cross section for resonant absorption ($\sigma_0 = 2.56 \times 10^{-18}$ cm^2), a_{57} is the isotopic abundance of ^{57}Fe ($a_{57} = 0.0219$), n is the number of iron atoms per gram in the absorber, and d is the weight per cross-sectional area of the absorber. However, this value of recoilless fraction is not very accurate, as it does not take into account the additional nonresonant intensity at the counter produced by the Compton scattering of higher-energy γ rays. Since we are only interested in a comparative study, the values of the recoilless fraction of this catalyst have been normalized relative to that of a bulk FeOOH sample at 12 K.

The resulting recoilless fractions determined for the as-received 30-Å sample, for the sample submitted to pressure, the sample frozen in carnuba wax, and the bulk α-FeOOH sample are shown in Fig. 4 (top). It can be seen that for the as-received sample the recoilless fraction f drops very sharply (75% between 10 and 45 K) and almost linearly with temperature. It can also be seen that the value of the recoilless fraction of the as-received samples is much reduced compared to the other samples, even at the lowest temperature. For the sample submitted to pressure and the sample frozen in carnuba wax, except for the absolute values of the recoilless fraction, which is lower for the sample frozen in carnuba wax, the behaviors of the decrease of the recoilless fractions with temperature are very similar. It can be seen from Fig. 4 that the recoilless fraction of the bulk sample is almost identical to that of the pressed sample, although the bulk sample does not show any superparamagnetic behavior, while the pressed sample exhibits significant superparamagnetic relaxation effects, consistent with its average particle size (30 Å). This indicates that for both the pressed and frozen samples, particle size does not play a major role in determining the recoilless fraction. Hayashi *et al.*[21] have shown that for iron particles (≈ 100 Å) embedded in various matrices, the Debye temperature does not differ much from the bulk value.

We will now discuss the different factors that affect the recoilless fraction. The Mössbauer effect is the "recoilless emission and absorption" of γ rays from a nucleus bound in a crystal lattice. However, the lattice as a whole (the lattice center of mass) always recoils after photon emission or absorption. So the essence of the Mössbauer effect is not photon emission or absorption without recoil, but rather is photon emission or absorption without transfer of energy to internal degrees of freedom of the lattice. The fraction of γ rays following this criteria is called the recoilless fraction. This fraction depends on the ratio of the mean-square vibrational amplitude $\langle x^2 \rangle$, of the emitting or scattering atoms to the square of the wavelength λ, of the scattered radiation,

$$f = \exp\left[-\left[\frac{4\pi^2 \langle x^2 \rangle}{\lambda^2} \right] \right] , \tag{5}$$

where $\langle x^2 \rangle$ is the mean-square amplitude of the vibration in the direction of emission of the γ ray averaged over an interval equal to the lifetime of the nuclear level involved in the γ-ray emission process. A number of simple conclusions may be drawn from an inspection of Eq. (5). For example, if $\langle x^2 \rangle$ is not bounded, the recoilless fraction will vanish. The contribution to $\langle x^2 \rangle$ comes from lattice vibration ($\langle x^2 \rangle_{\text{latt}}$) and the motion of the particle itself due to thermal agitation ($\langle x^2 \rangle_{\text{part}}$). With the assumption that there is no coupling between these modes, we can write

$$\langle x^2 \rangle_{\text{tot}} = \langle x^2 \rangle_{\text{latt}} + \langle x^2 \rangle_{\text{part}} \ . \tag{6}$$

As is well known, the contribution due to the lattice vibration can be best described by the Debye model. Equation (7) gives the mean-square amplitude of vibration as

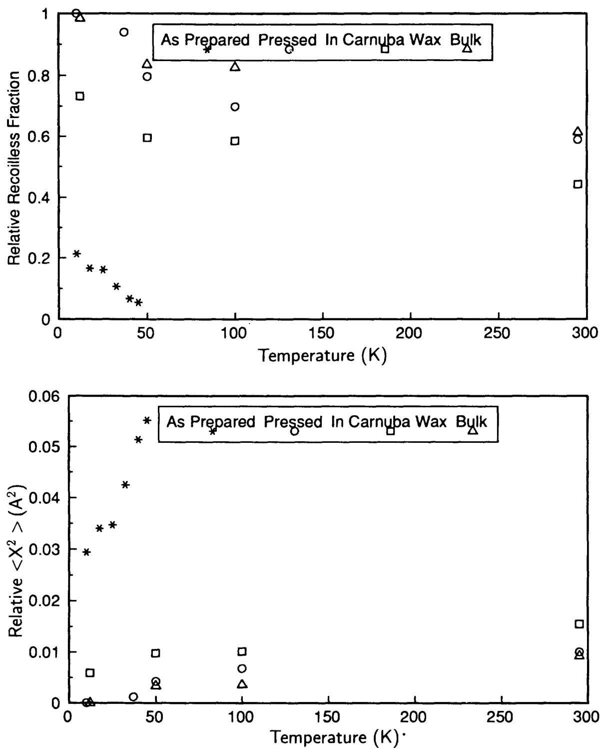

FIG. 4. Recoilless fraction and mean-square amplitude of vibration as a function of temperature for several samples.

defined by the Debye model, in the limit of low temperature:

$$\langle x^2 \rangle = \frac{3\hbar^2}{4Mk\Theta_D} \left[\frac{3}{2} + \frac{\pi^2 T^2}{\Theta_D^2} \right] , \quad T \ll \Theta_D , \tag{7}$$

where Θ_D is the Debye temperature defined by $\hbar\omega_{\text{max}} = k\Theta_D$.

The Debye expression for recoilless absorption [Eqs. (7) and (5)] is appropriate for bulk materials. The frequency spectrum of the lattice vibrations of extremely small crystals is expected to differ from the spectrum of bulk material. This difference can be due to finite boundary conditions causing a cutoff for long-wavelength phonons, thus enhancing f, or due to additional surface phonons on the large specific surface, thus reducing f.[2,4] A number of studies[1,9] have explained the temperature-dependent lowering of the recoil-free fraction of small particles in terms of smaller Debye temperatures for small particles compared to bulk material. Niemantsverdriet *et al.*[9] gave a value of 280 K for the Debye temperature of 200-Å α-FeOOH particles, compared to a Debye temperature of 500 K for bulk α-FeOOH, and attributed the reduction of the Debye temperature to the particle motion. For the current 30-Å FeOOH particles, the recoil-free fraction of 0.22 at 0 K gives a Debye temperature of 14 K, which is much too low. This indicates that the contribution from lattice vibrations is very small for these 30-Å particles and completely overshadowed by the particle motion.

The contribution to the mean-square amplitude of vibration due to particle motion can be approximated by comparing the 30-Å Fe-oxyhydroxide particle to a one-dimensional harmonic oscillator. Following the approach of Viegers and Trooster,[5] the mean-square amplitude of such a particle will be

$$\langle x^2 \rangle_{\text{part}} = \frac{\hbar}{2m\omega} \left[\frac{2}{e^{\hbar\omega/kT} - 1} + 1 \right] , \tag{8}$$

for

$$T = 0 , \quad \langle x^2 \rangle_{\text{part}} = \frac{\hbar}{2m\omega} = \frac{\hbar}{2\sqrt{qm}} , \tag{9}$$

where q is the binding force constant and m is the average particle mass.

The contribution to $\langle x^2 \rangle$ at $T=0$ due to particle motion can be calculated from Eq. (9). Assuming forces similar to those in molecular crystals,[5] the frequency $\bar{\omega}$ is estimated to be $\sim 10^{11}-10^{12}$ s^{-1}. Taking the single-particle mass of a 30-Å FeOOH sample, $\langle x^2 \rangle_{\text{part}}$ at $T=0$ is extremely small (0.0005 Å^2).

The recoil-free fraction is also dependent on the degree of packing. As pointed out by Van Wieringen,[8] a single particle can give rise to the Mössbauer effect if it is massive enough to absorb the γ radiation without recoiling, i.e.,

$$\begin{aligned} E_{\text{recoil}} &= E_\gamma^2 / 2Mc^2 \\ &\le \text{natural linewidth of } \gamma \text{ ray} \\ &= 4.6 \times 10^{-9} \text{ eV} . \end{aligned} \tag{10}$$

For ^{57}Fe, this equation gives a critical diameter of 250 Å.

The experimental fact that the Mössbauer effect can be seen for smaller particle sizes indicates that in these cases, γ recoil is shared by a large number of particles. For the current sample, the significant increase of the recoilless fraction on pressing the sample is a clear indication that the degree of packing plays an important role in determining the Mössbauer effect. In the as-received sample, most of the particles are bound to each other by very weak forces and can be considered as sufficiently independent to recoil individually upon absorption of a γ ray. The small contribution to recoilless absorption observed for this sample comes from a small percentage of particles that are clustered together and share the γ recoil. On submitting the as-prepared sample to some pressure, a large percentage of the particles get locked to each other and recoil as a rigid unit upon absorption of a γ ray, giving rise to a significant recoil-free fraction even at room temperature. Similarly, the particles frozen in carnuba wax exhibit a significantly increased recoilless fraction, although somewhat smaller than that of the particles in the pressed sample. The similarity of the recoilless fraction for the bulk and pressed samples indicates that the two samples have similar degrees of packing, although the particle sizes of the two samples are substantially different. The observation that the recoilless fraction of an ultrafine-particle sample fraction can be restored to close the bulk value by simply applying pressure has not been observed before. It implies that the ultrafine particles that come into contact form interparticle bonds that cause the larger multiparticle agglomerates to recoil as units.

It is of interest to study the behavior of $\langle x^2 \rangle$ as a function of temperature. The mean-square amplitude of vibration, $\langle x^2 \rangle$, at each temperature was determined from Eq. (5), using the normalized values of recoilless fractions relative to the recoilless fraction of the bulk sample at 12 K, as discussed before. Figure 4 shows the plot of the mean-square amplitude of vibration as a function of temperature for the as-received sample, the sample submitted to uniaxial pressure, the sample frozen in carnuba wax, and the bulk sample. Note that these are not the absolute value of $\langle x^2 \rangle$, but a mean vibrational amplitude relative to a zero vibrational amplitude of the bulk material at 12 K. It can be seen that for the as-received sample, the mean-square amplitude of vibration goes up very fast with the increasing temperature and has a nonzero value at $T=0$. The mean-square amplitudes for the sample subjected to pressure and the sample frozen in carnuba wax are similar to that for the bulk sample and go up very slowly with increasing temperature with an almost zero value at $T=0$.

As discussed earlier, the contribution to $\langle x^2 \rangle$ due to lattice vibration in this sample is almost negligible as compared to that due to particle motion, which was estimated to be very small at $T=0$ ($\langle x^2 \rangle_{\text{part}}$ at $T=0$ is

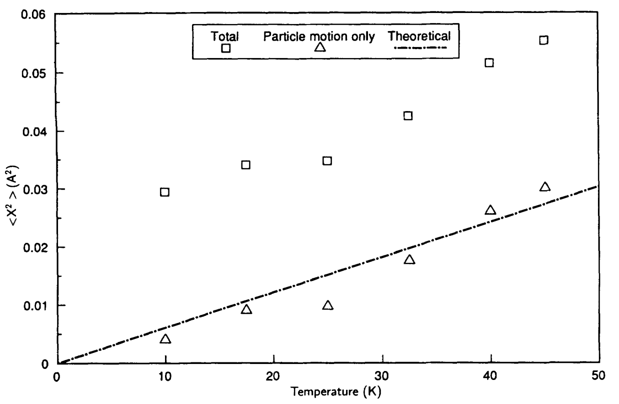

FIG. 5. Plot of $\langle x^2 \rangle$ as a function of temperature for the as-prepared sample. Theoretical line is plotted using Eq. (15) with $w = 2\times 10^{11}$.

$\sim$0.0005 Å^2). The apparent nonzero value of $\langle x^2 \rangle$ at $T=0$ ($\langle x^2 \rangle \approx 0.025$ Å^2), therefore, arises due to the recoil of a large percentage of particles upon absorption of the γ ray. This value is temperature independent and can be subtracted from the values of $\langle x^2 \rangle$ at all temperatures to give a good estimation of the mean-square amplitude of vibration due to particle motion, $\langle x^2 \rangle_{\text{part}}$. Figure 5 shows a plot of $\langle x^2 \rangle_{\text{part}}$ vs temperature. The squares are the values of $\langle x^2 \rangle_{\text{tot}}$ calculated from Eq. (5), and the triangles are the $\langle x^2 \rangle_{\text{part}}$ determined by subtracting $\langle x^2 \rangle_{T=0}$ from $\langle x^2 \rangle_{\text{total}}$. The solid line is the theoretical plot of $\langle x^2 \rangle$ vs T using Eq. (8). It is seen that $\langle x^2 \rangle$ approaches the linear approximation $\langle x^2 \rangle \approx kT/m\omega^2$. A value of $\omega = 2\times 10^{11}$ was found to give a slope that agreed well with the experimental data. The mass (m) in Eq. (8) is taken as the mass of a 30-Å particle of FeOOH assuming spherical particles. As discussed by Viegers and Trooster,[5] it is reasonable to assume binding forces similar to those in molecular crystals, which typically have vibration frequencies $\sim 10^{13}$ s^{-1} and molecular masses $\sim$2–10 times the mass of an FeOOH molecule. For the 30-Å Fe-oxide catalyst, with approximately 400 FeOOH molecular units per particle, a value of ω of the order of 10^{11} s^{-1} is therefore quite reasonable.

Assuming that the nonzero value of $\langle x^2 \rangle$ at $T=0$ arises mostly because of the recoil of the particles, its value can give an estimate of the percentage of particles that exhibit recoil-free absorption. By comparison of the $\langle x^2 \rangle$ value, it is found that the percentages of particles giving rise to recoilless absorption at $T=0$ K in the pressed sample and the sample frozen in carnuba wax are approximately 3 times larger than that in the as-prepared sample.

SUMMARY

Mössbauer results for an ultrafine iron oxide catalyst show a drastic lowering of the recoil-free fraction with increasing temperature. This behavior is attributed to the particle motion due to thermal vibration in this free-flowing catalyst. The mean-square vibrational amplitude of the particles as a function of temperature was determined from the recoil-free fraction. The temperature dependence of the mean-square vibrational amplitude is found to agree well with a simple harmonic-oscillator model.[5] The very low values of the recoil-free fraction and the apparent nonzero value of the mean-square vibration amplitude at $T=0$ are due to the fact that most of the particles in the as-prepared sample are loosely bound and recoil upon the absorption of γ radiation. A significant increase in the recoilless fraction is observed upon subjecting the sample to pressure or freezing it in carnuba wax. This indicates that most of the particles have become part of multiparticle units in the pressed sample or have their motion impeded in the frozen wax, and consequently exhibit recoil energies that are now less than the nuclear level width of the exited state of ^{57}Fe. This explanation of the observed effects offers the most conclusive experimental proof yet presented of how small particle recoil and vibration affect recoilless fraction.

ACKNOWLEDGMENTS

This research was supported by the U.S. Department of Energy under DOE Contract No. DE-FC22-90-PC90029, as part of the research program of the Consortium for Fossil Fuel Liquefaction Science. We are grateful to Bernard M. Kosowski of Mach I, Inc., for providing the sample used in this research.

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