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.

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. 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 \(I > 1/2\) 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 NQR probes.

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 electric field gradient (EFG) at the nucleus. The interaction can be described by the quadrupole Hamiltonian operator

\[
H_Q = \frac{eQV_{zz}}{4\sqrt{2}} \left[ 3I_+^2 - I(I + 1) + \frac{\eta}{2}(I_+^2 + I_-^2) \right]
\]

where \(e\) is the electronic charge, \(V_{zz}\) is the electric field gradient, \(I_+\) and \(I_-\) are the projection operators for the electric field gradient along the principal axis, \(\eta = (V_{xx} - V_{yy})/V_{zz}\) and \(0 \leq \eta \leq 1\).

Solving the Schrodinger equation using the quadrupole Hamiltonian gives eigenvalues which indicate that the energy 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 1/2, 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 \(\eta\), 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 $I_g = 1/2$ 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:

$$E_Q = \frac{eQV_{zz}}{4I(2I-1)} [3m_I^2 - I(I+1)](1 + \frac{\eta^2}{3})^{1/2}$$  \hspace{1cm} (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 energy levels of $^{57}$Fe with Figure 1(a) showing the unperturbed levels. Figure 1(b) shows the quadrupole split energy levels in $^{57}$Fe for which $Q_e = 0$ and $Q_z = +0.21b$.

For Mössbauer transitions between nuclear states with spin $1/2$ and $3/2$, (e.g. $^{57}$Fe and $^{119}$Sn), the spectra are simple doublets.

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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 $V_{zz}$.

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 $\pm 5\text{mm s}^{-1}$ 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 $\Delta E_Q$ in units of mm s$^{-1}$. Figure 2 shows the room temperature Mössbauer spectrum of a polycrystalline sample of iron monophosphide, FeP. The quadrupole split doublet has a separation of $\Delta E_Q = 0.656\text{mm s}^{-1}$. 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: $Q_e$, $Q_z$, $V_{zz}$ and $\eta$. For most Mössbauer isotopes, the quadrupole moments are known, either through NQR or other Mössbauer measurements using a material whose EFG is known. For the polycrystalline solid the Mössbauer spectrum cannot separate $V_{zz}$ and $\eta$. Also the sign of the EFG cannot be determined. Additional Mössbauer spectra must be
Peak asymmetry is lost if we probe the sample with gamma-rays traveling at a fixed angle to the EFG. Equation (4) allows the intensity ratio to be calculated as

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

For a positive quadrupole coupling constant, equation (5) ranges from 3 for $\Theta = 0^\circ$ to 0.6 for $\Theta = 90^\circ$. Figures 2(b) and 2(c) show the Mössbauer spectra of a single crystal of FeP recorded parallel to the crystalline a-axis (parallel to $V_{zz}$) and c-axis (perpendicular to $V_{zz}$). The asymmetry parameter $\eta$ 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 equation (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 1(c). 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 (Figure 3 (a)) and positive

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**Combined Magnetic and Quadrupole Interactions.**

![Diagram of combined magnetic and quadrupole interactions]

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

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 samples above the Neel temperature enabled the sign, magnitude and direction of $V_{zz}$ as well as $\eta$ 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.


### 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.

<table>
<thead>
<tr>
<th>Transition</th>
<th>$\Delta m$</th>
<th>Trans. Prob.</th>
<th>Angular Dependence</th>
<th>Powder $\theta = 0^\circ$</th>
<th>$\theta = 90^\circ$</th>
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<tbody>
<tr>
<td>1</td>
<td>+1/2 → +3/2</td>
<td>3</td>
<td>$9/4(1+\cos^2\Theta)$</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>2</td>
<td>-1/2 → +3/2</td>
<td>-1</td>
<td>$8/4(1+\cos^2\Theta)$</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>3</td>
<td>+1/2 → +1/2</td>
<td>0</td>
<td>$3\sin^2\Theta$</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>-1/2 → +1/2</td>
<td>0</td>
<td>$3\sin^2\Theta$</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>+1/2 → -1/2</td>
<td>-1</td>
<td>$3/4(1+\cos^2\Theta)$</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>6</td>
<td>-1/2 → +1/2</td>
<td>+1</td>
<td>$3/4(1+\cos^2\Theta)$</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>