Measurement of Nuclear Quadrupole Interactions using Mössbauer Spectroscopy *

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Z. Naturforsch. **51a,** 368–372 (1996); received November 20, 1995

Mössbauer spectroscopy is a useful probe for investigating nuclear quadrupole interactions. It enables the magnitude, sign and asymmetry of the electric quadrupole coupling constant to be determined. It is especially important for its ability to measure these parameters for excited nuclear states. The Mössbauer effect is used to measure excited state quadrupole moments in materials whose electric field gradient (EFG) is known. More commonly however, it is used to determine the EFG from which atomic bonding and electronic structure are determined. The technique also allows temperature dependent orientation of sublattice magnetization to be measured using the direction of the electric quadrupole coupling as a reference.

Key words: Mössbauer Effect, Electric Field Gradient, Quadrupole Interaction.

1. Introduction

Mössbauer spectroscopy is a popular analytical technique for measuring nuclear hyperfine interactions in both ground and excited state nuclei. The method involves the resonant absorption of gamma-rays between levels which have been perturbed through either the quadrupole and/or magnetic interactions [1–3].

A quadrupole split Mössbauer spectrum results from a nucleus with an electric quadrupole moment which experiences an electric field gradient (EFG). The quadrupole moment occurs when the nucleus has a spin greater than one-half, and all Mössbauer nuclei possess a quadrupole moment in either the ground or excited state or both, and are therefore able to undergo quadrupole splitting. The spectra are characterized by the quadrupole coupling constant, which is the product of V_{zz}, the principal component of the EFG, (often designated as eq), and eQ the electric quadrupole moment of the nucleus, where e is the proton charge. The quadrupole coupling constant is the same as that derived from pure nuclear quadrupole resonance (NQR) spectra. However, the Mössbauer technique has the dual advantage of being easier to practice, and of having a wider range of isotopes available, since in cases where the ground state has $Q=0$, (and is therefore NQR silent), the excited state always has a quadrupole moment. Additionally, for nuclear spin $I > 3/2$ the Mössbauer spectrum gives the sign of the quadrupole coupling constant directly [4, 5]; in other cases the sign can be determined from spectra of single crystal samples or with an applied magnetic field.

This paper discusses the use of Mössbauer spectroscopy to measure nuclear quadrupole interactions and the information which can be determined from the spectra. The origins of the EFG and nuclear quadrupole moments are not discussed as they are common to each of the available NQI probes.

2. Electric Quadrupole Interaction

All nuclear states with $I > 1/2$ have a non-zero electric quadrupole moment (Q) which can interact with an inhomogeneous electric field, described by the EFG at the nucleus. The interaction can be described by the quadrupole Hamiltonian operator

$$\mathscr{H}_Q = \frac{eQV_{zz}}{4I(2I-1)}\left[3I_z^2 - I(I+1) + \frac{\eta}{2}(I_+^2 + I_-^2)\right], \quad (1)$$

where in the principal axis system, the EFG tensor reduces to two independent parameters, $V_{zz}\,(=eq)$ and the asymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$. By convention, $|V_{zz}| \geq |V_{xx}| \geq |V_{yy}|$ and $0 \leq \eta \leq 1$. Solving Schrödinger equation using the quadrupole Hamiltonian gives eigenvalues which indicate that the energy

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* Presented at the XIIIth International Symposium on Nuclear Quadrupole Interactions, Providence, Rhode Island, USA, July 23–28, 1995.

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0932-0784 / 96 / 0500-0368 $ 06.00 © – Verlag der Zeitschrift für Naturforschung, D-72072 Tübingen

level splits into doubly degenerate sublevels characterized by m_I, the magnetic quantum number. Also important in the solution are the eigenvectors which are used to calculate the transition probabilities between the nuclear energy levels. This topic is important for interpretation of the quadrupole split Mössbauer spectra of single crystals and will be discussed below.

Mössbauer spectroscopy involves the absorption of gamma radiation to promote a nucleus from its ground state (E_g) to an excited state (E_e). If both levels have nuclear spin greater than ½, the quadrupole Hamiltonian must be solved for each energy level. Equation (1) now must be rewritten to include the different quadrupole moments (Q_g and Q_e) and nuclear spins (I_g and I_e) for the ground and excited states, respectively. The EFG parameters, V_{zz} and η, are independent of the nuclear state and therefore remain constant for each Hamiltonian.

As Q is constant for each particular nuclear state of a given Mössbauer nuclide, changes in the quadrupole interaction in different compounds of a given Mössbauer atom can only arise from changes in the EFG at the nucleus. Therefore all information about the molecular and electronic structure of the Mössbauer atom, as measured from the electric quadrupole interaction, originates from changes in the EFG. The interpretation of the quadrupole coupling constants therefore requires knowledge of the origin of the EFG and the way it is altered by chemical and physical influences.

As an introduction to the characteristics of nuclear quadrupole interactions measured by Mössbauer spectroscopy, the most popular Mössbauer isotope ^{57}Fe will be discussed. Recoilless gamma-ray absorption in ^{57}Fe occurs between the ground state having nuclear spin $I_g = ½$ and the 14.4 keV level having nuclear spin $I_e = 3/2$. The quadrupole Hamiltonian shows that only the excited state is split, having two doubly degenerate sublevels whose energies have been shifted by E_Q given by

$$E_Q = \frac{eQV_{zz}}{4I(2I-1)}\left[3m_I^2 - I(I+1)\right]\left(1+\frac{\eta^2}{3}\right)^{\frac{1}{2}}. \qquad (2)$$

The magnetic quantum number, m_I, has values of I_e, $I_e - 1, \ldots, -I_e$. The two doubly degenerate levels are now labelled $m_I = \pm 3/2$ and $\pm 1/2$, respectively. Figure 1 shows the nuclear levels of ^{57}Fe with Fig. 1a showing the unperturbed levels. Figure 1b shows the quadrupole split energy levels in ^{57}Fe for which $Q_g = 0$ and $Q_e = +0.21$ b. For positive V_{zz}, substitution of m_I into (2) shows the two sublevels equally shifted to each side of the equilibrium with the $m_I = \pm 3/2$ sublevel having the higher energy. Each separation is commonly designated as ∊ in Mössbauer spectroscopy. The total separation of the two excited state quadrupole split energy levels is called the "quadrupole split-

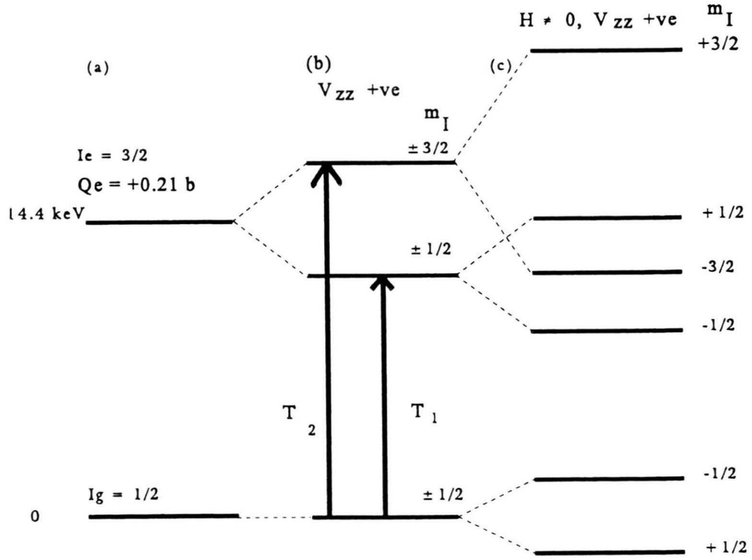

Fig. 1. Energy level diagram for the ground and first excited state of ^{57}Fe under the following hyperfine interactions, (a) none, (b) nuclear quadrupole and (c) magnetic and quadrupole.

ting" and is written as

$$\Delta E_Q = 2\epsilon = \tfrac{1}{2} e Q_e V_{zz} \left(1 + \frac{\eta^2}{3}\right)^{\frac{1}{2}}. \tag{3}$$

For Mössbauer transitions between nuclear states with spin ½ and $^3/_2$, (e.g. ^{57}Fe and ^{119}Sn), the spectra are simple doublets.

In Mössbauer spectroscopy, the 14.4 keV gamma-ray emitted from a decaying ^{57}Fe nucleus in a radioactive source is doppler shifted to allow it to be absorbed by the quadrupole split absorber. Generally a velocity range of ± 5 mm s^{-1} is sufficient for purely quadrupole split materials containing iron. Resonant absorption between the ground and excited states occurs at two different velocities, the difference of which measures ΔE_Q in units of mm s^{-1}. Figure 2a shows the room temperature Mössbauer spectrum of a polycrystalline sample of iron monophosphide, FeP. The quadrupole split doublet has separation of $\Delta E_Q =$ 0.656 mm s^{-1}. The area under of each peak is equal and represents the number of absorbed photons at that velocity. Equation (3) shows that there are four parameters controlling the quadrupole splitting, Q_g, Q_e, V_{zz} and η. For most Mössbauer isotopes, the quadrupole moments are known, either through NQR or other Mössbauer measurements using a material whose EFG is known. For a polycrystalline solid the Mössbauer spectrum cannot separate V_{zz} and η. Also the sign of the EFG cannot be determined. Additional Mössbauer spectra must be recorded to determine these parameters. One method involves the recording of the Mössbauer spectrum using a single crystal or textured sample. Under these conditions the transition probabilities, and therefore absorption areas, depend on the angles between the gamma-ray direction and the principal quantization axis (defined here by the direction of V_{zz}).

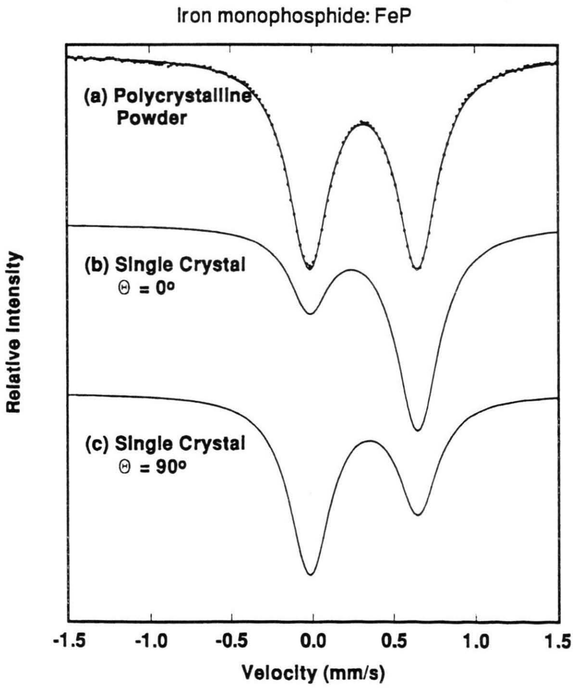

Fig. 2. Quadrupole split Mössbauer spectra of Iron Monophosphide recorded using (a) powder and single crystals with gamma-rays (b) parallel and (c) perpendicular to V_{zz}.

The transition probabilities (Mössbauer spectrum line intensities or probability of a gamma-ray being absorbed) are controlled by the spin and parity of the ground and excited nuclear states, multipolarity of the transition and direction of the gamma-ray with respect to the principal quantization axis. The geometric arrangement of the experimental set-up can provide valuable information concerning the nuclear quadrupole interactions. Again for the ^{57}Fe transitions having multipolarity M1 (magnetic dipole, $L=1$), the probability P for a nuclear transition from the ground state $|I_g, m_{I_g}\rangle$ to the excited state $|I_e, m_{I_e}\rangle$ is given by

$$P\left(\frac{3}{2} m_{3/2}, 1\, m \,\middle|\, \frac{1}{2} m_{1/2}, \Theta, \Phi\right) = \left|\left\langle \frac{3}{2} m_{3/2}, 1\, m \,\middle|\, \frac{1}{2} m_{1/2} \right\rangle F_{\mathrm{L}}^{m}(\Theta, \Phi) \langle I_1 \| 1 \| I_2 \rangle\right|^2, \tag{4}$$

where Θ, Φ are the polar and azimuthal angles of the principal quantization z-axis and the direction of the gamma-ray. $\langle I_g, m_{I_g}, Lm | I_e, m_{I_e}\rangle$ are the Clebsch-Gordon coefficients coupling together the three vectors I_g, L and I_e, and $\langle I_g \| 1 \| I_e \rangle$ is the reduced matrix element. The angular functions $F_{\mathrm{L}}^{m}(\Theta, \Phi)$ give the angular intensity of the gamma-rays having the magnetic quantum number m_I. For a polycrystalline sample, the quantization axis is randomly oriented with respect to the gamma-ray direction. The transition probabilities are calculated by integrating (4) over Θ and Φ. Table 1 summarizes the probabilities of transmission in ^{57}Fe between the doubly degenerate ground state and the two doubly degenerate excited states for a quadrupole split specimen. The transition probabilities are given for polycrystalline (random orientation) and for $\Theta = 0°$ and 90°. For simplicity it is assumed that $\eta = 0$, which eliminates the Φ depen-

Table 1. Summary of the transition probabilities, angular dependence of radiation absorption and intensities of the 6 allowed transitions in ^{57}Fe Mössbauer spectra of polycrystalline (powder) and single crystals for the gamma-ray direction parallel or perpendicular to the principal quantization axis.

	Transition	Δm	Trans. Prob.	Angular Dependence	Powder	$\Theta = 0°$	$\Theta = 90°$
1	$+\frac{1}{2} \geq +\frac{3}{2}$	+1	3	$\frac{9}{4}(1+\cos^2\Theta)$	3	3	3
2	$-\frac{1}{2} \geq -\frac{3}{2}$	−1	3	$\frac{9}{4}(1+\cos^2\Theta)$	3	3	3
3	$+\frac{1}{2} \geq +\frac{1}{2}$	0	2	$3\sin^2\Theta$	2	0	4
4	$-\frac{1}{2} \geq -\frac{1}{2}$	0	2	$3\sin^2\Theta$	2	0	4
5	$+\frac{1}{2} \geq -\frac{1}{2}$	−1	1	$\frac{3}{4}(1+\cos^2\Theta)$	1	1	1
6	$-\frac{1}{2} \geq -\frac{1}{2}$	+1	1	$\frac{3}{4}(1+\cos^2\Theta)$	1	1	1

dence. The six allowed transitions are between the doubly degenerate ground state and the two doubly degenerate excited states. For a polycrystalline material, the total transition probability to the excited $m_{I_e} = \pm 3/2$ state (transitions $1+2=T_2$ on Fig. 1b) is the same as to the $m_{I_e} = \pm 1/2$ state (transitions $3+4+5+6=T_1$). The quadrupole split doublet of the Mössbauer spectrum is therefore symmetric, with both peaks having the same intensity. It can be quickly determined from Fig. 1 that reversing the sign of V_{zz} results in an identical Mössbauer spectrum.

Peak asymmetry is lost if we probe the sample with gamma-rays travelling at a fixed angle to the EFG. Equation (4) allows the intensity ratio to be calculated as

$$\frac{T_2}{T_1} = \frac{3(1+\cos^2\Theta)}{5-3\cos^2\Theta}. \tag{5}$$

For a positive quadrupole coupling constant, (5) ranges from 3 for $\Theta = 0°$ to 0.6 for $\Theta = 90°$. Figures 2b and 2c show the Mössbauer spectra of a single crystal of FeP recorded parallel ot the crystalline a-axis (parallel to V_{zz}) and c-axis (perpendicular to V_{zz}). The asymmetry parameter η can also be determined from the single crystal spectra. The off-diagonal terms in the quadrupole Hamiltonian matrix lead to nuclear substates which are no longer pure m_I states of $|I, m_I\rangle$, but linear combinations of these. The new eigenstates modify the probability equation (4), and the effect is observed as a modification to the intensity ratio given by (5).

The sign of the EFG can also be determined if the Mössbauer nucleus experiences a magnetic field (either externally applied or internal due to magnetic exchange). The magnetic hyperfine interaction now splits the ground and excited states with no degeneracy, as shown in Figure 1c. The general Mössbauer spectrum is now a sextet whose peaks are not equally spaced due to the quadrupole interaction. Figure 3 shows typical spectra for a magnetically ordered material which has a negative (Fig. 3a) and positive (Fig. 3b) EFG. In most magnetic iron materials, the quadrupole interaction is much smaller than the magnetic interaction. Therefore accurate determination of the nuclear quadrupole interaction is difficult. This problem can be overcome by recording the Mössbauer spectra at an elevated temperature which decreases the magnetic hyperfine field.

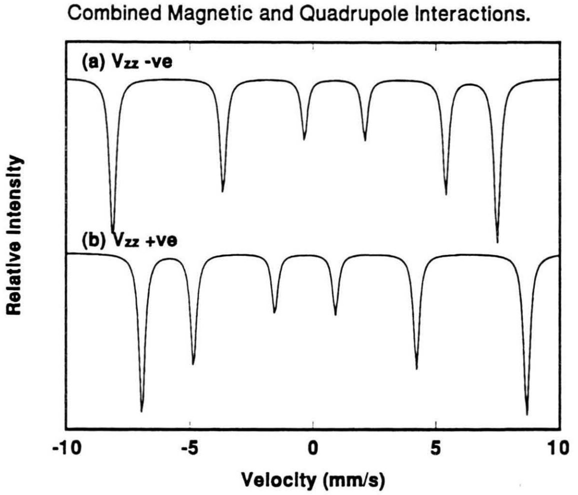

Fig. 3. Mössbauer spectra showing the effect of combined magnetic and quadrupole interactions for (a) negative EFG and (b) positive EFG. The negative EFG displaces the four central peaks to the right. For a positive EFG the asymmetry is reversed.

3. Other Applications

In most materials the EFG is nearly temperature independent. With V_{zz} also fixed in direction, the nuclear quadrupole interaction can be used as a reference to determine the direction of the sublattice magnetization in magnetic materials. The phenomenon of temperature dependent canting of the sublattices in antiferromagnetic gadolinium aluminate has been demonstrated at low temperatures [6, 7]. Recording the Mössbauer spectra of single crystal and powder sample above the Néel temperature enabled the sign, magnitude and direction of V_{zz} as well as η to be determined. Cooling the samples showed that with the onset of magnetic ordering the magnetic dipole alignment resulted from competition between the temperature dependent exchange and dipole interactions with the temperature independent crystalline electric field. The result was a canting of the sublattices from a direction nearly parallel to V_{zz} at T_N through 45° as the temperature decreased.

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