General Aspects of Nuclear Hyperfine Interactions in Salts of the Rare Earths

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INTRODUCTION

Most of the experimental studies of recoilless nuclear resonance absorption performed until now have been using the 14.4-keV transition in Fe$^{57}$. The low energy of this transition, the long lifetime of the relevant nuclear level, the long lifetime of the parent isotope, and, last but not least, the vast number of problems which could be tackled, made Fe$^{57}$ the favorite isotope in the entire field covered by this conference. In increasing numbers, however, experimental and theoretical studies are progressing which involve nuclear isotopes other than Fe$^{57}$.

The rare-earth elements provide the largest group of isotopes which are suitable for recoilless resonance absorption studies in chemically similar atoms. This results first of all from the fact that nuclei of the rare-earth elements conveniently exhibit low-lying first excited nuclear states. Furthermore, the nuclear hyperfine interactions in rare-earth isotopes appreciably exceed the widths of the relevant gamma lines, thus permitting direct measurements of hyperfine splittings of gamma lines.

The present article attempts to discuss some of the general features which one encounters in recoilless resonance absorption studies of hyperfine interactions in salts of the rare earths. Experimental results will be presented which have been selected primarily in order to illustrate the general discussion.

The magnetic and optical properties of salts of the rare earths are intimately connected with the presence of a partially filled 4f electron shell. The rare-earth series extends from lanthanum with a completely empty 4f shell (4f$^0$) to lutecium with a com-
pletely filled 4f shell ($4f^{n+}$. The trivalent state of the rare-earth ions is the one most frequently encountered in ionic compounds. The point-group symmetries associated with the rare-earth sites in ionic crystals are usually rather low. In particular, the preference for a trivalent ionization state renders it difficult to obtain the rare-earth ion in a surrounding of cubic symmetry, i.e., in a lattice position with a vanishing electric field gradient and thereby with a vanishing electric quadrupole interaction. This difficulty has rather inconvenient consequences for gamma-resonance experiments, in that it rather often renders it difficult to produce radioactive sources emitting a single (unsplit) line.

The electric and magnetic moments of a rare-earth nucleus interact with the electric and magnetic fields produced in a salt by the surrounding ions and by the atomic electrons of the ion which contains the particular nucleus. A knowledge of the position of the surrounding ions and a knowledge of the electronic state of the ion in its surrounding are, therefore, prerequisites for a description of the nuclear hyperfine interactions. The direct interaction of the magnetic moments of the surrounding ions and magnetic fields has not been observed thus far in gamma-resonance studies. This direct interaction usually escapes observation, although in favorable cases one can expect to obtain so much enhancement of the externally applied field by the atomic electrons that it might become possible to observe the direct interaction.

THE INTERACTION WITH THE CRYSTALLINE ELECTRIC FIELD (CEF)

The rare-earth ion interacts in a salt with the other ions which surround its position. The dominant effect is the interaction of the CEF produced by the surrounding ions with the 4f electrons in the partially filled shell. This interaction is weak in comparison with the spin–orbit interaction, in contrast to the situation prevailing in the case of iron transition elements. As a result, the total angular momentum $J$ remains a good quantum number for rare-earth ions incorporated in crystals, while it ceases to be a good quantum number for ions of iron transition elements.

The CEF produced by the ions surrounding the central ion may, in good approximation, be regarded as a static electric field produced by point charges, dipoles, etc. Covalent bonding of the magnetic 4f electrons in salts of the rare earths is generally much smaller than for the 3d electrons in salts of iron transition elements. If one then assumes that the wave functions of the surrounding ions do not overlap the central paramagnetic ion, one may express the potential $V(r, \theta, \phi)$ of the CEF in terms of the parameters $A_n^m$ and $B_n^m$, which are defined by the following expansion in terms of spherical harmonics

$$V(r, \theta, \phi) = \sum_{n,m} [A_n^m Y_n^m(\theta, \phi) + (-1)^m Y_n^{-m}(\theta, \phi)] + B_n^m Y_n^m(\theta, \phi) - (-1)^m Y_n^{-m}(\theta, \phi)).$$

General symmetry and parity considerations yield the results that one needs to consider only terms with $n = 2, 4, 6$ in the case of rare-earth ions. Symmetry properties of the surroundings (point-group symmetries) further reduce the number of contributing terms.

The interaction of the CEF with the 4f electrons in rare-earth ions results in a partial or complete removal of the spatial degeneracy in the orientation of the total angular momentum $J$ of each electronic state. The $(2J + 1)$-fold degenerate electronic level of each multiplet component of a free rare-earth ion is split by the CEF into a number of levels. The actual number of crystalline levels depends on the symmetry of the CEF, which is given by the symmetry of the spatial arrangement of the surrounding ions, while the level spacing depends on the strength of the interaction between the CEF and the 4f electrons. The angular part of each degenerate or non-degenerate crystalline level $\alpha$ may be described by wave functions of the type

$$\psi^{(\alpha)} = \sum_{m=-J}^{+J} a_{m}^{(\alpha)} \psi_{m} + \sum_{m=-J'}^{+J'} b_{m}^{(\alpha)} \psi_{m} + \cdots,$$

where $J, J', \cdots$ specify the total angular momenta of the different components of the electronic ground multiplet, and $\psi_{J}, \psi_{J'}, \cdots$ are the associated eigenfunctions. The constants $a_{m}^{(\alpha)}, b_{m}^{(\alpha)}, \cdots$ are readily obtained if one treats the potential $V(r, \theta, \phi)$ defined by Eq. (1) as a perturbation of the degenerate electronic ground state of the free ion. The actual calculations are greatly facilitated by employing the operator equivalent techniques developed by Elliott and Stevens.\footnote{R. J. Elliott and K. W. H. Stevens, Proc. Roy. Soc. (London) A218, 553 (1953).}


\footnote{Experimental results are usually expressed in terms of parameters $A_2^0, A_4^0$ which obey Eq. (1) if one employs spherical harmonics which are not normalized to unity, a procedure which eliminates inconvenient numerical factors.}

\footnote{3}
MAGNETIC HYPERFINE INTERACTION

The Hamiltonian describing the magnetic interaction with the nucleus of the electrons in partially filled shells is given by

$$H_n = \sum \left( 2\beta \mu N / \mathbf{I} \right) \mathbf{I} \cdot \mathbf{r}_i - \mathbf{s} \cdot \mathbf{r}_i^2 + 3\mathbf{r}_i \cdot (\mathbf{s} \cdot \mathbf{r}_i) / \mathbf{r}_i^2 + \frac{9}{4} \pi \mathbf{s} \cdot \mathbf{I},$$

where $\beta$ is the Bohr magneton, $\beta$ the nuclear magneton, $\mathbf{I}$ the nuclear spin, $\mathbf{r}$ the electron radius vector, and $\mathbf{s}$ and $\mathbf{r}$ are the orbital and spin angular momenta.

For $s$ electrons only the last term, the so-called Fermi contact term, remains finite. For other electrons, the last term vanishes. In paramagnetic crystals of the rare earths one may neglect the contribution of the Fermi contact term to the magnetic hyperfine interaction. This procedure appears justified on the grounds that one does not observe any appreciable hyperfine interaction in cases of vanishing orbital angular momentum, as for instance in the case of gadolinium. The magnetic hyperfine interaction depends then only on the first three terms in Eq. (3), with the summation extended over all electrons in the partially filled $4f$ shell. The evaluation of the matrix elements of $H_n$ between the different crystalline field levels is greatly facilitated by employing the operator equivalent techniques developed by Elliot and Stevens. Within a manifold of states $\psi_j^{(m)}$ spanned by the vector $\mathbf{J}$ we may replace the angular part of the interaction operator which appears as a factor of the operator $\mathbf{I}$ in Eq. (3) by the vector equivalent operator $\mathbf{J}$:

$$\langle \psi_j^{(m)} | \sum \left( \mathbf{I} \cdot \mathbf{r}_i + 3\mathbf{r}_i \cdot \mathbf{s} \cdot \mathbf{r}_i / \mathbf{r}_i^2 \right) | \psi_j^{(m')}. \rangle = \langle \mathbf{J} | \langle \mathbf{N} | \mathbf{J} \psi_j^{(m')}. \rangle.$$

The conversion factors $\langle \mathbf{J} | \langle \mathbf{N} | \mathbf{J} \rangle$ were tabulated by Elliot and Stevens. The magnetic hyperfine interaction energy within a (nondegenerate) state $\psi_j^{(m)}$ is given by (neglecting the contribution of higher multiplet components and considering terms of zeroth and first order only)

$$E_j^{(m)} = \langle \psi_j^{(m)} | H_n | \psi_j^{(m)} \rangle + \sum_{m'} | \langle \psi_j^{(m)} | H_n | \psi_j^{(m')} \rangle |^2 / E_j^{(m')} - E_j^{(m)}. \quad (5)$$

Equations (3) and (4) demonstrate the dependence of the magnetic hyperfine interaction upon the matrix elements of $\mathbf{J}$ within the manifold of crystalline field levels associated with the state vector $\mathbf{J}$.

INVARIANCE AGAINST TIME REVERSAL AND ITS INFLUENCE UPON MAGNETIC HYPERFINE INTERACTIONS

The total Hamiltonian $H$ which describes the paramagnetic ion within the CEF is invariant against the operation of time reversal, as long as the crystal is not subjected to externally applied magnetic fields. This particular invariance holds even in the presence of a spin–orbit coupling term $\xi (\mathbf{L} \cdot \mathbf{S})$, since both $\mathbf{L}$ and $\mathbf{S}$ change their sign under the operation of time reversal. The invariance against time reversal will be briefly discussed since it bears profoundly upon the nuclear hyperfine interactions.

The Schrödinger equation of the paramagnetic ion within the CEF can be given by

$$H \psi (t) = H \psi e^{-i\omega t} = -\left( \frac{\hbar}{i} \right) \frac{\partial \psi (t)}{\partial t} = E \psi e^{-i\omega t}. \quad (6)$$

Applying time reversal and taking into account that $H$ remains invariant under the operation of time reversal, we have

$$H \psi^{-1} (t) = H \psi^{-1} e^{i\omega t} = -\left( \frac{\hbar}{i} \right) \frac{\partial \psi^{-1} (t)}{\partial t} = E \psi^{-1} e^{i\omega t}. \quad (7)$$

In the case of rare-earth ions, $\psi$ may be considered to have the form given by Eq. (2). The common time-reversal operator $a$ yields for the time-reversed function

$$\psi^* = \sum_{m-j} a_j (1)^{j-m} \psi_j^m + \sum_{m-j} b_j (1)^{j-m} \psi_j^m + \cdots. \quad (8)$$

The symmetries inflicted upon the wave functions of the crystalline levels by the invariance under time reversal depend on the degeneracies of the levels. In case of cubic lattice symmetries ($O, O_h, T_d$) three- and fourfold degenerate levels would occur. The rare-earth ions, however, preferentially crystallize in rather low symmetries. We therefore shall limit ourselves to the two cases of nondegenerate and twofold degenerate (time-reversed) levels.

**Nondegenerate Levels**

According to Eqs. (6) and (7), both $\psi$ and $\psi^*$ must be simultaneous eigenfunctions of the Schrödinger equation in order for a level to be nondegenerate. On comparing Eqs. (2) and (8) one obtains the conditions

$$a_{-m} = a_m (-1)^{j-m}; b_{-m} = b_m (-1)^{j-m}; \cdots. \quad (9)$$

As an immediate consequence, we obtain for the expectation values of all components of the total angular momentum $J$ within a manifold of states spanned by the vector $\mathbf{J}$:

$$
\langle \psi^{(a)}_J | J_i | \psi^{(a)}_J \rangle = \langle \psi^{(a)}_J | J_J | \psi^{(a)}_J \rangle = \langle \psi^{(a)}_J | \mathbf{J}_J | \psi^{(a)}_J \rangle = 0 ,
$$

that is, the total angular momentum in nondegenerate levels is quenched in rare-earth elements. We may compare this situation with the one prevailing in iron transition elements, where the invariance under time reversal yields a quenching of the orbital angular momentum only, leading to spin-only paramagnetism. The spin momentum is, in first order, not influenced by the CEF in the iron transition elements, since the CEF acts directly only upon the electron orbits. The spin–orbit coupling interaction, which in comparison with the crystalline field interaction is very weak in iron transition elements, may only partially lift the orbital degeneracy. In contrast, the spin–orbit coupling in rare-earth transition elements is very large in comparison with the crystalline electric field interaction; the spin is strongly coupled to the orbit and the total angular momentum is quenched.

The quenching of the total angular momentum caused by the CEF in nondegenerate electronic states has the consequence that the expectation values of the electronic magnetic moment $\mathbf{m}$ vanish:

$$
\langle \psi^{(a)}_J | \mathbf{m}_J | \psi^{(a)}_J \rangle = \langle \psi^{(a)}_J | \mathbf{m}_m | \psi^{(a)}_J \rangle = \langle \psi^{(a)}_J | \mathbf{m}_J | \psi^{(a)}_J \rangle = 0 ,
$$

that is, the magnetic interaction vanishes in zero order for all nondegenerate levels, independent of temperature. This quenching of the total angular momentum in nondegenerate electronic states of rare-earth ions is, however, of somewhat less importance as the quenching of the orbital angular momentum in iron transition elements. The total spacing of the crystalline levels in rare-earth ions is of the order of room temperature only, a result of the limited strength of the interaction between the CEF and the $4f$ electrons. In some cases, nondegenerate and degenerate levels are situated closely enough to produce an instantaneous magnetic interaction through the first-order terms appearing in Eq. (5).

**Twofold-Degenerate Levels**

The degeneracy may be a Kramer’s-type degeneracy or an accidental degeneracy, the latter one resulting in the case of an ion with an even number of electrons which is exposed to a CEF of sufficiently high symmetry. In either case we may choose the wave functions of Eqs. (2) and (8) as representations for the twofold-degenerate levels. Orthogonality then requires (neglecting for simplicity higher multiplet components)

$$
\langle \psi^{(a)}_J | \psi^{(a)*}_J \rangle = 0 = \sum_a c_{a+m}^{(a)} d_{a-m}^{(a)} (-1)^{J-m} .
$$

Similar conditions hold for all mutually orthogonal crystalline levels. This leads to the conditions $a_0 = 0$ and $a_n = 0$, $a_{-m} \neq 0$ or $a_{-m} = 0$, $a_n \neq 0$. The observation of nuclear hyperfine splittings of gamma lines is limited to temperatures where the spin-lattice relaxation times are long enough to permit the measurement of instantaneous magnetic interactions rather than of average interactions. At elevated temperatures, spin-lattice relaxation times are short in comparison with all other relevant times, thus, preventing a direct observation of the magnetic hyperfine interactions in the individual crystalline levels. One may only observe a value of the magnetic interaction which is the time average taken over all crystalline levels, weighted according to their Boltzmann factors. This averaging process leads to a vanishing magnetic interaction. The observation of the magnetic hyperfine interaction, therefore, is limited to rather low temperatures.

The degeneracies of the crystalline levels populated at these temperatures play a dominant role. In the case of ions with an odd number of electrons, i.e., with electronic levels exhibiting Kramer’s degeneracy, one may, in general, expect a strong magnetic hyperfine interaction, with the exception of gadolinium, which has a $S$ ground state. In cases of nuclear ground states with zero spin, the magnetic interaction may still exist in the nuclear excited states.

In the case of ions with an even number of electrons, the appearance of a magnetic interaction depends on the presence of levels with accidental degeneracies, usually twofold-degenerate levels, or of nondegenerate levels grouped as to be nearly degenerate. In particular, we do not, in general, expect observable magnetic hyperfine interactions in those ions with an even number of electrons, where the point-group symmetry at the rare-earth ion site is sufficiently low to completely remove any degeneracy, as is the case in the rhombic, triclinic, and monoclinic groups.

As an example we consider the two cases Er$^{3+}$ in Er$_2$O$_3$ and Tm$^{3+}$ in Tm$_2$O$_3$. Er$^{3+}$ represents a system exhibiting Kramer’s degeneracy, while Tm$^{3+}$ is an example for a system without Kramer’s degeneracy. The rare-earth ions in both Er$_2$O$_3$ and Tm$_2$O$_3$ occupy two different nonequivalent lattice sites; 1/2 of the ions occupy sites exhibiting the symmetry of the point group $C_2$, while 1/2 of the ions occupy sites associated
with the symmetry $C_3$. The symmetry of the point group $C_3$ is sufficiently low so as to remove completely any degeneracy other than Kramer’s degeneracy. This leads, for the case of the ions associated with the $C_2$ positions, to $2J + 1 = 13$ levels in the case of Tm$^{3+}$ and to $\frac{1}{2}(2J + 1) = 8$ levels in the case of Er$^{3+}$ (Table I). As a result, one expects at low temperatures a strong magnetic hyperfine interaction in the case of Er$_2$O$_3$, while no magnetic interaction is expected for the case of Tm$_2$O$_3$ (disregarding the presence of the ions at the less populated positions with symmetry $C_3$). Measurements of hyperfine interactions in Er$_2$O$_3$ and Tm$_2$O$_3$ at low temperatures are confronted in Figs. 1 and 2.$^8$

The discussion presented above duly applies also to the case where the magnetic hyperfine interaction is studied in paramagnetic salts as a function of an externally applied magnetic field. An external magnetic field likewise lifts the degeneracy of electronic levels with either Kramer’s degeneracy or accidental degeneracy. The magnetic moment induced in the electronic states by the external magnetic field may greatly enhance the value of the magnetic field produced at the nuclear sites, the actual value often appreciably exceeding the value of the externally applied field. Likewise, the resulting magnetic interaction will usually be observable only at low temperatures, due to the requirement of either long enough spin-lattice relaxation times or large enough population differences of the magnetically split electronic states.

**NUCLEAR QUADRUPOLE INTERACTION**

Studies of the nuclear magnetic hyperfine interaction in salts of the rare earths usually require the application of rather low temperatures, as has been discussed above. This is an immediate consequence of the fact that the over-all splitting of the crystalline levels is of the order of room temperature only. Any averaging process over the levels at elevated temperatures yields nearly equal contributions from states $\psi^+$ and $\psi^-$, thus leading to a vanishing net magnetic moment of the electronic states at elevated temperatures. Studies of the nuclear quadrupole interaction,

<table>
<thead>
<tr>
<th>Atomic number</th>
<th>$Z = 68$</th>
<th>$Z = 69$</th>
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<tr>
<td>Number of electrons per ion</td>
<td>65</td>
<td>66</td>
</tr>
<tr>
<td>Free ion electronic ground state</td>
<td>$4f^{11}$ $4f^{10}$</td>
<td>$4f^{13}$ $2H_4$</td>
</tr>
<tr>
<td>Number of crystalline field levels (degeneracy)</td>
<td>$\frac{1}{2}(2J + 1) = 8$ [2]</td>
<td>$2J + 1 = 13$ [1]</td>
</tr>
</tbody>
</table>

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7 F. W. Stanek, Z. Physik 166, 6 (1962).

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**Fig. 1.** Recoilless resonance absorption in the 80.6-keV first excited state in Er$^{166}$. Transmitted intensities measured as a function of relative velocity between source (Ho$_2$O$_3$, $T = 20^\circ$ K) and absorber (Er$_2$O$_3$, $T = 20^\circ$ K). (See Stanek, Ref. 7.)
on the other hand, usually do not require the application of low temperatures. The averaging process over the populated crystalline field levels does not wipe out the quadrupole interaction, because this interaction depends on the squares of the projection quantum numbers \( m \) rather than on the different \( m \) values themselves. The nuclear quadrupole interaction, in fact, can be observed over a wide range of temperatures.

The nuclear quadrupole moment interacts with the field gradients produced by the ions surrounding the central rare earth in the paramagnetic salts. The total electric field gradient at the nuclear sites consists of several different contributions, the most important ones resulting from the following effects:

1. The \( 4f \) electrons, distorted by the CEF, produce an electric field gradient \( e q^{(4f)} \) at the nuclear sites.

2. The charged ions surrounding the central rare-earth ion in the paramagnetic crystal produce a direct field gradient \( e q^{(im)} \) at the nuclear site. This direct contribution \( e q^{(im)} \) to the total field gradient is usually negligible in comparison with the contribution \( e q^{(4f)} \) from the distorted \( 4f \) electrons.

3. The CEF not only interacts with the electrons in the partially filled \( 4f \) shell, it also interacts with the electrons in the closed shells or subshells. The interaction of the CEF with these core electrons induces a distortion (multipole polarization) in the closed shells. The quadrupole part of this distortion produces a contribution \(-\gamma e q^{(im)}\) to the electric field gradient at the nuclear site. The proportionality factor \(-\gamma\) represents a shielding \((\gamma > 0)\) or anti-shielding \((\gamma < 0)\) factor. It is a scalar quantity, i.e., the same factor multiplies each component of the field gradient tensor.

4. The distorted \( 4f \) electron shell interacts with the core electrons, thereby inducing an additional multipole polarization in the closed electron shells. The quadrupole part of this polarization likewise contributes to the electric field gradient at the nuclear site, through the term \(-Req^{(4s)}\), where \(-R\) represents a shielding \((R > 0)\) or anti-shielding \((R < 0)\) factor. \( R \), again, is a scalar quantity.

Collecting the different contributions, we obtain for any component \( e q_{ij} \) of the electric field gradient tensor

\[
e q_{ij} = (1 - \gamma)(q^{(im)}_{ij} + (1 - R)q^{(4s)}_{ij}) \quad i,j = 1,2,3.
\]

The first factor in each term gives the direct contribution, while each second factor gives the contribution from electronic shielding.

The Hamiltonian \( H_Q \) describing the nuclear quadrupole interaction is given by

\[
H_Q = \frac{\mathcal{E} Q}{4I(2I-1)} \left\{ (1 - R)q^{(4s)}_{ij}(3I_i^2 - I(I+1)) + \left( \frac{1}{2} \eta^{(4f)} \right) (I_j^2 + I_i^2) \right\} + \left( \frac{1}{2} \eta^{(im)} \right) (I_j^2 + I_i^2).
\]

(10)

\( Q \) is the nuclear quadrupole moment, defined in the usual way as the expectation value of the quadrupole operator in the substate \( |I, m_i = I > \), \( I \) is the nuclear spin, \( \eta = (q_{ee} - q_{mm})/q_{ee} \), while the operators \( I_x \) are defined by the relations \( I_x = I_x \pm i I_y \); all other quantities have been introduced earlier. It should be emphasized that Eq. (10) holds in the principal axes system of the electric field gradient tensor. In cases of very low symmetry, this system does not necessarily coincide with a system whose axes coincide with axes of major symmetry of the CEF.

The Determination of the Matrix Elements of the Components of the Electric Field Gradient Tensor

The components \( q^{(im)}_{ij} \) and \( \eta^{(im)} = [q^{(im)}_{22} - q^{(im)}_{33}]/q^{(im)}_{xx} \) can, in principle, be determined by lattice sum calculations. In most cases this procedure is impractical, partly because of insufficient knowledge of the position coordinates of the surrounding ligand point charges, dipole moments, etc., and because of the slow convergence of the corresponding lattice sums. Other uncertainties may result from the fact that the position coordinates often are accurately known only at a fixed temperature, and also because the position
of very light elements, which are inaccessiible to determinations by x-ray measurements, are only rather vaguely known. The quantities \( q^{(l)}_{\gamma} \) and \( \eta^{(l)} \) can in many cases be determined by using optical, specific heat, susceptibility, or electron paramagnetic resonance data. Such measurements provide information on the position of the crystalline field levels and thereby on the values \( A^{\pi}(r^*) \), where \( r^* \) denotes the value of \( r^* \) averaged over the 4f electron shell. The quantities \( q^{(l)}_{\gamma} \) and \( \eta^{(l)} \) may be expressed in terms of the parameters \( A^{\pi}_\gamma \), using the definition \( e_{\gamma\iota} = \partial^2/\partial x^2 \partial x \Sigma (-V/e) \), where \( V \) is the interaction energy defined by Eq. (1). We obtain the relations

\[
e_{\gamma\iota}^{(l)} = -4A^0_\gamma/e \quad \eta^{(l)} = A^0_\gamma/A^0_0.
\]

(11)

The quantities \( q^{(l)}_{\gamma} \) are defined through the relation

\[
e_{\gamma\iota}^{(l)} = \partial^2/\partial x^2 \partial x \Sigma (-e/r_\iota),
\]

where the sum extends over all 4f electrons in the partially filled shell and the \( r_\iota \) represent radius vectors of the 4f electrons. With this definition we obtain for the expectation values of \( q^{(l)}_{\gamma} \) and \( \eta^{(l)} \) for a crystalline field level:

\[
\langle \psi | q^{(l)}_{\gamma} | \psi \rangle = -\sum_\iota \langle \psi | J_\iota | \psi \rangle (r^*)_\iota \langle \psi | J_\iota | \psi \rangle,
\]

(12a)

\[
\langle \psi | \eta^{(l)} | \psi \rangle = \langle \psi | J_\iota | \psi \rangle (r^*)_\iota \langle \psi | J_\iota | \psi \rangle + J_\iota^2 | \psi \rangle.
\]

(12b)

**The Antishielding and Shielding Factors \( \gamma^* \) and \( R \)**

Electronic shielding effects (Sternheimer effects) play a major role in the nuclear quadrupole interaction of the rare-earth isotopes. Theoretical calculations of the values of the Sternheimer factors are rather difficult to perform, because of the lack of sufficiently accurate electronic wave functions for heavy atoms. Calculations have nevertheless been conducted for a series of cases, including some rare-earth ions. These calculations exhibit the following general trend: The factor \( \gamma^* \) is negative for all but the very lightest positive ions, thus, representing an antishielding effect which leads to an enhancement of the direct field gradient produced by the surrounding ions at the nuclear site; the factor \( \gamma^* \) gradually increases in absolute value with increasing atomic number, its value being of the order of \(-100\) for trivalent rare-earth ions. The contribution \( q^{(l)}_{\gamma} \) to the electric field gradient is usually negligible in comparison with the contribution \( q^{(l)}_{\eta} \). The contribution \(-\gamma^* q^{(l)}_{\gamma}\), on the other hand, in general yields a substantial contribution to the total field gradient at the nuclear site.

Theoretical values for the factor \( R \) of rare-earth ions are equally difficult to obtain. Sternheimer calculates some values for the (dominant) angular contributions \( R' \) to \( R \), arriving at shielding effects \((R' > 0)\) of the order of \(10\%\). Some theoretical values for \( \gamma^* \) and \( R' \) are presented in Table II.\(^{10-12}\)

**The Temperature Dependence of the Nuclear Quadrupole Interaction**

Most gamma resonance absorption studies of the nuclear quadrupole interaction in salts of the rare earths were performed under conditions, where the spin-lattice relaxation time was fast enough to average the acting electric field gradients over the contributing crystalline field levels. Under these conditions, one obtains components \( q^{(l)}_{\gamma} \) of the net field gradients which are given by

\[
\langle q^{(l)}_{\gamma} \rangle = \sum_\iota \langle \psi(a)|J_\iota|\psi(a)\rangle e^{-E(a)/kT} \sum_\iota e^{-E(a)/kT}.
\]

With an over-all splitting of the CEF levels of the order of room temperature, one expects a strong variation of the field gradient \( q^{(l)}_{\gamma} \) in the range below room temperature. At elevated temperatures, where the crystalline levels approach equal population, the 4f shell assumes a net spherical symmetry, yielding \( \langle q^{(l)}_{\gamma} \rangle = 0 \). The necessary temperatures are typically of the order of room temperature. The total field gradient, nevertheless, does not vanish at elevated temperatures, since then the nucleus still experiences the contribution from the term \((1 - \gamma^*) \times q^{(l)}_{\gamma}\). Thus it becomes possible to isolate this latter contribution by applying sufficiently high temperatures. Figure 3 gives an example.\(^9\) The case of \( \text{Tm}^{3+} \) is particularly favorable, because the first excited

\[\text{Table II. Sternheimer shielding and antishielding factors.}
\]

<table>
<thead>
<tr>
<th>Ion</th>
<th>( R' )</th>
<th>( \gamma^* )</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Pr}^{3+} )</td>
<td>-16.4</td>
<td></td>
<td>Ray(^a)</td>
</tr>
<tr>
<td>( \text{Pr}^{4+} )</td>
<td>-105</td>
<td></td>
<td>Wikner and Burns(^b)</td>
</tr>
<tr>
<td>( \text{Tm}^{3+} )</td>
<td>-61.5</td>
<td></td>
<td>Wikner and Burns(^b)</td>
</tr>
<tr>
<td>( \text{Eu (4f orbital)} )</td>
<td>+0.29</td>
<td></td>
<td>Sternheimer(^c)</td>
</tr>
<tr>
<td>( \text{Lu (4f orbital)} )</td>
<td>+0.23</td>
<td></td>
<td>Sternheimer(^c)</td>
</tr>
</tbody>
</table>

\(^a\) See Ref. 12.
\(^b\) See Ref. 10.
\(^c\) See Ref. 11.

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\(^9\) R. M. Sternheimer, Phys. Rev. 84, 244 (1951); 95, 736 (1954); 105, 158 (1957); 130, 1423 (1963); H. M. Foley, R. M. Sternheimer, and D. Tycio, ibid. 93, 734 (1954); R. M. Sternheimer and H. M. Foley, ibid. 102, 741 (1956).


\(^11\) R. M. Sternheimer, Phys. Rev. 84, 244 (1951); 95, 736 (1954).


\(^9\) R. M. Sternheimer, Phys. Rev. 84, 244 (1951); 95, 736 (1954); 105, 158 (1957); 130, 1423 (1963); H. M. Foley, R. M. Sternheimer, and D. Tycio, ibid. 93, 734 (1954); R. M. Sternheimer and H. M. Foley, ibid. 102, 741 (1956).
electronic level of the free ion ($^7H_4$) lies some 8300 cm$^{-1}$ above the ground level ($^5H_6$), thus, permitting the application of rather high temperatures without substantially populating the next higher multiplet component.

![Graph showing temperature dependence of quadrupole splitting in $\text{Tm}_2\text{O}_3$.](image)

**Fig. 3.** Temperature dependence of the nuclear quadrupole splitting in the 8.4-keV level in $\text{Tm}^{169}$. Sources of $\text{ErF}_3 (T = 550^\circ \text{K})$ and absorbers of $\text{Tm}_2\text{O}_3$ were used for temperatures of the absorber in the range $11^\circ \text{K} < T < 700^\circ \text{K}$. Absorbers of thulium ethyl sulfate ($T = 300^\circ \text{K}$) and sources of $\text{Tm}_2\text{O}_3$ were used for temperatures of the source in the range $T > 700^\circ \text{K}$. (See Mössbauer and Poindeexter, Ref. 13.)

The fact that the contributions $(1 - R)(q_{\pi}^{(4)}) \gamma_\pi + (1 - \gamma_\pi)q_{\pi}^{(0)}$ to the total field gradient often carry opposite signs in salts of the rare earths can be used conveniently to solve the problem of preparing a source which does not exhibit a net quadrupole interaction, thus, emitting a single line. This can, in principle, be achieved by using a source with a proper symmetry of the rare-earth ion and choosing a temperature $T_0$, at which the conditions hold

\[
(1 - R)(q_{\pi}^{(4)}) \gamma_\pi + (1 - \gamma_\pi)q_{\pi}^{(0)} = 0, \quad (13a)
\]

\[
(1 - R)(q_{\pi}^{(4)}) \gamma_\pi + (1 - \gamma_\pi)q_{\pi}^{(0)} = 0. \quad (13b)
\]

These two conditions cannot, in general, be simultaneously fulfilled. It therefore becomes necessary to choose a symmetry of the surroundings producing an axially symmetric field gradient ($\eta = 0$).

The technique of choosing a proper temperature in order to eliminate the quadrupole splitting in the radioactive source was first applied by Cohen et al.\textsuperscript{14}


in the case of $\text{Tm}_2\text{O}_3$. Choosing rare-earth oxides provides, however, only a partial solution, since the rare-earth ions within the oxides occupy in the ratio 3:1 two lattice sites which differ in the symmetries of their surroundings. Although the time average of the quadrupole interaction at one lattice site vanishes at a certain temperature, one is always left with the residual quadrupole interaction at the other side. Therefore, using oxides, it is principally impossible to reduce the linewidth of the resonance lines down to their natural limit. Barnes et al.\textsuperscript{15} have chosen dehydrated rare-earth fluorides in order to remove the quadrupole splitting in the resonance lines. The rare-earth fluorides chosen not only host all rare-earth ions at lattice sites with equivalent symmetry, but also possess sufficient chemical stability at the required temperatures. They do not, however, exhibit field gradients with axial symmetry. All symmetry requirements are fulfilled in thulium ethyl sulfate. Figure 4 shows the widths of the 8.4-keV resonance line in $\text{Tm}^{169}$ for different combinations of sources and absorbers, all at their optimal temperatures $T_0$.

Measurements of the nuclear quadrupole interaction would, at least in principle, permit a determination of the nuclear quadrupole moments of the nuclear excited and ground states, assuming that the electric field gradients are known. The existing uncertainties in the crystalline shielding factors make such a procedure at the present rather doubtful. Gamma resonance measurements of the temperature dependence of the nuclear quadrupole interaction may, on the other hand, be used to obtain direct experimental information on the shielding factors, employing theoretical or experimental values of the nuclear quadrupole moments. Such a procedure was applied in the case of $\text{Tm}^{2+}$ by Barnes et al.\textsuperscript{16}

**Experimental Determination of Electronic Shielding Factors in Thulium Ethyl Sulfate**

Barnes et al.\textsuperscript{16} investigated the temperature dependence of the nuclear quadrupole interaction in the 8.4-keV level of $\text{Tm}^{169}$ in thulium ethyl sulfate, $\text{Tm}(\text{C}_2\text{H}_5\text{SO}_4)_2 \cdot 9\text{H}_2\text{O}$. Recoilless nuclear resonance absorption was measured in the temperature range $10^5\text{K} < T < 300^5\text{K}$, using sources of activated $\text{ErF}_3$ and absorbers of thulium ethyl sulfate. The source was kept at $550^5\text{K}$ in order to restrict the emission spectrum to a single line, applying the technique described above. The measured temperature

\textsuperscript{15} R. G. Barnes, R. L. Mössbauer, and J. M. Poindeexter (unpublished).

dependence reflects the temperature dependence of the contribution $q^{(2)}$ to the total field gradient. The spin-lattice relaxation time was short in comparison with all other relevant times, thus, leading to effective averaging over the individual field gradient components associated with each crystalline level. The point-group symmetry of the thulium ion in ethyl sulfate is $C\alpha$; in this case one deals with an axially symmetric field gradient ($q = 0$). The spins of the nuclear ground state and of the 8.4-keV excited state in Tm$^{169}$ are $\frac{1}{2}$ and $\frac{3}{2}$, respectively; thus only the excited state contributes to the quadrupole interaction. If we express the contribution $q^{(2)}$ to the field gradient in terms of the parameter $A^{2}_{2}$ defined in Eq. (11), we obtain for the splitting $\Delta E$ of the gamma absorption line in Tm$^{169}$, using the Hamiltonian $H_{q}$ in Eq. (10),

$$|\Delta E(T)| = \frac{1}{2} \tilde{e}^{2} Q [(1 - R) q^{(4)}_{4} - 4 (1 - \gamma_{\omega}) A^{2}_{2}/\tilde{e}^{2}].$$

(14)

Figure 5 shows the experimental data points and two theoretical curves. Plotted in each case is the ratio of the quadrupole splitting of the gamma lines $\Delta E(T)/\Delta E(0)$. The theoretical curves were obtained by using the crystalline field parameters $\langle r^{6}\rangle A^{2}_{2}(\text{opt})$, determined from optical measurements by Wong and Richman,\textsuperscript{17} in order to evaluate $\langle q^{(4)}_{4} \rangle_{T}$ and $A^{2}_{2}$. In these calculations, Barnes et al.\textsuperscript{18} used the values $\langle r^{6}\rangle_{T} = 0.19 \AA^{6}$ (Judd and Lindgren\textsuperscript{19}) and $\langle r^{6}\rangle_{T} = 75.5 \AA^{-3}$ (Lindgren\textsuperscript{19}). It has to be emphasized that an important difference exists between the parameter $A^{2}_{2}(\text{opt})$, deduced from optical experiments, and the parameter $A^{2}_{2}$ which appears in Eq. (14). This difference arises from the fact that the 4f electron shell is partially shielded from the interaction with the crystalline electric field, described by the parameter $A^{2}_{2}$. The 5s$^{2}$p$^{1}$ electronic subshell that effectively surrounds the 4f shell is the major source

\textsuperscript{19} I. Lindgren, Nucl. Phys. 32, 151 (1962).
for a screening of the $4f$ electrons, which as a result do not experience the CEF described by the parameters $A^\tau$. The crystalline level splitting is caused by that CEF which actually acts on the $4f$ electrons, rather than by the unshielded crystalline field. The optically determined parameters $A^\tau_{\text{opt}}$, therefore, describe the reduced rather than the original CEF. We define new shielding factors $\sigma_n$, in order to account for the shielding of the $4f$ electron shell, using the (simplified) definition

$$A_n^\tau_{\text{opt}} = (1 - \sigma_n)A_n^\tau.$$  

Furthermore, introducing the notation $\rho = (1 - \gamma_\omega)/(1 - R)(1 - \sigma_\omega)$, we obtain from Eq. (14):

$$\frac{\Delta E(T)}{\Delta E(0)} = \left[\frac{[q_{4s}^{(4f)}(T) - 4\rho A_0^s_{\text{opt}}(\text{opt})/\epsilon^2]}{([q_{4s}^{(4f)}_o - 4\rho A_0^s_{\text{opt}}(\text{opt})/\epsilon^2]}. \right.$$  

The curves in Fig. 5 illustrate two cases, one where electronic shielding is completely neglected (curve A; $\rho = 1$) and one where electronic shielding was included by adjusting the parameter $\rho$ so as to obtain the best fit to the experimental data (curve B; $\rho = 287$). In this way one obtains a first relation between the three shielding factors $\gamma_\omega$, $R$, $\sigma_\omega$, namely, $(1 - \gamma_\omega)/(1 - R)(1 - \sigma_\omega) = 287$. Furthermore, by using the theoretical value $Q = 1.5 \times 10^{-7}$ eV, Eq. (14) yields another relation for the three shielding factors. Using the theoretical value $\gamma_\omega = - 61.5$, calculated by Wiikner and Burns, the quantities $R$ and $\sigma_\omega$ can be evaluated. As a result, one obtains $R = 0.12$ and $\sigma_\omega = 0.75$, both factors being positive, thus representing shielding effects. Comparison of this value of $R$ may be made with the value of $R = 0.16$ obtained by interpolation from papers by Sternheimer.

(contrast Table II). The value $\gamma_\omega/(1 - \sigma_\omega) = \gamma_\mu/\gamma_\mu = -246$, obtained by Barnes et al., may be compared with the absolute value 550, deduced for lanthanum ethyl sulfate by Edmonds from nuclear magnetic resonance measurements and with the average value -400 deduced for rare-earth ethyl sulfates by Block and Shirley from nuclear orientation measurements. A calculation by Lenander and Wong for the $4f$ electrons in LaCl$_3$ yields a shielding of the second-order term in the crystal field expansion which is similar in magnitude to the one observed in thulium ethyl sulfate. Ray's calculation yields $\sigma_\omega = 0.48$ for the case of Pr$^{3+}$ in PrCl$_3$. It should be noted that a calculation by Burns indicates that the higher multipole terms $(A^\tau, B^\tau, A^F, B^F)$ in the expansion of the potential produced by the surrounding ions suffer only a relatively small shielding effect (of the order of 10%).

The resonance absorption measurements in thulium ethyl sulfate lead to the conclusion that the effect of electronic shielding via the $A^\tau$ parameter plays a major role in both the crystalline field splitting of electronic levels and in the quadrupole splitting. The electronic shielding effect is supposedly substantial for most rare-earth ions and many values of the nuclear quadrupole moments deduced from measurements of the nuclear quadrupole interaction require correction due to electronic shielding.

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22. J. Blok and D. A. Shirley (private communication).
23. C. J. Lenander and E. Y. Wong (to be published).