Mössbauer-Effect Studies in Hafnium-Metal Single Crystals*

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The Mössbauer effect in Hf^{178} has been studied with oriented single-crystal absorbers of hafnium metal at the temperature of liquid helium. Along the [0001] axis, only the $|\Delta m|=1$ component of the quadrupole spectrum is observed, and along the [10$\bar{1}$0] axis only the $|\Delta m|=1$ and $|\Delta m|=2$ components are observed. Combining these observations with those made using a polycrystalline hafnium-metal absorber, the magnitude of the electric field gradient was found to be $V_{zz}=(0.95\pm0.04)\times10^{18}$ V/cm^2, and the asymmetry parameter $\eta<0.1$. The Debye temperature of hafnium carbide has been estimated to be (350 ± 10)°K, and the Debye temperature of hafnium metal has been found to be (227 ± 10) and (192 ± 13)°K, for γ rays propagating parallel and perpendicular to the c axis, respectively.

I. INTRODUCTION

WHEN the nuclear Zeeman components of a Mössbauer line are not well resolved, the application of an external magnetic field will impose an axis of quantization; along the field direction some of the components will be suppressed and the remaining ones will be more clearly resolved. In this paper, we demonstrate that it is possible to improve the resolution of electric quadrupole spectra in the Mössbauer effect by performing polarization experiments with oriented single-crystal absorbers.[1] This method suppresses some of the quadrupole components. The success of the technique lies in the strikingly different radiation patterns of the quadrupole components relative to the axis of quantization.

We have applied this technique to the study of the nuclear quadrupole interaction in hafnium metal using the 93-keV γ ray in hafnium-178[2–5] with oriented single-crystal absorbers of hafnium metal. The 2-nsec 2^+ first excited state of hafnium-178 [6] emits a pure electric quadrupole radiation, as indicated in Fig. 1(a). In the presence of an axially symmetric quadrupole interaction (asymmetry parameter $\eta=0$), only the $|\Delta m|=1$ component is excited along the z axis of the electric field gradient (EFG), and only the $|\Delta m|=1$ and $|\Delta m|=2$ components are excited along directions perpendicular to the z axis of the EFG, as shown in Fig. 1(b). This arises from the nature of the radiation patterns of the quadrupole transition, which are shown in Fig. 1(c). The point group symmetry of hafnium metal in the (hcp) α phase[7] ($P6_3/mmc$) requires the z component of the EFG to lie along the crystallographic c axis. Since V_{zz} lies along a threefold axis of rotational symmetry, it follows that the EFG should be axially symmetric.[8] It may be pointed out

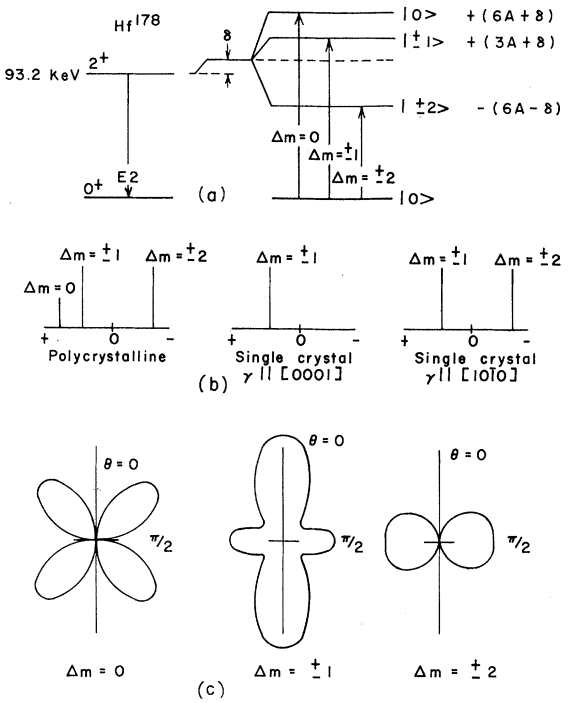

FIG. 1. (a) Quadrupole interaction in hafnium metal; (b) relative intensities of the quadrupole components of the Mössbauer line in polycrystalline hafnium metal and in oriented single crystals of hafnium metal; and (c) angular distributions of the $\Delta m=0$, $|\Delta m|=1$, and $|\Delta m|=2$ quadrupole components with respect to the z axis of the EFG.

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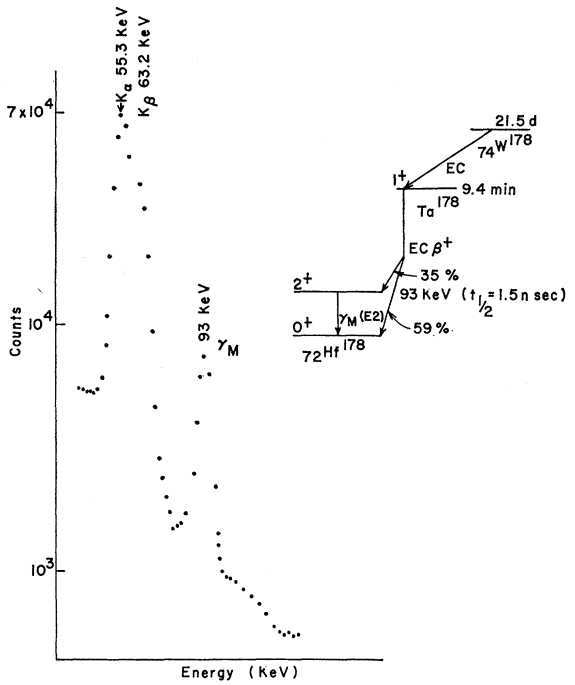

FIG. 2. Partial decay scheme of the $A=178$ chain: pulse-height spectrum of the K x rays and Mössbauer γ ray taken with a 25-cm^3 Ge(Li) detector.

that the EFG in hafnium metal has been extensively studied through the perturbed angular correlation of the γ rays of tantalum-181 in polycrystalline hafnium-metal lattice,[9–11] and the asymmetry parameter η has been found to be 0.3. However, Salomon *et al.*[12] studied the perturbed angular correlation of the γ rays of tantalum-181 in oriented hafnium-metal single crystals and concluded that η is zero. Apart from the inconsistency of these results, it is not clear that this method measures the EFG at a regular site in hafnium metal.

II. SOURCES AND ABSORBERS

Twenty-day $_{76}W^{178}$ decays to 9.4-min $_{75}Ta^{178}$, which feeds the 93-keV state of $_{74}Hf^{178}$ with a 35% branch, as indicated in Fig. 2(a). Sources of W^{178} were made by bombarding 0.010-in. tantalum-metal foils with 43-MeV protons in the cyclotron of the Lawrence Radiation Laboratory, Berkeley. No chemical separation was needed: The tantalum-metal foil was merely etched to remove the oxidized surface layer and then annealed *in vacuo* for about 1 day at about 1000°C. The spectrum of low-energy γ rays taken with a 25-cm^3 Ge(Li) detector is shown in Fig. 2(b): The 93-keV γ ray is clearly resolved from the x rays and stands well above the background. Sources of W^{178} were also made by the bombardment of tantalum-carbide targets with 43-MeV protons and by the bombardment of enriched hafnium oxide (Hf^{177}) with 40-MeV α particles.

For the absorbers, thin platelets of hafnium metal were spark-cut along the [0001] and [10$\bar{1}$0] axes from a large single-crystal rod.[13] The single-crystal cut along the [0001] direction was etched to a thickness of 125 ± 10 μ, and the crystal cut along the [10$\bar{1}$0] direction was etched to a thickness of 75 ± 10 μ. The single-crystal absorbers could be oriented to within $\frac{1}{2}°$ of arc using the back-reflection Laue technique; however, the angular resolution of the Mössbauer-effect experiments was about 2° of arc for the source-absorber distance used.

III. EXPERIMENTS AND RESULTS

The Mössbauer-effect experiments were performed with both the source and the absorber at the temperature of liquid helium in a cryostat described earlier.[14,15] The γ rays were detected in a Ge(Li) detector 3 mm thick and 4 cm^2 in area. In early experiments, sources of W^{178} in the tantalum-carbide host lattice were used. Although a large effect was observed because of the high Debye temperature of tantalum carbide, the narrowest line observed with this source and an

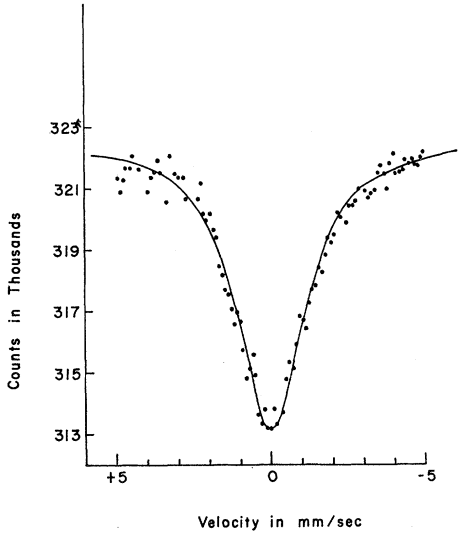

FIG. 3. Mössbauer spectrum taken with a W^{178} source in a tantalum-metal host lattice and a natural hafnium-carbide absorber, both at the temperature of liquid helium.

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absorber of hafnium carbide had a full width at half-maximum (FWHM) of 4 mm/sec, which is twice 2Γ.

A Mössbauer spectrum taken with the source of W^{178} in the tantalum-metal host and a natural hafnium-carbide absorber (10 mg/cm^2 of Hf^{178}) is shown in Fig. 3. The FWHM is 2.6 ± 0.1 mm/sec, which is 1.3 times 2Γ. The excess width is entirely attributable to the finite thickness of the absorber. Spectra were taken with different thicknesses of hafnium carbide, and from the observed excess width of the Mössbauer lines, the Debye temperature of hafnium carbide was calculated[16] to be (350 ± 10)°K at the temperature of liquid helium. In making this calculation, we took the total internal conversion coefficient[17] to be 4.72 and the maximum resonance cross section to be 14×10^{-19} cm^2.

A Mössbauer spectrum taken with the polycrystalline absorber of hafnium metal is given in Fig. 4(c). Spectra made with the polycrystalline metallic absorbers were fitted by the method of least squares to three Lorentzians, with no restrictions on line positions or intensities. The interval between the $\Delta m=0$ and $|\Delta m|=1$ components, 0.85 ± 0.11 mm/sec, was very nearly equal to one-third the interval between the $|\Delta m|=1$ and $|\Delta m|=2$ components, 2.2 ± 0.1 mm/sec, from which it is concluded that $\eta<0.10$, which is consistent with the expectation from the crystal symmetry that η be zero.

The Mössbauer spectrum taken with a hafnium-metal single crystal oriented so that the γ rays were transmitted parallel to the c axis shows a single line [Fig. 4(a)], while the spectrum taken with the γ rays transmitted perpendicular to the c axis and parallel to the $[10\bar{1}0]$ axis shows only two lines [Fig. 4(b)]. It is clear that these spectra confirm the predicted suppression of the quadrupole components. It can be noted that the positions of the $|\Delta m|=1$ and $|\Delta m|=2$ lines in the spectrum made with the polycrystalline absorber coincided with those in the spectra made with the single-crystal absorbers. From the interval observed in Fig. 4(b), the quadrupole interaction in hafnium metal at the temperature of liquid helium is found to be $e^2qQ=-1.83\pm0.06$ μeV. Using the electronically measured mean life[6] of the 93-keV state of Hf^{178} and the theory of transition rates among the rotational levels of deformed nuclei,[17,18] we obtain

$$B(E2)_{ex}=4.08\times10^{-61}\,E_\gamma^{-5}\tau^{-1}[1+\alpha_T]^{-1}$$
$$=Q_0^2 5/16\pi$$

and

$$Q(I,K)=Q_0[3K^2-I(I+1)]/(I+1)(2I+3),$$

for $B(E2)_{ex}$ in cm^4 with E_γ in MeV and τ in sec, where α_T is the total internal conversion coefficient and the electric quadrupole moment of the 93-keV state was calculated to be $Q=-1.93\pm0.05$ b. The value of the EFG is then $V_{zz}=+(0.95\pm0.04)\times10^{18}$ V/cm^2.

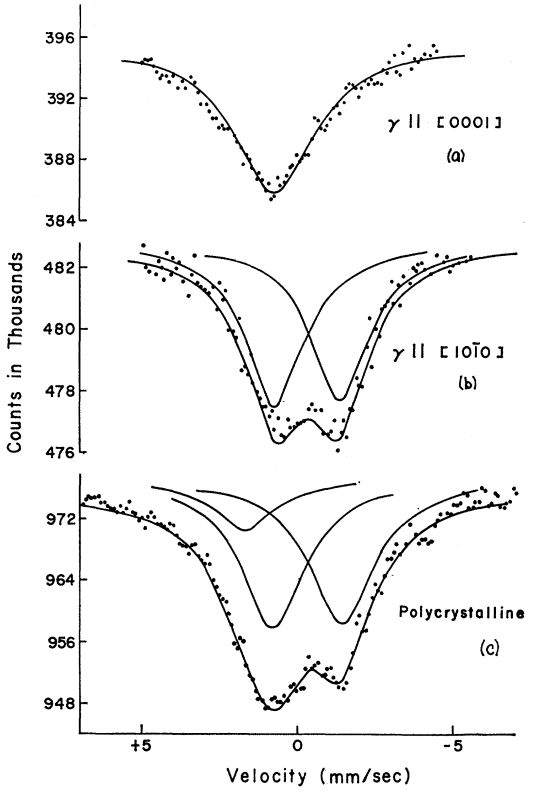

FIG. 4. Mössbauer spectra with hafnium-metal absorbers; (a) oriented single-crystal absorber with γ rays propagating parallel to the c axis; (b) oriented single-crystal absorber with γ rays propagating perpendicular to the c axis; and (c) polycrystalline absorber.

The room-temperature perturbed angular correlation studies of Marklund *et al.*[11] and of Sommerfeldt *et al.*[10] gave $\eta=0.3$ as mentioned above, and their results for the EFG are considerably smaller than ours. Although it seems likely that the magnitude of the EFG should decrease as the temperature increases, it is difficult to imagine that the asymmetry parameter, a quantity intimately tied to the structural symmetry of the lattice, would change with temperature and develop a nonvanishing value.

Gerdau *et al.*[3] obtained a Mössbauer spectrum with a polycrystalline hafnium absorber and a supposed single-line source. They fitted their spectrum to three Lorentzians assuming $\eta=0$, and they obtained a value of -1.752 ± 0.024 μeV for the quadrupole interaction and a value of $+(0.90\pm0.03)\times10^{18}$ V/cm^2 for the EFG. By a similar procedure, Snyder *et al.*[5] obtained a value of -1.84 ± 0.01 μeV for the quadrupole interaction energy in hafnium metal.

Finally, it may be pointed out that the three components of the Mössbauer spectrum taken with the

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polycrystalline hafnium-metal absorber were found to have relative intensities of $(0.36\pm0.12):1:1$, which suggests that the Debye-Waller factor is somewhat anisotropic; but because of the uncertainty in the intensity estimate, no definite conclusion can be drawn. The FWHM of the Mössbauer lines with the single-crystal absorbers were found to be 3.2 ± 0.1 mm/sec for the γ rays propagating parallel to the c axis and 2.67 ± 0.14 mm/sec for the γ rays propagating perpendicular to the c axis. Since η is practically zero, the broadening of these Mössbauer lines must be attributed entirely to the effective thickness of the absorbers. The observed broadenings correspond to Debye temperatures of (227 ± 10)°K for the γ rays propagating along the c axis and (192 ± 13)°K for the γ rays propagating perpendicular to the c axis.

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Alpha-Particle Stopping Cross Section in Solids from 400 keV to 2 MeV†

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Stopping cross sections of α particles from 400 keV to 2 MeV have been measured to an accuracy of ±3.6 to $\pm4.9\%$ in 17 elements (Be, C, Mg, Al, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Ge, Pd, Ag, In, and Sn). The experimental method consists of the elastic scattering of α particles from a thick Ta backing onto which a thin layer of target element has been evaporated. The energy loss of α particles in the target film is determined by the difference in energy between α particles scattered from clean Ta and α particles scattered from Ta after having gone through the thin layer of target element. The results are compared with measurements by Porat and Ramavataram and by Gobeli and with estimates by Whaling; the discrepancies range from 1 to 20%. Structure in and a decrease of the α-particle stopping cross section ϵ_α with stopping element atomic number Z_2 are noticed in the region $Z_2=22$–29. This dependence is not predicted by the Bethe-Bloch formalism valid at higher velocities, nor by the Firsov or the Lindhard formalism valid at lower velocities. The oscillatory structure of ϵ_α on Z_2 is discussed qualitatively by comparing $\epsilon_\alpha(E_\alpha)$ versus Z_2 with a Hartree-Fock-Slater potential $\phi(r)$ versus Z, with E_α related to the radius r by a velocity comparison. An empirical formula for $\epsilon_\alpha=\epsilon_\alpha(E_\alpha,Z_2)$ has been constructed from the present measurements.

I. INTRODUCTION

In 1963 Ormrod and Duckworth[1] discovered that the electronic stopping cross section ϵ_{ion} has an oscillating dependence on Z_{ion}. This oscillatory dependence (or periodic structure) of ϵ_{ion} on Z_{ion} has been verified at low energies in boron, carbon, and aluminum thin films[2,3] and in gaseous media[4,5] at higher energies (0.1–1.5 MeV) and $Z_{\text{ion}}\lesssim39$ in thin carbon films,[6,7] and has also been verified in the channeling of heavy ions in oriented W single crystals[8] and Si crystals.[9] This oscillating phenomenon is of interest in that it was not predicted by the theories of Firsov[10] or of Lindhard, Scharff, and Schiøtt[11] applicable in the low-velocity region of the incident ion. Several theoretical treatments[12] obtaining Z_{ion} oscillations from Hartree-Fock wave functions have recently been made. El-Hoshy and Gibbons[13] have correlated the periodic structure with electronic shell structure of the atoms. These treatments modify Firsov's or Lindhard's formalism in one way or another, and the authors successfully interpret the ϵ_{ion}

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