

MÖSSBAUER DETERMINATION OF THE E2/M1 MIXING RATIO OF THE 77 keV TRANSITION IN ^{197}Au AND OF THE SIGN OF THE ELECTRIC FIELD GRADIENT IN $\text{KAu}(\text{CN})_2$

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A Mössbauer measurement of the E2/M1 mixing ratio of the 77 KeV transition in ^{197}Au yielded $\delta = -0.352 \pm 0.005$. With this result, Mössbauer absorption spectra of $\text{KAu}(\text{CN})_2$ single crystals show that the electric field gradient at ^{197}Au in this compound is negative. This implies that the field gradient is mainly produced by $6p_z$ electrons. The data also indicate a large vibrational anisotropy of Au in $\text{KAu}(\text{CN})_2$.

1. Introduction

The interpretation of electric quadrupole interactions in solids in general requires the knowledge of the sign as well as the magnitude of the electric field gradient. Thus two different explanations have been proposed for the large electric quadrupole interaction observed in $\text{KAu}(\text{CN})_2$, one invoking [1,2] the $6p_z$ electron population arising from covalent bonding and the other [3] the delocalization of $5d_{xz,yz}$ electrons as the prime source of the electric field gradient at the gold nuclei. The former suggestion predicts a negative sign for the electric field gradient and the latter a positive one. A measurement of the sign therefore can rule out one of the two explanations.

Mössbauer spectroscopy generally is sensitive to the sign of electric quadrupole interactions and thus permits one to determine the sign of the electric field gradient, if the sign of the nuclear quadrupole moment is known as is usually the case. In the special case of Mössbauer transitions involving nuclear states with spins $I = \frac{3}{2}$ and $I = \frac{1}{2}$, however, one cannot obtain the sign of the quadrupole interaction from the pure quadrupole pattern of polycrystalline samples, since such spectra consist of merely two lines with equal intensities. To determine the sign of the quadrupole

coupling constant in these cases, one can either apply an external magnetic field, or one can use samples with a preferred orientation of the principal axes of the electric field gradient. The latter is best achieved by the use of single crystals. Alternatively, a sample with a strong texture may be used. For textured samples or single crystals the sign of the electric quadrupole interaction can be extracted from the asymmetry in the line intensities of the quadrupole doublet.

In the case of the 77 keV transition in ^{197}Au the magnetic moment of the $I^\pi = \frac{3}{2}^+$ groundstate is so small [4] that, with the fields produced by commonly available superconducting magnets, no detectable asymmetric line broadening can be expected. One therefore has to resort to the use of single crystals to determine the sign of electric field gradients in gold compounds. The application of this method is, however, complicated by the mixed E2/M1 multipolarity of the 77 KeV transition. In this case, the relative intensities $J_M(\theta)$ observed for transitions between individual nuclear sublevels can be written as [5]

$$\begin{aligned}
 J_0(\theta) &= \frac{3}{2} \begin{pmatrix} I_e & 1 & I_g \\ m_e & 0 & -m_g \end{pmatrix}^2 \sin^2\theta + \frac{15}{8} \begin{pmatrix} I_e & 2 & I_g \\ m_e & 0 & -m_g \end{pmatrix}^2 \delta^2 \sin^2 2\theta, \\
 J_{\pm 1}(\theta) &= \frac{3}{4} \begin{pmatrix} I_e & 1 & I_g \\ m_e & \pm 1 & -m_g \end{pmatrix}^2 (1 + \cos^2\theta) \\
 &\quad \pm \frac{1}{2} \sqrt{15} \begin{pmatrix} I_e & 1 & I_g \\ m_e & \pm 1 & -m_g \end{pmatrix} \begin{pmatrix} I_e & 2 & I_g \\ m_e & \pm 1 & -m_g \end{pmatrix} \delta (\cos^2\theta + \cos 2\theta) \\
 &\quad + \frac{5}{4} \begin{pmatrix} I_e & 2 & I_g \\ m_e & \pm 1 & -m_g \end{pmatrix}^2 \delta^2 (\cos^2\theta + \cos^2 2\theta), \\
 J_{\pm 2}(\theta) &= \frac{5}{4} \begin{pmatrix} I_e & 2 & I_g \\ m_e & \pm 2 & -m_g \end{pmatrix}^2 \delta^2 (\sin^2\theta + \frac{1}{4} \sin^2 2\theta), \tag{1}
 \end{aligned}$$

where θ is the angle between the axis of quantization and the direction in which the gamma rays are observed, and δ is the E2/M1 mixing parameter. The subscripts e and g denote the excited state and the groundstate of the nucleus, m is the orientation quantum number of the nuclear spin I , and the coefficients

$$\begin{pmatrix} I_e & L & I_g \\ m_e & M & -m_g \end{pmatrix}$$

are Wigner $3j$ -symbols [6]. Except for the use of $3j$ -symbols instead of Clebsch-Gordan coefficients, eqs. (1) are identical with the expressions given by Kistner [7].

They apply for both emission and absorption Mössbauer spectra. The sign convention used for δ is the one generally adopted [8–10] in angular correlation work for cases where the mixed transition is the lower one in a γ – γ cascade.

For the case of ^{197}Au in an axially symmetric electric field gradient the individual components given by eqs. (1) yield two hyperfine lines corresponding to the transitions from $m_e = \pm\frac{1}{2}$ to $m_g = \pm\frac{3}{2}$ and from $m_e = \pm\frac{1}{2}$ to $m_g = \pm\frac{1}{2}$, respectively. For the ratio of the intensities of these two lines eqs. (1) yield

$$R(\theta, \delta) = \frac{J(\pm\frac{1}{2}; \pm\frac{3}{2})}{J(\pm\frac{1}{2}; \pm\frac{1}{2})} = \frac{(3 - 2\sqrt{3}\delta + 5\delta^2) + 3(1 + 2\sqrt{3}\delta - \delta^2)\cos^2\theta}{(5 + 2\sqrt{3}\delta + 3\delta^2) - 3(1 + 2\sqrt{3}\delta - \delta^2)\cos^2\theta}$$

$$= \frac{2(\sqrt{3} + \delta)^2 - 3(1 + 2\sqrt{3}\delta - \delta^2)\sin^2\theta}{2(1 - \sqrt{3}\delta)^2 + 3(1 + 2\sqrt{3}\delta - \delta^2)\sin^2\theta}, \quad (2)$$

where θ is the angle between the axis of the electric field gradient and the axis of the Mössbauer spectrometer. In fig. 1 the function $R(\theta, \delta)$ is plotted for $\theta = 0$ and $\theta = 90^\circ$.

For $\delta = \sqrt{3} \pm 2$ one finds $R = 1$ for all angles θ . Obviously the sign of the electric field gradient then cannot be determined by the single-crystal method. For the 77 keV transition in ^{197}Au conversion electron data have yielded $|\delta| = 0.33 \pm 0.05$ [11,12]. This result practically includes the value $\delta = \sqrt{3} - 2 = -0.27$ for which the

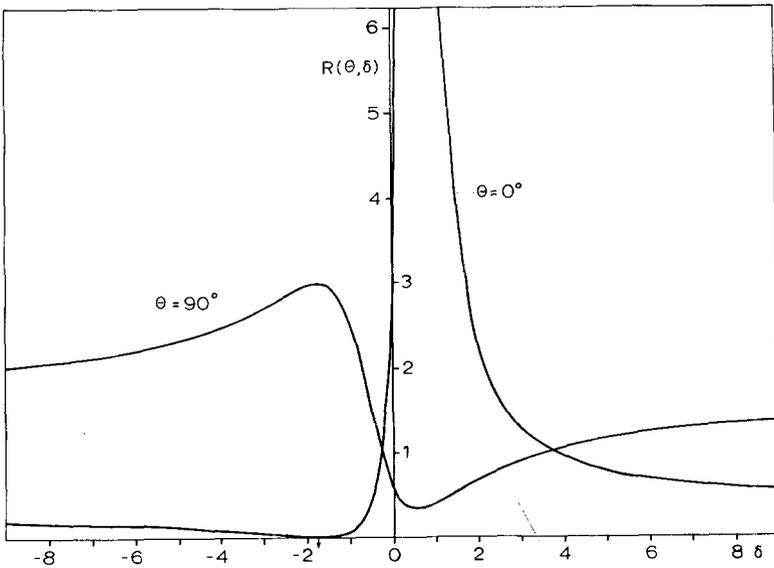


Fig. 1. Intensity ratio $R(\theta = 0)$ and $R(\theta = 90^\circ)$ of the two components of the quadrupole doublet as a function of the E2/M1 mixing parameter δ of a transition between nuclear states with spins $I = \frac{1}{2}$ and $I = \frac{3}{2}$.

two lines of the quadrupole doublet have equal intensities for all values of θ . We have therefore determined the sign and a more accurate value for the magnitude of δ before applying the single-crystal method to $\text{KAu}(\text{CN})_2$. To this end we have measured the Mössbauer emission spectrum of a source of ^{197}Pt in an iron matrix that was polarized parallel to the axis of the spectrometer by an external magnetic field. From the experimental line intensities in the emission Zeeman pattern and eqs. (1) the sign and magnitude of δ were obtained. With this result the Mössbauer spectra of single-crystal absorbers of $\text{KAu}(\text{CN})_2$ could be interpreted in terms of the sign of the electric field gradient.

2. Experiments and results

The measurements were performed with a Mössbauer spectrometer consisting of a liquid He cryostat, an electromechanical velocity drive providing the sinusoidal motion of the source, a Ge(Li) detector and a multichannel analyzer operated as a multiscaler. The ^{197}Pt activity feeding the 77 keV transition was produced by neutron irradiation of either natural Pt or enriched ^{196}Pt .

For the measurement of the mixing parameter δ , we used radioactive Pt and iron of 99.99% purity to prepare a $\text{Pt}_{0.01}\text{Fe}_{0.99}$ alloy. A foil of 40 mg/cm² of metallic gold was used as absorber. The source was magnetized by means of a superconducting solenoid. Two spectra were taken with source and absorber at 4.2 K and external fields of 4.0 T (fig. 2) and 6.0 T at the source. The absorber was exposed to fringing fields of 1.4 T and 2.1 T, respectively. Taking the resulting unresolved splitting of the Mössbauer line of the absorber and the circular polarization of the emission and absorption lines into account, one has to fit a superposition of eight Lorentzian lines to these spectra. The line drawn in fig. 2 is the result of such a fit. From eqs. (1) one finds that the ratio of the areas under the outer and the inner pair of peaks in these spectra is equal to $R(\theta = 0)$ as given by eq. (2). The values obtained for this ratio from the spectra taken at 4.0 T and 6.0 T are $R = 0.737 \pm 0.013$ and 0.715 ± 0.022 , respectively. The agreement between these two results shows that the source had already been fully magnetized at 4.0 T. From the weighted mean, $R = 0.731 \pm 0.011$, one obtains $\delta = -0.354 \pm 0.005$. The second solution of eq. (2), yielding a value of δ close to +5, is ruled out by conversion electron data and Mössbauer measurements with unmagnetized samples [11,12]. Our value for δ is in good agreement with a value recently obtained by the Oak Ridge group [13]. For the ratio of g -factors the measurements at 4.0 T and 6.0 T yielded $g_{\frac{1}{2}}/g_{\frac{3}{2}} = 8.72 \pm 0.05$ and 8.60 ± 0.10 , respectively. With $\mu_{\frac{3}{2}} = +0.14487 \mu_{\text{N}}$ [4] we obtain $H_{\text{hf}} = -(126.9 \pm 2.5)$ T for hyperfine field at Au in an iron matrix. This is in good agreement with previous results [11]. It should be noted that the present results were obtained in source experiments and are therefore unaffected by finite absorber thickness. Moreover, the poor geometry enforced by the superconducting solenoid renders effects of finite solid angle negligible.

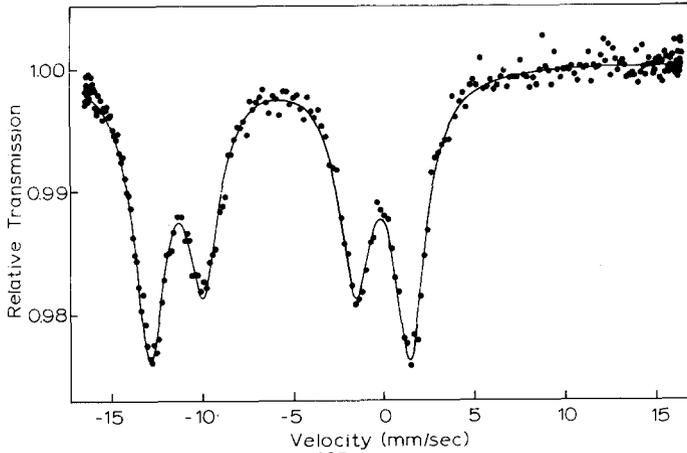


Fig. 2. Mössbauer spectrum of a source of ^{197}Pt in a $\text{Pt}_{0.01}\text{Fe}_{0.99}$ alloy and an absorber of metallic gold. The source was magnetized in a longitudinal external field of 4.0 T.

The single crystals of $\text{KAu}(\text{CN})_2$ used for the determination of the sign of the electric field gradient were grown from an aqueous solution. The crystals had sizes of several millimeters. The crystal structure of $\text{KAu}(\text{CN})_2$ has been found to be rhombohedral [14] with 9 equivalent Au atoms in the unit cell. The trigonal bipyramidal shape exhibited by most of the crystals results from twinning. We have prepared two composite absorbers with the crystallographic c -axis parallel and perpendicular to the direction of the gamma rays. The thickness of both absorbers was about 500 mg/cm^2 of $\text{KAu}(\text{CN})_2$. The Mössbauer spectra obtained with these absorbers and a source of ^{197}Pt made of isotopically enriched ^{196}Pt metal are shown in fig. 3.

The $\bar{1}$ point symmetry of the Au positions in the space group R3 found for $\text{KAu}(\text{CN})_2$ [14] does not enforce axial symmetry on the electric field gradient at the Au sites and gives little clue as to the directions of the principal axes. The existence of nearly linear NC-Au-CN entities and the idea that the dominating contribution to the electric field gradient at the gold nuclei arises from the intrinsic electronic structure of these $\text{Au}(\text{CN})_2^-$ molecules, however, suggest that the field gradient is, to a good approximation, axially symmetric around the molecular axis. The axes of the individual $\text{Au}(\text{CN})_2^-$ entities have different orientations in the unit cell, all being tilted by an angle of about 20° with respect to the crystallographic c -axis [14]. Single crystals of $\text{KAu}(\text{CN})_2$ thus do not permit one to align the electric field gradients at angles of $\theta = 0^\circ$ and $\theta = 90^\circ$, but the partial alignment achieved by the use of $\text{KAu}(\text{CN})_2$ single crystals is sufficient for the sign of the electric quadrupole interaction to be determined.

For the hypothetical case of complete alignment we expect the intensity ratio of the lines in the quadrupole pattern to be $R(\theta = 0) = 0.73 \pm 0.01$ and $R(\theta = 90^\circ) = 1.17 \pm 0.01$. The ratios actually found from the single-crystal spectra of $\text{KAu}(\text{CN})_2$

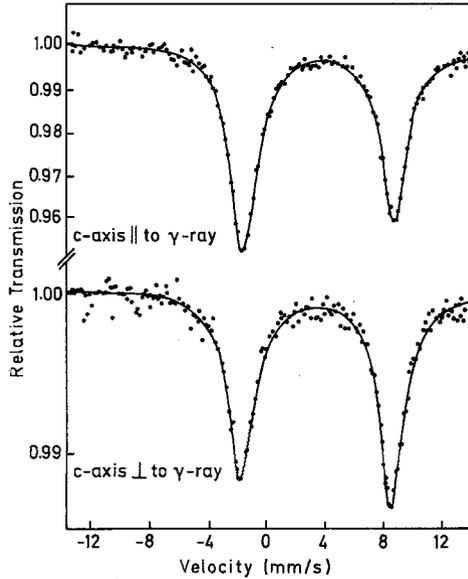


Fig. 3. Mössbauer spectra of $\text{KAu}(\text{CN})_2$ single crystal absorbers, in which the rhombohedral c -axis was oriented parallel (upper spectrum) and perpendicular (lower spectrum) to the direction of the gamma rays.

are $R_{\parallel} = 0.83 \pm 0.06$ and $R_{\perp} = 1.14 \pm 0.10$, if the line at positive velocities (see fig. 3) is attributed to the transitions between $m_g = \pm\frac{3}{2}$ and $m_e = \pm\frac{1}{2}$. A comparison with the values expected for $\theta = 0$ and $\theta = 90^\circ$ shows that this choice is correct. This implies that eQV_{zz} is negative. Since the electric quadrupole moment of the ground-state of ^{197}Au is $Q = +0.58 \text{ b}$ [13,15,16], we conclude that the electric field gradient V_{zz} is negative. Quantitatively we obtain $(c/E_\gamma)^{\frac{1}{2}} eQV_{zz} = -(10.2 \pm 0.2) \text{ mm/s}$ from the Mössbauer spectra and hence $V_{zz} = -9.1 \cdot 10^{18} \text{ V/cm}^2$. Since the value of Q was obtained without the application of a Sternheimer correction [15,16], we estimate the error of V_{zz} to be about 30%.

The intensity ratio R_{\parallel} can straightforwardly be interpreted in terms of an effective tilting angle θ between the axis of the electric field gradient and the direction of the gamma rays. Neglecting effects of finite absorber thickness we obtain $\theta = (30 \pm 10)^\circ$ from eq. (2). This is in fair agreement with the X-ray data [14].

An inspection of fig. 3 shows that the relative intensity of the Mössbauer absorption is much larger for the absorber through which the gamma rays passed parallel to the rhombohedral c -axis of $\text{KAu}(\text{CN})_2$ than for the other one. Since both absorbers had about the same thickness and the other experimental conditions in the two measurements were also equal, this difference indicates that the recoilless fraction is larger by about a factor of three for gamma rays with wave vectors parallel to the c -axis than for ones with wave vectors perpendicular to it.

This conclusion is supported by measurements with a carefully prepared polycrystalline absorber of 300 mg/cm^2 of $\text{KAu}(\text{CN})_2$, for which we found an intensity ratio of $R = 0.95 \pm 0.01$. If this ratio were due to a texture of the absorber, this texture would have to be such that the c -axes are preferentially oriented perpendicular to the plane of the absorber. This seems to be improbable if one considers the shape of the $\text{KAu}(\text{CN})_2$ crystals. We thus conclude that the intensity ratio of $R = 0.95$ found in the polycrystalline samples is due to the anisotropy of the recoilless fraction, i.e. to the Goldanskii-Karyagin effect [17]. In fact, both the polycrystalline and single crystal data yield a value of $a \approx -1.1$ for the vibrational anisotropy parameter [17] defined as $a = k^2(\langle z^2 \rangle - \langle x^2 \rangle)$. From this value of a one deduces $\langle z^2 \rangle - \langle x^2 \rangle \approx -7 \times 10^{-4} \text{ \AA}^2$.

3. Discussion

The electric field gradient in $\text{KAu}(\text{CN})_2$ is the largest found to date in any gold compound. Theoretical estimates [1,2] show that the lattice contribution to the electric field gradient is so small that it can be neglected in the qualitative discussion that will be given in the following. Ionic Au^+ has a closed-shell $5d^{10}$ configuration that does not give rise to an electric field gradient at the gold nucleus. The large field gradient actually observed in $\text{KAu}(\text{CN})_2$ therefore must essentially arise from the effects of covalent bonding on the electron configuration of the gold ion in the solid.

Neglecting inner-shell contributions, one can visualize the electric field gradient at the gold nuclei as arising from (i) holes in the $5d^{10}$ configuration and (ii) a non-zero $6p_z$ (a_{2u}) population.

Since the $5d_{x^2-y^2}$ and $5d_{xy}$ (e_{2g}) orbitals are non-bonding in the linear $\text{Au}(\text{CN})_2^-$ molecule, covalent bonding will affect only the $5d_{z^2}$ (a_{1g}) and $5d_{xz,yz}$ (e_{1g}) populations. Holes in the $5d_{z^2}$ and $5d_{xz,yz}$ orbitals will result in a positive contribution to the electric field gradient. Since the cyanide ligands are strong σ -donors and π^* -acceptors, it is reasonable to assume that in $\text{KAu}(\text{CN})_2$ the $5d$ contribution to the electric field gradient arises mainly from the reduced $5d_{xz,yz}$ population. Danon has shown [3] that, with reasonable assumptions for this population, one obtains a value of $V_{zz} = +8 \times 10^{18} \text{ V/cm}^2$ for the $5d$ contribution to the electric field gradient. The fact that the actual electric field gradient in $\text{KAu}(\text{CN})_2$ is negative, however, shows, that the dominating contribution arises from the $6p_z$ electrons rather than from $5d$ electrons. The $6p_z$ contribution is indeed expected to be large in a compound with strongly σ -donating ligands. Interpretations of the electric field gradients in $\text{Au}(\text{I})$ compounds based on the dominance of the $6p_z$ electrons have previously been given by Bartunik et al. [2] and by Faltens and Shirley [1]. Neglecting the positive contribution from the $5d$ electrons, the latter authors already concluded that the effective $\langle r^{-3} \rangle_{6p}$ values in $\text{Au}(\text{I})$ compounds must be considerably larger than, for instance, the value of $8.9 a_0^{-3}$ found for Hg in HgCl_2

[1]. This is *a fortiori* true if one takes the positive 5d contribution into account. With Danon's [3] estimate of $V_{zz,5d} = +8 \times 10^{18} \text{ V/cm}^2$ we obtain $V_{zz,6p} = -17 \times 10^{18} \text{ V/cm}^2$ for the $6p_z$ contribution. If one assumes this to be produced by two $6p_z$ electrons, i.e. the maximum number possible, and neglects the Sternheimer shielding factor, one obtains a lower limit of about $11 a_0^{-3}$ for the effective $\langle r^{-3} \rangle_{6p}$ in $\text{KAu}(\text{CN})_2$.

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