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EFFECT OF CRYSTAL SIZE ON MÖSSBAUER RECOIL-FREE FRACTION IN Au^{197}

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We have observed the Mössbauer effect in Au^{197} microcrystals of mean diameter 60 and 200 Å. The microcrystals were grown in a hydrosol and bound in gelatin. Mössbauer absorption measurements were made with the absorber temperature ranging from 4.2 to 63°K while the Pt^{197}(Au) source was maintained at 4.2°K. Our result indicates that the crystal surfaces are loosely bound to the gelatin and that the recoil-free fraction is greater in the smaller microcrystals than in the larger ones. The results of Mössbauer measurements on the two microcrystal samples are shown in Fig. 1.

Au^{197} was chosen for this work in preference to the more common Mössbauer isotope, Fe^{57}, primarily because the preparation of gold hydrosols with a well-defined size distribution is straightforward, while iron microcrystals cannot be readily prepared due to the chemical activity of iron. Growth of particles smaller than 60 Å has not yet been attempted since distribution of particle size of the smaller crystals is difficult to control. The shape of the particles grown for these experiments is cube-octahedron, but since this shape is nearly spherical it is common to speak of the particle dimension as a "diameter." Particle size and distribution were determined by electron microscopy. Considerable care was exercised in preparation of the absorbers to insure uniform deposition of gold.

The γ-ray sources were 0.005-inch enriched platinum foils containing 21 mg of Pt^{196}. They were irradiated at the Oak Ridge National Laboratory Research Reactor for 24 hours, and the total initial activity of a source upon receipt was approximately 25 mCi. The radiation from this source contained an appreciable component

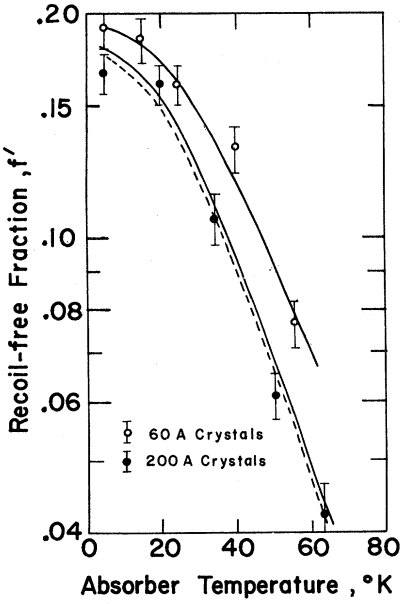

FIG. 1. Recoil-free fractions versus absorber temperature for gold microcrystals. Source temperature is 4.2°K. The solid curves are least-squares fits to the data points using Eq. (1). The dashed curve is calculated for bulk gold using $\Theta_M = 0$°K and $\Theta_D = 163$°K.

of gold x rays as well as γ rays from other platinum isotopes which were not resolved from the 77-keV γ ray used in these experiments. Consequently, careful measurements of the background were obtained using nonresonant critical absorbers of platinum and iridium.

The source and absorbers were mounted in a variable temperature liquid-helium cryostat. An electromechanical transducer similar to that used by Roberts and Thomson[1] was used to apply sinusoidal motion to the absorber. A multiple absorber provision allowed any one of the absorbers used in this experiment to be placed in counting position without warming the assembly. After passing through the absorber and the liquid-helium Dewar, the radiation was counted by a NaI(Tl) scintillation counter located external to the cryostat. The 77-keV γ rays were selected by a differential discriminator, and the resulting Mössbauer spectrum recorded on an RCL 512-channel analyzer operating in the multiscaler (time) mode. The single-line absorption spectra were analyzed with least-squares computer programs discussed elsewhere.[2]

Values for the Mössbauer recoil-free fraction in an absorber, f', were calculated on the basis of the absorption integrals for each experiment. For an absorber it is convenient to define a dimensionless thickness $t = n\sigma_0 f'$, where n is the number of Mössbauer nuclei/cm^2 and σ_0 is the resonant-absorption cross section. For $t \leq 2$ the absorber is said to be thin, and analysis of the data is relatively simple.[3] For the absorber composed of 60-Å microcrystals, $t = 1.8$ at 4.2°K, while for the 200-Å absorber, $t = 1.3$ at the same temperature. Details of absorber preparation, the experimental procedure, and the calculations will follow in a separate paper.

The Mössbauer recoil-free fraction depends on the detailed nature of the phonon spectrum of the solid. Small crystalline particles have phonon spectra different from the bulk material for two primary reasons: Long-wavelength phonons cannot be sustained in small crystals; and a large percentage of the atoms in these small crystals reside on the surface producing surface waves. Montroll[4] gives a phonon distribution function for surface waves. To complete a description of the phonon spectrum within the Debye continuum framework, it is necessary to cut off the range of phonon frequencies so that phonons whose wavelengths are considerably longer than the dimension of the crystal are not allowed. Thus, a suitable distribution function containing surface modes for the phonons must be cut off at both a low-frequency and the usual high-frequency limit. Physically this requirement is imposed because a classical elastic standing wave must "see" boundaries separated by at least half a wavelength. The presence of surface waves and a long-wavelength limit for "volume" phonons turns out to be both mathematically and physically inseparable. When the Debye-like frequency spectrum is renormalized to $3N-6$ modes, N being the number of atoms in the crystal, one finds that f' is increased, since it is the long-wavelength phonons which readily participate in nonrecoilless events. It might be remarked that this effect should be partially offset by the decreased binding of surface atoms, since in the 60-Å crystals almost half the atoms lie on the surface (assumed to be two atoms thick).

The long wavelength cutoff can be described by a characteristic temperature, Θ_M. An expression for $f'(T)$ has been derived on the basis of the Debye theory using Θ_M, as well as the customary short wavelength cutoff, Θ_D:

$$\ln f' = -\frac{3h}{mk\lambda^2}\left\{\Theta_D{}^2\left[\frac{1}{4}+\left(\frac{T}{\Theta_D}\right)^2\varphi\left(\frac{\Theta_D}{T}\right)\right]-\Theta_M{}^2\left[\frac{1}{4}+\left(\frac{T}{\Theta_M}\right)^2\varphi\left(\frac{\Theta_M}{T}\right)\right]+\frac{3cTh}{4kd}\ln\left[\frac{\sinh(\Theta_D/2T)}{\sinh(\Theta_M/\pi T)}\right]\right\}$$

$$\times\left[\Theta_D{}^3-\Theta_M{}^3+\frac{9ch}{8kd}\left(\Theta_D{}^2-\frac{4\Theta_M{}^2}{\pi^2}\right)\right]^{-1}, \qquad (1)$$

where h is Planck's constant, k is Boltzmann's constant, m is the mass of the recoiling atom, λ is the wavelength of the gamma ray, c is the phonon progagation velocity, d is the crystal "diame-

ter," and

$$\varphi(z)=\int_0^z \frac{y\,dy}{e^y-1}.$$

We can express Θ_M in terms of d. If the boundaries of the particles are rigidly fixed, they act as nodes and we would expect $\Theta_M = hc/2kd$. On the other hand, if the boundaries are free, Love[5] has shown that $\Theta_M = 3.66hc/2kd$. For microcrystals 60 Å in diameter, we would expect to find $\Theta_M = 7.8°K$ for spherical crystals with fixed boundaries and $\Theta_M = 28.7°K$ for spherical crystals whose boundaries are free. When the data are analyzed by a least-squares computer program, we find $\Theta_M = 23°K$. Likewise for microcrystals 200 Å in diameter we would expect to find $\Theta_M = 2.3°K$ for spherical crystals with fixed boundaries and $\Theta_M = 8.6°K$ for crystals with free boundaries, while the data yield $\Theta_M = 8°K$. These data indicate that the gold microcrystals embedded in gelatin are loosely bound to the gelatin, so that their surfaces are free, but since the recoil-free fraction is not a strong function of Θ_M at low temperatures, these values of Θ_M could be in error by as much as 25%. The experimentally determined values of Θ_D for the 200-Å and the 60-Å samples are 163 and 173°K, respectively.

The measurements described here are the results of three data runs on the same set of microcrystal absorbers. More extensive measurements of this type covering a wider range of crystal size as well as other crystalline materials are planned.

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ULTRAHIGH RESOLUTION $\Delta F = 0, \pm 1$ $(He^3)^+$ HFS SPECTRA BY AN ION-STORAGE COLLISION TECHNIQUE*

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We have studied the hfs spectra of ground-state $(He^3)^+$ ions contained in a quadrupole rf ion trap. Linewidths as narrow as 10 Hz have been obtained thus far, demonstrating the long phase-memory times of the internal precession realizable in our technique.

The hfs levels of $(He^3)^+$ in a magnetic field are split according to the Breit-Rabi formula [Fig. 1(a)] and the following transitions between the sublevels are possible:

$$a\text{: } 00 \leftrightarrow 11 \text{ at } \nu_a = \Delta\nu - \nu_z + \delta,$$

$$b\text{: } 00 \leftrightarrow 10 \text{ at } \nu_b = \Delta\nu + 2\delta,$$

$$c\text{: } 00 \leftrightarrow 1\,{-1} \text{ at } \nu_c = \Delta\nu + \nu_z + \delta,$$

$$d\text{: } 11 \leftrightarrow 10 \text{ at } \nu_d = \nu_z + \delta,$$

$$e\text{: } 11 \leftrightarrow 1\,{-1} \text{ at } \nu_e = \nu_z \text{ (double quantum)},$$

$$f\text{: } 10 \leftrightarrow 1\,{-1} \text{ at } \nu_f = \nu_z - \delta.$$

Here $\Delta\nu \approx 8665.649$ MHz is the absolute value of the zero-field hfs separation, ν_z is defined by $2h\nu_z = -(g_I + g_J)\mu_0 H$, and δ may be expressed as $\delta = \nu_f(\nu_f/\Delta\nu)[1-(4g_I/g_J)+(2\nu_f/\Delta\nu)]$. We have observed all listed transitions in a magnetic field H corresponding to $\nu_f = 10 \times (1 \pm 5 \times 10^{-5})$ MHz (about 7.23 G) and $\delta = 11\,512$ Hz which was stabilized by a potassium optical pumping magnetometer. While the field-dependent transitions showed linewidths $\delta\nu$ of about 2 kHz, due to residual field inhomogeneities and hum, it was possible to reduce that of the only weakly field-dependent b transition to as low as 10 Hz.