Interpretation of Unresolved Mössbauer Spectra in Compounds of I$^{129}$*

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The $I^{129}$ Mossbauer-effect absorption spectra of the rare earth tri-iodides, La$I_3$, Gd$I_3$ and Er$I_3$ show evidence of unresolved quadrupole splitting. We propose that the electric field gradient (EFG) responsible for the interaction can be associated with a partially filled p hole ($h_p$) in the $5s^25p^6$ electronic configuration of I$^-$. The quadrupole coupling parameters and isomer shifts are determined from a least squares fitting of the data using as initial estimates the Cl$^{35}$ NQR data for equivalent rare earth tri-chlorides. For La$I_3$, Gd$I_3$ and Er$I_3$, these are $e^2qQ = -80 \pm 8$ MHz, $-115 \pm 8$ MHz, $-144 \pm 8$ MHz; $\eta = 0.20, 0.50, 0.44$; $h_p = 0.18, 0.20, 0.21$; and $\delta = -0.285 \pm 0.033$ mm/sec, $-0.273 \pm 0.033$ mm/sec, $-0.249 \pm 0.033$ mm/sec, respectively. The degree of covalent bonding in these compounds is discussed in terms of an overlapping orbital model.

1. Introduction

Recently, unresolved $I^{129}$ Mossbauer spectra of the rare earth tri-iodide compounds La$I_3$, Er$I_3$ and Gd$I_3$ have been reported$^1$.

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It seemed very interesting to correlate these results with known Nuclear Quadrupole Resonance (NQR) measurements\(^2\) of quadrupole interactions in similar tri-chloride compounds in order to estimate the quadrupole interactions expected for the tri-iodides. In this paper, we report these estimate values obtained by a least squares fit to the experimental Mössbauer spectra with theoretical curves calculated using the estimated quadrupole interaction parameters. The interpretation of the electric field gradients derived and the departure of ionicity are based on the theory of covalent bonding described by Townes and Schawlow\(^3\) and the theory of overlapping orbitals, described by Owen and Thornley\(^4\).

2. Estimative of the Electric Field Gradients and the Quadrupole Interaction Parameters

It has been reported\(^1\) that the \(^{129}\text{I}\) Mössbauer-effect spectra of the rare earth iodides, \(\text{LaI}_3\), \(\text{GdI}_3\) and \(\text{ErI}_3\) exhibit unsplit absorption resonances. However, the preliminary attempts to fit the resonances with single Lorentzian peaks resulted in questionable values for the isomer shift.

Recently, it was shown\(^5\) that the presence of unresolved quadrupole splitting can affect the determination of isomer shift values in cases where the Mossbauer transitions involve nuclear levels with spin larger than 3/2.

The reevaluation of the original \(^{129}\text{I}\) data indicates that this indeed may be the situation. In particular, the "single line" resonance associated with each of the compounds exhibit a definite asymmetry. Furthermore, the relative line widths of the resonances cannot be correlated to thickness broadening effects. Both of these observations would be consistent with the idea of unresolved quadrupole splitting.

In fact, this possibility is quite reasonable, if one considers the \(^{35}\text{Cl}\) Nuclear Quadrupole Resonance (NQR) data\(^2\) for the equivalent rare earth tri-chloride compounds. In this latter series, a non-zero quadrupole coupling was observed.

The origin of the electric field gradients (EFG) responsible for the quadrupole interaction is by itself an interesting point. In particular, if one assumes that the halide ions possess ionic valence of 1-, then the electronic configuration for both the \(\text{I}^- (5s^2 5p^6)\) and \(\text{Cl}^- (3s^2 3p^6)\) consist of closed shells and consequently cannot contribute to the EFG. This would imply that these gradients are associated entirely with the lattice electric field.
However, it was pointed out in the NQR study of the rare earth tri-chlorides that the observed quadrupole couplings cannot in fact be explained by such purely "ionic" model. Moreover, monopole sum calculation for the rare earth tri-iodide compounds indicated that the quadrupole coupling constants associated with the lattice EFG are much smaller than the natural line width of $I^{129}$ and therefore inconsistent with the broadening and asymmetry observed in the Mossbauer data.

One is led then to consider that departures from the purely ionic model could be responsible for the quadrupole couplings. For $I^{129}$, the consequences of such a departure become evident when one considers the relationship between the number of $p$ holes, $h$, in the $5p$ electronic shell and the isomer shift. In particular, it has been shown that

$$\delta = 1.36 h_p - 0.54 \text{ (mm/sec)},$$

(1)

where $-0.54 \text{ mm/sec} (= \delta_0)$ is the isomer shift of "ionic" $I^-$ relative to a $\text{ZnTe}^{129}$. 

From relation (1) and the "average" isomer shifts reported for the rare earth tri-iodides, we see that $h \neq 0$. Such departures from ionicity result in a partially occupied $p$-hole in the $5p$ electronic shell which could account for the EFG responsible for the observed quadrupole interaction.

These so-called covalent effects have been considered by Townes and Schawlow. In particular if the ionic bond between the iodine and rare earth-ligands has a fractional importance $x$ in the structure and the pure covalent bond an importance $1 - x$, then each contributes an amount to the EFG ($\text{eq}_r$) given by the products of the fractional importance and the values of the EFG associated with each type of bond; i.e.,

$$eq_I = (1 - x)eq_{510} + x(o) = (1 - x)eq_{510},$$

(2)

where, in the notation of Ref. 3, $eq_{510}$ is the field gradient due to a $5p$ hole.

The quantity $(1 - x)$ is called the amount of unbalanced $p$ electrons (or holes), $U_p$, oriented along the bond. For any type of bond, the net effect of the valence $p$ electrons may be expressed as the number of unbalanced $p$ electrons, $U_p$, oriented along the bond. We then have that the quadrupole coupling constant is given by:

$$e^2 q_{\text{mol}} = U_p e^2 q_{\text{at}} Q,$$

(3)

where $eq_{\text{at}}$ is the EFG due to the lowest $p$-hole state in the closed shell $5p^6$. 

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This implication that the EFG in the rare earth tri-halides may be associated with an unbalanced $5p$ hole allows us to estimate the quadrupole coupling constant in the rare earth tri-iodides from the NQR data of the tri-chloride series.

In particular, the EFG for atomic Cl or I, having electronic configurations $3s^23p^5$ and $5s^25p^5$, respectively, is given by:

$$eq_{at}(p\,\text{z hole}) = \frac{4}{3}e\langle r^{-3}\rangle_n,$$

where $n$ is the principal quantum number of the p shell.

The ratio of the quadrupole coupling constants becomes

$$R_1 = \frac{e^2 q_{at} Q(Cl)}{e^2 q_{at} Q(I)} = \frac{Q(Cl)}{Q(I)} \cdot \frac{\langle r^{-3}\rangle_3}{\langle r^{-3}\rangle_5}.$$  

Using the calculated values of $\langle r^{-3}\rangle$ given by Mann and the experimental values of the quadrupole moments $g$ for $Cl^{35}$ and $I^{129}$ (see Table I), we obtain:

$$R_1 = 0.066 \pm 0.002.$$  

<table>
<thead>
<tr>
<th>Atom</th>
<th>Configuration</th>
<th>$\langle r^{-3}\rangle$</th>
<th>$Q_{as}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl$^{35}$</td>
<td>$3p^5$</td>
<td>6.768695</td>
<td>-0.079 $\pm$ 0.004*</td>
</tr>
<tr>
<td>I$^{129}$</td>
<td>$5p^5$</td>
<td>14.86653</td>
<td>-0.55 $\pm$ 0.02*</td>
</tr>
</tbody>
</table>

Table I - Calculated values of $\langle r^{-3}\rangle$ (atomic units) for chlorine and iodine atoms from Mann and experimental values of the quadrupole moments (in barns) of $Cl^{35}$ and $I^{129}$ from Nuclear Data tables. *Rounded-off values for the ground state.

Supported by the data given in Table II, which shows the ratios of the quadrupole couplings of various solid halide compounds to gaseous ones, we make the assumption that this theoretical ratio for atomic quadrupole coupling constants is approximately equal to the molecular one; i.e.,

$$R_2 = \frac{e^2 q_{mol} Q(Cl^{35})}{e^2 q_{mol} Q(I^{129})} \simeq 0.066.$$  

Using the quadrupole interaction parameters measured by Carlson and Adams (Table III), we can estimate the quadrupole coupling for the rare earth iodides. These values are given in Table IV.
The values of the constants are given in Table 8.1 of Ref. 13.

<table>
<thead>
<tr>
<th>Compound</th>
<th>( v_0 ) (MHz)</th>
<th>( e^2qQ ) (MHz)</th>
<th>( \eta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaCl(_3)</td>
<td>4.084 ± 0.001*</td>
<td>8.168 ± 0.002*</td>
<td>0.50 ± 0.02</td>
</tr>
<tr>
<td>GdCl(_3)</td>
<td>5.23 ± 0.01*</td>
<td>10.47 ± 0.02*</td>
<td>0.425 ± 0.01</td>
</tr>
<tr>
<td>ErCl(_3)</td>
<td>4.445 ± 0.005*</td>
<td>8.31 ± 0.01*</td>
<td>0.525 ± 0.02</td>
</tr>
</tbody>
</table>

Table III - NQR frequencies, \( v_0 \equiv \frac{1}{2} e^2qQ (1 + \eta^2/3)^{1/2} \), quadrupole coupling constants \( e^2qQ \) and \( \eta \) values of Cl\(_{35}\) in LaCl\(_3\), GdCl\(_3\), and ErCl\(_3\). Ref. 2.
*These values come from interpolation to \( \sim 100^\circ K \).

<table>
<thead>
<tr>
<th>Compound</th>
<th>( e^2qQ(129) ) (MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaI(_3)</td>
<td>123 ± 7</td>
</tr>
<tr>
<td>GdI(_3)</td>
<td>158 ± 19</td>
</tr>
<tr>
<td>ErI(_3)</td>
<td>135 ± 8</td>
</tr>
</tbody>
</table>

Table IV - Estimated values of \( e^2qQ \) for \( I^{129} \) in LaI\(_3\), GdI\(_3\), and ErI\(_3\) using relation (7) and from Table III.

Such estimates serve as a starting point to a least squares fit to the \( I^{129} \) data. This fitting procedure consists of varying the parameters associated with the quadrupole interaction and the isomer shift for \( I^{129} \) in order to produce the best possible fit to the data.
Figure 1 - Energy levels for a $Te^{129m}$ source and an $I^{129}$ absorber. The nuclear level splittings in the absorber are shown assuming $eq$ as positive.
In particular, the absorption spectrum of a iodine 129 compound (with quadrupole interaction), shown in Fig. 1, consists of eight allowed nuclear transitions between the 7/2+ ground to the 5/2+ first excited nuclear state. The line positions are related to the quadrupole coupling, the asymmetry parameter $\eta$, and the isomer shift $\delta$ by\textsuperscript{10}:

$$E_{ij} = A\{Rf(I^*, m^*, n) - f(I, m_j, n)\} + 6,$$  \hspace{1cm} (9)

where $A = e^2 qQ_{GS}/4$, $f(I, m, n)$ is related to the spin Hamiltonian eigenvalues for the case of non-axial symmetric electric field and $R$ is the quadrupole moment ratio of $I^{129}(=Q^*_{ES}/Q_{GS} = 1.23)$\textsuperscript{11}.

![Figure 2 - Line positions of the $I^{129}$ absorption spectrum in velocity units. The conversion factor is $c/E_r$, where $c$ is the speed of light and $E_r = 27.8$ keV.](image)

The theoretical Mossbauer absorption spectra consist of a sum of Lorentzian curves with positions and amplitudes represented by the lines in Fig. 2. The intensity and position of these peaks depend on the spin Hamiltonian parameters. In the actual fitting procedure, the position of the absorption lines (and widths) were varied so as to produce the best possible fit to the experimental spectrum. After this adjustment, the values of the quadrupole interaction parameters and isomer shift were extracted.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$e^2q_{mol} Q(I^{129})(\text{MHz})$</th>
<th>$\eta$</th>
<th>$\delta$ (mm/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaI$_3$</td>
<td>$-80 \pm 8$</td>
<td>0.20</td>
<td>$-0.285 \pm 0.033$</td>
</tr>
<tr>
<td>GdI$_3$</td>
<td>$-115 \pm 8$</td>
<td>0.50</td>
<td>$-0.273 \pm 0.033$</td>
</tr>
<tr>
<td>ErI$_3$</td>
<td>$-144 \pm 8$</td>
<td>0.44</td>
<td>$-0.249 \pm 0.033$</td>
</tr>
</tbody>
</table>

Table V - Estimated values of $e^2qQ$, $\eta$ and isomer shift $\delta$ for $I^{129}$ in the R. E. tri-iodides, obtained by least squares fitting.
Figure 3 - Experimental Mossbauer spectrum of $LaI_3$. The solid line is the theoretical absorption curve obtained by a least squares fitting.
Figure 4 - Experimental Mössbauer spectrum of \( \text{Gd}_3 \). The solid line is the theoretical absorption curve obtained by a least squares fitting.
Figure 5 - Experimental Mossbauer spectrum of $ErI_3$. The solid line is the theoretical absorption curve obtained by a least squares fitting.
Figures 3, 4 and 5 show the comparisons between the theoretical and experimental spectra for the rare earth tri-iodides and Table V contains the final parameters obtained.

These values represent the best overall fits to the data (including the original fits with single Lorentzian peaks) consistent with the idea of unresolved quadrupole splittings.

### 3. Interpretation and Conclusions

The experimental evidence of atomic EFG in the rare earth tri-iodides of the type AI, leads us to consider that covalent effects are present. The electronegativity of iodine is larger than the one of the rare earth elements, which implies that the isomer shift is related only to the number of p-holes, h. Both aspects suggest that the chemical bonding can be understood in terms of the description of orbital overlap given by Owen and Thornley. The s and d electrons from the outer electronic configuration of La, Gd and Er, hybridize in the bonding with iodine 5-p electrons leaving a p-hole partially occupied. In this sense $U_p$ is given by $(1-x)$, where x is the amount of hybridization between the s and d electrons from the ligands. This approach differs from the one given by Townes and Daily, where s and d orbitals hybridize of the same atom are considered. However, from either approach, the expression for $U_p$ is the same.

The quantity $U_p$ is related to the p electron distribution in the x, y and z directions (p,, $p_y$ and $p_z$ populations) by the following expression:

$$U_p = -U_z + \frac{1}{2}(U_x + U_y),$$

where $U_z$, $U_x$ and $U_y$ are related to the asymmetry parameter, $\eta$, and the number of p holes in the $5s^2 5p^6$ configuration by:

$$\eta = \frac{3}{2} \frac{U_x - U_y}{U_p},$$

$$h_p = 6 - (U_x + U_y + U_z).$$

Using relations (1), (3), (8)-(10) and Table V, taking $e^2 q_{at} Q$ as $-1223.5 \text{ MHz}$, and the relationship between h, and the isomer shift for $I^{129}$, namely

$$\delta = 1.36 h - 0.54 (\text{mm/s}),$$

we constructed Table VI.
Table VI - Estimated values $U_p, h_p, V, U_y$ and $U_z$ for $I^{129}$ in $LaI_3$, $GdI_3$, $ErI_3$ using relations (1), (3), (8) - (10) and Table V. The value of $\epsilon^2 q Q$ is $- 1223$ MHz, accordingly to (r-1) and $Q(I^{129})$ from Table I.

The large ionicity, $\sim 0.80$, is consistent with the ionic character of these crystals, $\sim 0.75$. The fractional importance of the ionic bond $x \approx 90\%$, leaving $1 - x \approx 10\%$ fractional importance for the covalent bond.

The amount of hybridization that accounts for covalent effects changes from bond to bond and no simple rules are yet known. If we assume that the bonding in the rare earth tri-iodide compounds is simple covalent, the number of unbalanced p-electrons would be given by $U_p = 1 - s + d$, which means a hybridization between $s$ and $d$ electronic wave functions of the rare earth ligands. It should be noted that we are using a hybridization due to an orbital overlapping of the wave functions of the ligands instead of a hybridization of the $s$ and $p$ type wave functions of the iodine as described by Owen and Thornley. The average numerical value derived for $U_p (\sim 0.10)$ can be understood as resulting from an admixture of $60\%$ of $s$-wave function and $30\%$ of $d$-wave function of the ligands to the $p$-wave function of the iodine. Small deviations can be explained by the presence of $f$-electrons in the bonding. The small departure from complete ionicity and the estimated values for the quadrupole coupling explain quite reasonably the unresolved Mossbauer spectra for the $I^{129}$ compounds of rare earths.

From these studies, we can estimate the NQR frequencies for the tri-iodides reported in this paper. In particular, associated with the $5/2$ nuclear ground state of $I^{127}$ are the two NQR transitions $5/2 \rightarrow 3/2$ and $3/2 \rightarrow 1/2$, with the NQR frequencies given by:

$$v_1^2 = \frac{3e^2 q Q}{10} \left(1 - \frac{11}{54} \eta^2\right),$$
$$v_2^2 = \frac{3e^2 q Q}{20} \left(1 + \frac{5}{54} \eta^2\right),$$

respectively.
Table VII - Estimated $I^{1127}$ NQR frequencies, $v_Q$, given by relations (11) and the $e^2 qQ's$ from Table V. The conversion from $I^{1129}$ to $I^{1127}$ is given by the ratio of the ground state quadrupole moments $Q(I^{1129})/Q(I^{1127}) = 0.701$ from Ref. 7.

From Table V, relations (11) and using the measured ratio of the ground state quadrupole moments of $I^{1129}$ and $I^{1127}$, $Q(I^{1129})/Q(I^{1127}) = 0.7017$, one obtains the estimated frequencies given in Table VII.

An experimental evaluation of these frequencies through NQR measurements would be complementary to this work and would provide additional confirmation to the present approach to understand the quadrupole interaction in these almost "ionic" compounds.

One of us (M. I. da Costa, Jr.) thanks Tullio Sonnino for suggesting the experimental work on $I^{1129}$ compounds. We thank John D. Rogers and Celso Müller for supplying the least squares fit program with display on line.

References and Notes

6. We wish to thank Adalberto Vasquez for supplying the monopole sum calculation program.