A study of crystalline electric fields in some thulium aluminum compounds

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A study of crystalline electric fields in some thulium aluminum compounds

by

Thomas Gerald Pinter

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I. INTRODUCTION

A. General Discussion

For many years the absorption of low energy photons by atoms has been observed in optical spectroscopy. Due to the recoil energy lost in the scattering process, it was assumed that absorption could not be observed for more energetic photons. When Moessbauer demonstrated in 1958 (1) that atoms bound in solids cannot arbitrarily recoil, a new area of spectroscopy was opened to experimental and theoretical research. The reader is referred to standard reviews of the subject for a more complete discussion than what follows here (2,3).

The energy transitions of interest here are nuclear transitions caused by the absorption of gamma rays in which no energy is given up to the lattice, i.e., zero phonon processes. In this case the widths of the nuclear levels involved in the transitions alone determine the linewidth of the zero phonon component. For thulium, the nuclear lifetime is roughly $3.9 \times 10^{-9}$ sec. By employing the uncertainty principle, one obtains a corresponding linewidth of about $1.2 \times 10^{-7}$ eV. This linewidth is smaller than the energy splitting due to the interaction of nuclei with their crystal-line environment. Hence, some of the most useful applications of the Moessbauer effect (ME) occur in the realm of solid state physics, viz., the study of magnetic and electrostatic interactions of a nucleus with its surrounding.

Consider a radioactive nucleus which emits a photon in the decay to its ground state. By moving this nucleus, the frequency, hence the energy, can be shifted by an amount $\pm vE_0/c$ where $v$ is the velocity of the nucleus or source, $E_0$ is the energy of the emitted photon, and $c$ is the velocity of
light. By this means photons of desired energy can be created to be absorbed by the substance to be investigated. A velocity scan is obtained which produces a continuous spectrum of photon energies. The width of the necessary velocity scan varies from a few mm/sec in the case of $^{57}$Fe to perhaps ±50 cm/sec for $^{169}$Tm in its ordered state. These velocities are easily obtainable in the laboratory.

The energy dependence of the absorption cross section is given by the Breit-Wigner formula

$$\sigma(E) = \frac{\lambda^2}{2\pi} \frac{1+2I_e}{1+2I_g} \frac{1}{1+i\alpha} \left[1+4((E-E_0)/\Gamma)^2\right]^{-1}$$

where $E_0$ is the nuclear transition energy, $\Gamma$ is the full width of the resonance at half maximum, $I_e$ and $I_g$ are the spins of the excited and ground states of the nucleus respectively, $\alpha$ is the internal conversion coefficient. For thin absorbers, the experimentally observed linewidth is just twice the linewidth of the gamma ray if the natural linewidth is realized in both emission and absorption processes.

B. Crystalline Electric Field Interactions in Rare-Earth Compounds

The rare-earth elements are particularly suited to the study of the internal crystal field since the interaction of the unfilled 4f shell with the surrounding charge ions, or crystal field, can be treated as a perturbation on the interactions of the free ion. Unlike the 3d transition series, in which the crystal-field interaction is strong, the weak 4f interaction is several orders of magnitude below the free ion energies.

The crystal field acts to remove the degeneracy of the ground state of the unfilled shell. In thulium, the ground state multiplet is some
100-300 cm\(^{-1}\) in overall extent; whereas, the first excited level is some
8500 cm\(^{-1}\) above the ground state. This crystal field is shielded by the
outer filled shells and interacts with the nucleus mainly by distorting
the unfilled 4f level. This produces an electric field gradient (EFG) at
the nuclear site which is observed in Mössbauer effect experiments.

In the case of intermetallics, however, additional complications
arise due to the presence of conduction electrons. One would expect some
contribution to the EFG at the nuclear site from these electrons, but the
exact nature of this contribution is not clearly understood.

There has been considerable discussion about the way to treat the
crystal field in rare-earth compounds. Since the effect of the crystal
field is small compared to the spin-orbit interaction, J is a good quantum
number. This is not true for the iron transition series which behaves as
if the orbital angular momentum of the electrons is zero. Treating the
crystal field as large compared to the spin-orbit interaction accounts for
the quenching of the orbital angular momentum. Since the unfilled shell in
the iron series lies at the outside of the ion, it has been conjectured
(4-7) that the shielding of the 4f shell by the 5s\(^2\)p\(^6\) electrons may be
responsible for the weaker crystal-field interaction with the 4f shell in
the rare-earth ion.

Burns (8,9) has suggested that these shielding effects are negligible
in the rare-earths. He claims that the larger rare-earth ions would see
smaller crystal fields since the charges would necessarily be further away.
Axe and Burns (9) noted the breakdown of purely electrostatic theory when
applied to an ion in a cubic environment. They attempted to account for
the difference by employing a covalency model. A semi-empirical fit has
been employed in this respect to some degree of success. Thus, Burns has reported some experimental evidence which suggests that covalency and overlap may not be so easily cast aside as it was once thought, at least not in the higher symmetry fields.

Sternheimer (10) has recently performed new calculations on the shielding parameters for the outer closed shells in various rare-earths. His results indicate a shielding parameter of about 0.6 for the second-order term. However, his results suggest little shielding or even anti-shielding for the fourth- and sixth-order terms, in agreement with the ideas of Burns. However, semi-empirical fits with the data for various rare earth materials (7,11-15) indicate some agreement with the second-order shielding term. Unfortunately, these experiments are not conclusive in regards to higher-order terms.

Theoretical attempts which have been made, allowing for the effects of covalency and overlap in the calculation of the crystal field interaction with the 4f electrons in PrCl$_3$, using a molecular orbital model have led to some degree of success (16). However, these calculations have been important only in accounting for the fourth- and sixth-order terms in the crystal field expansion. They are indefinite as to the effect of covalency and overlap on the second-order term.

Since the rare-earth ions are further apart in the lattice than the iron transition ions, the point-ion model should have some validity. This seems to be a reasonable assumption in the case of the second-order terms in the crystal-field potential expansion. These second-order terms are slowly converging. Ions several lattice spacings away will contribute appreciably to the magnitude of this term. This is not the case for the
higher order terms which converge much more rapidly, making nearest neighbor contributions more important. Many of the attempts to include covalency and overlap include only these nearest neighbors. This makes it reasonable to suggest that these effects might only be important for the higher order terms in the expansion.

It should be noted that potential sources of error exist in the point-ion approximation. These errors arise from the imprecise determination of the lattice constants. There is also some temperature dependence in the value of the ionic positions which is uncertain. These are small compared to the very real problem of obtaining precise theoretical calculations of the various parameters which appear in the formalism.

C. Introductory Remarks

In his dissertation, D. J. Genin (17) observed several inconsistencies in the ME spectra. The resonance broadened considerably as the temperature was decreased. This is opposite to the expected decrease in broadening and corresponding increase in intensity due to an increasing recoilless fraction. The cause of this phenomenon was not ascertained. He also noticed an asymmetry in the spectrum which varied as a function of temperature. An anisotropy in the recoilless fraction and paramagnetic relaxation effects were considered as possible sources of this asymmetry. The latter was not deemed practical due to relatively fast spin-lattice relaxation times in metallic compounds. It should be remarked that the data presented by Genin were fit to Lorentzian lineshapes and a two line pattern was always obtained.
The ME data for Tm$_3$Al$_2$ shows these effects even more pronouncedly than the previous studies. Figure 1 shows the effect of applying a perturbing magnetic field to the quadrupole levels of the nucleus. This changes the transition energies so that the spectrum becomes a composite of five individual Lorentzian lines. The effects noted above are consistent with this interpretation of the data, i.e., an effective magnetic field perturbs the quadrupole levels of the nucleus at high temperatures, and this field, becoming more intense as the temperature is decreased, thus spreads out the spectrum and causes it to become more asymmetric. It should be remarked that it is impossible to fit the Tm$_3$Al$_2$ data with pure Lorentzian lineshapes.

The presence of an indirect exchange coupling of the rare-earth magnetic ions by the conduction electrons is generally accepted as the cause of magnetic ordering in these systems. Much study of this interaction has been performed by using nuclear magnetic resonance (NMR) techniques to examine the nonmagnetic ion in rare-earth aluminide intermetallics. Compounds of the form RAl, RAl$_2$, and RAl$_3$ have been studied extensively in this respect where R stands for a rare-earth ion (18-20).

An exchange interaction, called s-f exchange, occurs between the highly localized 4f band and the conduction electrons. This interaction results in an effective magnetic field at the nucleus of the nonmagnetic ion in addition to the normal Pauli spin paramagnetism when the compound under study is placed in a magnetic field. This causes the resonance of the nonmagnetic ion to be shifted with respect to the resonance of the same ion in a diamagnetic compound. The part of the Knight shift arising from s-f exchange is temperature dependent unlike that due to Pauli
Figure 1. Energy level diagram showing the effect of a perturbing magnetic field on the nuclear quadrupole levels. The lineshape realized from the energy transitions is also shown, slightly exaggerated.
paramagnetism. Workers have measured this temperature dependence in order to obtain values for the exchange parameter and the ordering temperature (18-20).

The exchange parameter calculated from NMR experiments is negative in the rare-earth aluminides for those rare-earths with at least a half-filled 4f shell. The negative exchange parameter indicates that the conduction electron spin density polarization is negative in the sense that it is antiparallel to the local moment. Watson et al.(21) suggested that interband transitions between the conduction band and the highly localized 4f band are responsible for the negative exchange parameter.

Tm$_3$Al$_2$ is an ideal compound to work with in the sense that both ME experiments and NMR experiments can be performed. In this way the effect of the crystalline environment on both the magnetic ion and the nonmagnetic ion can be observed. This is not possible with some of the other rare-earth intermetallics. The point symmetry of some of the sites may be too high, e.g., in RAl$_2$ compounds, the symmetry is that of the cubic Laves phase and the R ion sits at a site of cubic symmetry; the same is not true for the aluminum ion, however. ME experiments, therefore, show a single line at all temperatures. NMR experiments are not always feasible to perform with some of the rare-earth intermetallics employed in ME experiments for various reasons, e.g., low abundance of the isotope.

The NMR experiments are also useful in the sense that quadrupole coupling parameters can be obtained at the aluminum sites. These values can be compared with the crystal-field calculations. Such parameters have been calculated for many of the rare-earth aluminides and are collected in van Diepen's dissertation (19). These measurements indicate that the
effective charge at the aluminum site may not be trivalent. It is assumed for these calculations that the rare-earth ion has a trivalent valence with the exception of Eu and Yb.

The purpose of this investigation is to attempt to correlate both the electrostatic and magnetic interactions discussed above. It is believed that the conduction electrons play an important role in this respect. However, in the paramagnetic region, the electrostatic and magnetic effects can be treated independently to a reasonable approximation. Exchange effects at high temperatures are probably quite important in rare-earth intermetallics. These points will be taken up again after the presentation of the data.
II. THEORY

A. General Hamiltonian of the Free Ion

Consider a free ion whose nucleus interacts with its surrounding electrons. The general Hamiltonian operator will contain the following terms: the kinetic energy of the electrons $T$; the electrostatic interaction energy $V_{en}$; the mutual electrostatic energy of the electrons $V_{ee}$; the spin-orbit interaction of the electrons $V_{so}$.

For a nucleus with a quadrupole moment and a spin, two additional interactions will be present: the dipole-dipole interaction between the nuclear spin and the magnetic moments for the electrons $V_n$; and the electrostatic interaction of the electrons with the quadrupole moment of the nucleus $V_q$. These terms in the rare-earths are sufficiently weak so as to be treated as perturbations on the spin-orbit term $V_{so}$. They will be treated as such in the following discussion.

Observations of the optical spectra of different atoms has led to the conclusion that there exist two general categories into which these interactions fall in regards to their relative strength.

1. For most atoms, the term $V_{ee}$ is the largest of the terms after $T$ and $V_{en}$. The spin-orbit term $V_{so}$ is considerably smaller. Here $L$, $S$, $J$, and $m_J$ are good quantum numbers with the energy levels degenerate in $m_J$. This is the case in the rare-earths.

2. For some atoms, however, the spin-orbit dominates. In this case $L$ and $S$ are no longer good quantum numbers, but are replaced by the total angular momenta of the individual valance electrons.
B. Effect of the Static Crystalline Field

The interactions of the free ion are modified when the ion is placed in a crystalline environment. A paramagnetic ion will be surrounded by a distribution of charges from the neighboring ions. The wave functions of this distribution will overlap the electronic charge distribution of the ion under consideration to some extent. Attempts to calculate the effects of this overlap on the free ion energy levels are being attempted with some degree of success. However, at present these calculations have been carried out primarily on the higher order terms in the crystalline potential (10,16).

To avoid the problem of overlap, the crystal has traditionally been treated as a lattice of point charges. In rare-earths this treatment is acceptable as a first approximation due to the relatively small extent of the electron core of the ions combined with the relatively large separation between neighboring ions. This procedure has given semi-empirical agreement with the theoretical calculations. The reader is referred to Hutchings (22) for a good review of this subject.

In the rare-earths, the unfilled 4f shell is distorted by the presence of the other nuclei in the crystal. This distortion effectively interacts with the quadrupole moment of the nucleus to remove the $m_J$ degeneracy of the spin-orbit interaction. Consider then a charge $Ze$, where $e = |e|$, at spherical coordinates $R, \alpha, \beta$. The potential at some point $r, \theta, \phi, (r<R)$ is given by the expression

$$V = Ze \sum_{N+1} P_N(\cos \gamma)$$

(2)
where $P_N$ are Legendre polynomials. To get the total potential at the point $r, \theta, \phi$; a sum is performed over all of the charges $Ze$, in this case the lattice sites of the crystal. It should be noted that this expansion is valid only in a region in which Laplace's equation holds; hence the necessity of neglecting overlap effects.

By use of the addition theorem for spherical harmonics, $P_N(\cos \gamma)$ can be expressed in terms of $\alpha, \beta, \theta, \phi$. The potential can then be written

$$V = \sum_i Z_i e^\sum_{N=0}^{\infty} \frac{r^N}{N!} \left[ P_N(\cos \alpha_i)P_N(\cos \theta) + 2 \sum_{M=1}^{N} \frac{(N-M)!}{(N+M)!} P_N^M(\cos \alpha_i)P_N^M(\cos \theta) (\cos M \beta_i + \sin M \phi \sin M \alpha_i) \right]$$

where the sum $i$ is over all of the lattice sites of the crystal. Since the $P_N^M(\cos \theta)$, the associated Legendre polynomials, are not normalized to one, it is convenient to define new functions $\Theta^M_N$ such that

$$\Theta^M_N = \frac{2N+1}{2} \frac{(N-M)!}{(N+M)!} P_N^M(\cos \theta).$$

It can be shown that the functions $\sin M \phi, \cos M \phi/\pi^{1/2}$, and $1/(2\pi)^{1/2}$ form an orthonormal set over the interval $(0,2\pi)$. In view of this, the following tesseral harmonics are then defined:

$$V_N^M = \Theta^M_N \sin M \phi/\pi^{1/2} \quad V_N^0 = \Theta^0_N/(2\pi)^{1/2} \quad V_N^M = \Theta^M_N \cos M \phi/\pi^{1/2}$$

which forms a complete set of basis functions in which the potential can be expressed. See Prather (23) for a complete listing of these functions through $N=6$.

The potential can now be written in the form

$$V = (1/e) \sum_{N=0}^{\infty} r^N \sum_{M=-N}^{N} A^M_N V_N^M$$
where
\[ A_N^M = \frac{4\pi e^2}{2N+1} \sum_{i} (z_i R_i^{N+1}) V_N^M(\alpha_i, \beta_i) \]

The above terms can be expanded into a set of the spherical harmonics rather than the tesseral harmonics employed. However, the potential is expressed more conveniently in the above form for the purposes of the later calculations. It is more convenient to redefine the functions in the following manner:

\[ V_N^M = a_N^M V_N^M \quad \text{with} \quad A_N^M = a_N^M A_N^M \]

where \( a_N^M \) are the numerical coefficients of the \( V_N^M \). Now the \( V_N^M \) contain only the \( x, y, z \) dependence of the \( V_N^M \) and the \( A_N^M \) are constants depending on the structure of the crystal involved. The potential can now be expressed in the form

\[ V = (1/e) \sum_{N=0}^{\infty} r_N^{N} \sum_{M=-N}^{N} A_N^M v_N^M. \]

It is these \( A_N^M \)'s which are to be calculated on the basis of the point-ion approximation.

A number of terms can be eliminated in the expansion for \( V \) by symmetry arguments. For \( f \) electrons \( N \) only goes to six in the wave function expansion so all matrix elements formed with \( V_N^M \), \( N \) greater than six, will be zero due to the orthogonality properties of the wave functions. Also, the wave functions for the \( f \) electrons have definite parity. Thus, since

\[ V_N^M(x, y, z) = -V_N^M(-x, -y, -z) \]

for odd \( N \), these matrix elements will be zero since
\[ \int x^d \varphi^m_N(x) d\tilde{x} = -\int x^d \varphi^m_N(x) d\tilde{x} = 0 \]  
(9)

The \( N=0 \) term is constant. Its only effect is to shift all of the energy levels by the same amount; hence, it may be neglected. The only values of \( N \) to be considered then are \( N=2,4,6 \). Some of these coefficients may also be zero due to the symmetry properties of the lattice. Prather (23) lists the non-zero coefficients for various crystal symmetries.

For \( m = C_s \) point symmetry, the situation for all of the sites for \( \text{Tm}_3\text{Al}_2 \), the relevant terms are \( N=2,4,6 \) and \( M=\pm2,\pm4,\pm6 \).

The explicit form of the potential for \( C_s \) symmetry is

\[
e V_{C_s} = A_2^0(2z^2-x^2-y^2) + A_2^2(x^2-y^2) + A_4^0(35z^4-30r^2z^2+3r^4)
+ A_4^2(6z^2-x^2-y^2)(x^2-y^2) + A_4^{-2}(6z^2-x^2-y^2)2xy + A_4^4(x^4-6x^2y^2+y^4)
+ A_4^{-4}4xy(x^2-y^2) + A_6^0(231z^6-315r^2z^4+105r^4z^2-5r^6)
+ (A_6^2(x^2-y^2) + A_6^{-2}2xy)(33z^4-18r^2z^2+r^4) + (A_6^4(x^4-6x^2y^2+y^4)
+ A_6^{-4}(4x^2y-4xy^2))(10z^2-x^2-y^2) + A_6^6(x^6-15x^4y^2+15x^2y^4-y^6)
+ A_6^{-6}(3x^2-y^2)(x^2-3y^2)2xy
\]  
(10)

The term \( A_2^{-2} \) can be eliminated by a suitable choice of the axes, so it has not been included here.

The Hamiltonian which describes this interaction for the crystal field with the 4f electrons can be expressed as follows
\[ H_{CEF} = -e_k V(r_k, \theta_k, \phi_k) = -\sum_{k} \sum_{N=0}^{6} r_k^N \sum_{M=-N}^{N} A_{N}^M V_{N}^M(\theta_k, \phi_k) \] (11)

where the summation \( k \) is over all of the electrons in the 4f shell.

This Hamiltonian removes the \( m_J \) degeneracy of the LS levels. These levels will now interact with the quadrupole moment of the nucleus through the term \( V_q \) mentioned above. The crystal-field Hamiltonian has been tuned up to transform the potential operators into equivalent angular momentum operators. That such operator equivalents are valid can be verified by using the Clebsch-Gordan coefficients to give the values of the matrix elements of the potential functions. Care must be taken to allow for the noncommutation of various angular momentum operators with each other in the transformation process. Thus

\[ H_{CEF} = -\sum_{N,M} A_{N}^M r_4f \langle J_{\|} | J_{\|} J_{\|} \rangle <J_{m_j}|0_{N}(J_X, J_Y, J_Z)|J_{m_j}> \] (12)

where \( r_4f = U_{4f} |r_{4f}|U_{4f}^\dagger \) and \( \theta_N = \alpha, \beta, \gamma \) for \( N=2,4,6 \). \( U_{4f} \) here is the radial part of the electronic wave functions for the 4f shell. The functions \( \phi_{N}^M(J_X, J_Y, J_Z) \) are the operator equivalents. The expressions \( <J_{\|} | \phi_{N} | J_{\|}> \) are reduced matrix elements and are found in the literature (22).

For the experimental determination, it is desirable to define the crystal-field parameters

\[ C_N^M = A_{N}^M r_4f \] (13)

Although it is customary to introduce a factor here to account for the shielding of the outer electrons, it will not be done at this time due to the uncertainty about the significance of such a term.
The wave functions of the crystal-field levels are linear combinations of the eigenvectors of the total angular momentum $J$

$$\psi_i = U(r) \sum_{m_J} c_i^{m_J} \psi_{m_J}$$

(14)

The expansion coefficients $c_i^{m_J}$ and the energy eigenvalues $E_i$ are obtained from the diagonalization of the interaction matrix $H_{m_J, m_J}$. 

C. Nuclear Quadrupole Interaction

In part B the Hamiltonian for a point-charge crystal field was derived. Here the effect of the crystal field on the free ion shall be discussed. The interaction of the crystal field with the 4f electrons partially or completely removes the spatial degeneracy in the orientation of the total angular momentum $J$ of each electronic state. The levels are split into multiplets which interact with a nucleus having a quadrupole moment $Q$. Thus the interaction $V_q$ mentioned in part A becomes relevant.

Consider now the possible sources of the electric field gradient interacting with the quadrupole moment of the nucleus (24). Several contributions are expected, the most important being:

1. The unfilled 4f shell is distorted by the crystal field to produce an EFG $4f$ at the nucleus.

2. The ions situated at the lattice sites produce a direct EFG $4f_{\text{lat}}$ at the nucleus. This EFG is usually negligible compared with $4f$.

3. The crystal field interacts with the electrons in the closed shells to induce a polarization of these shells. The quadrupole
part of this distortion produces a contribution \(-\gamma \omega_0 \text{eq lat}\) to the EFG at the nucleus. The proportionality constant \(-\gamma \omega\) represents a scalar shielding or antishielding factor.

(4) The distorted unfilled 4f shell also interacts with the core electrons. The quadrupole part of this term produces an EFG \(-R_q \text{eq}^{4f}\) at the nucleus. \(-R_q\) also represents a scalar shielding or antishielding factor.

(5) The electrons in the conduction band also produce an EFG \(\text{eq}^{ce}\) at the nucleus. This term exists only for metals and intermetallics, however.

Thus the EFG tensor acting at the nucleus can be written

\[
\text{eq}_{ij} = (1-\gamma \omega)\text{eq}_{ij} \text{lat} + (1-R_q)\text{eq}_{ij}^{4f} + \text{eq}_{ij}^{ce} \tag{15}
\]

The Hamiltonian describing the interaction between the EFG tensor and the quadrupole moment of the nucleus can be written

\[
H_Q = \frac{e^2}{4I(2I-1)}[q_{zz} (3I_z^2-I^2) + q_{xx} (3I_z^2-I^2)] \tag{16}
\]

This expression is valid only in the principal axis system of the EFG tensor. Since the tensor is traceless, due to LaPlace's equation, only two parameters are needed to specify it in diagonal form: \(q_{zz}\), the field gradient, and \(n = (q_{xx}-q_{yy})/q_{zz}\), the asymmetry parameter.

Using the value for \(\text{eq}_{ij}\) in Equation 15, the following relation for the crystal field Hamiltonian can be written

\[
H_Q = \frac{e^2}{4I(2I-1)}[((1-\gamma \omega)q_{zz} \text{lat} + (1-R_q)q_{zz}^{4f} + q_{zz}^{ce})(3I_z^2-I^2)]
\]
In general, the EFG tensor is defined by the relation

\[ \varepsilon_{ij} = \left. \frac{d^2 \Psi(r, \theta, \phi)}{dx_i dx_j} \right|_{r=0} \]  

Using Equation 10, the lattice contribution to the EFG tensor can be written

\[ e^2 q_{zz}^{\text{lat}} = 4A_2^0; \quad e^2 q_{zz}^{\text{lat}} = 4A_2^1. \]  

The 4f electron contribution to the EFG tensor can be obtained from the second derivatives of the point charge potential. These results are

\[ q_{zz}^{4f} = \sum_k \frac{d^2}{dz^2} \left( -\frac{1}{r_k} \right) = -\varepsilon_k \left( 3r_k^2 - r_k^5 \right) \]

\[ = -\langle 4f \mid \sum J \mid 4f \rangle \langle r^{-3} \rangle \]

\[ n q_{zz}^{4f} = \varepsilon_k \left[ \frac{d^2}{dx^2} \left( -\frac{1}{r_k} \right) - \frac{d^2}{dy^2} \left( -\frac{1}{r_k} \right) \right] \]

\[ = -\varepsilon_k \left( 3x_k^2 - 3y_k^2 \right) r_k^5 = -\langle 3/2 \rangle \langle J_2 \rangle \langle r^{-3} \rangle 4f \langle J_2^2 \rangle \]

The summation over all of the electrons in the 4f shell. A similar expression, except for the operator equivalents, can be obtained for the conduction electrons.

There exists a temperature range for which the crystal-field levels will not be equally populated. In the thulium intermetallics, the upper limit of this temperature range is usually between 100 and 200 degrees Kelvin. This roughly corresponds to the splitting of the ground state multiplet by the crystal field. Since the next excited state in the LS
scheme is roughly 12,000 degrees above the ground state, effects due to its splitting will not be included in these calculations. For temperatures sufficiently low, then, the contribution to the EFG tensor from the 4f electrons will be the expectation value of the contribution for each level weighted by the Boltzmann factor, \( \frac{1}{\exp(E/kT) + 1} \), viz.,

\[
q_{ij}^{4f} = \sum_{\nu=1}^{2J+1} q_{ij}^{4f} \left( \frac{1}{\exp(E_{\nu}/kT) + 1} \right)
\]

Combining the results of Equations 13, 15, 19, 20, and 21 the total Hamiltonian describing the average quadrupole interaction at some temperature \( T \) may now be written

\[
H_Q(T) = \frac{e^2}{2(2I-1)} \left[ <q_{zz}^T > (3I^2 - I^2) + \frac{1}{2} <q_{zz}^0 > (I^2 - I^2) \right]
\]

where

\[
<q_{zz}^T > = -\langle J||s||J\rangle(1-R_Q)\langle r^{-3} \rangle_{4f} <3J_z^2 - J^2 >_T
\]

\[
-4C^0_z(1-\gamma_e)/e^2<r^2>_{4f} + q_{zz}^{ce}
\]

\[
<q_{zz}^0 > = -(3/2)\langle J||s||J\rangle(1-R_Q)\langle r^{-3} \rangle_{4f} <J^2 + J^2 >_T
\]

\[
-4C^0_z(1-\gamma_e)/e^2<r^2>_{4f} + \eta^{ce}q_{zz}^{ce}.
\]

Here the term \( <Q>_T \) indicates the operator used in the Boltzmann average of Equation 21. The temperature dependence of \( q_{ij}^{1at} \) and \( q_{ij}^{ce} \) has been neglected here as the error introduced will be within experimental error.

At this point it is desirable to discuss the specific case of \(^{169}\)Tm. The pertinent Moessbauer transition is an 8.4 keV transition between the ground state and the first excited state. The ground state possesses a spin of 1/2. Since this spin reflects a spherically symmetric state, there
is no quadrupole interaction and the level is unsplit by the crystal field. The excited state possesses a spin of 3/2 which does interact with the EFG of the crystal. This interaction partially removes the m degeneracy of the excited level. The unperturbed level will be split into two levels, one labeled by the quantum numbers ±3/2 and the other by the numbers ±1/2. This quadrupole splitting of the nuclear level is shown in Figure 1.

To calculate the energy splitting requires the diagonalization of a 4x4 matrix. However, this matrix reduces to two 2x2 identical blocks as argued above. The characteristic equation for the energy eigenvalues can be solved in a straightforward manner. The resultant energy splitting is

$$<\Delta E>_T = e^2Q[<q_{zz}^2>_T + (1/3)<\eta q_{zz}^2>_T]^{1/2}$$  \hspace{1cm} (23)

This splitting, however, is not measured directly in the experiments when Tm₃Al₂ is used as the absorber. The experimental parameters actually measured will be discussed further below.

It is desirable to introduce dimensionless parameters to be fit empirically from the data, due to the uncertainty of the theoretical calculations for some of the quantities appearing in Equation 23, as follows

$$\rho'_1 = e^2Q<\mathcal{J}/\mathcal{N}>(1-R_Q)<r^{-3}>_{4f}/C_2^0$$

$$\rho'_2 = Q(1-\gamma_\omega)/<r^2>_{4f} - e^2Q_{zz}ce/4C_2^0.$$

The primes have been included on the ρ's to differentiate between these parameters and those defined by Barnes et al.(7) for salts, which contain
shielding parameters and do not contain a conduction electron contribution. This results in the final form for the energy splitting of the excited state

\[
\langle \Delta E \rangle_T = \frac{1}{2} \left\{ [p_1 c_2^0 J_2^2 - J_2^2]_T + 4c_2^0 \right\}^2 \\
+ \frac{1}{3} \left\{ [(3/2)p_1 c_0^0 J_2^2 + J_2^2]_T + 4c_2^0 \right\}^2 \frac{n_{\text{lat}}}{2} \frac{1}{2}.
\] (25)

where \( n_{\text{ce}} \) has been assumed to equal \( n_{\text{lat}} \) and \( c_2^2 = n_{\text{lat}} c_2^0 \). If the conduction electrons were uniformly distributed throughout the crystal, then the net field gradient at the nucleus due to the conduction electrons would be zero. However, it is more reasonable to suppose that the distribution of the conduction electrons reflects the symmetry of the crystal to some extent. Since the experiments seem rather insensitive to this point, the assumption is made in order that the number of variable parameters can be kept to a minimum in the fitting routines.

D. Magnetic Hyperfine Interactions

Since both nuclei and electrons possess spin, there exists a dipole-dipole interaction of the form \( V_N \) mentioned in part A of this chapter. In metals this interaction is probably not observable due to fast spin-lattice relaxation times. The nucleus "sees" an effective magnetic field which oscillates rapidly with respect to the nuclear precession time. This means that this effective field due to all of the electrons in the unfilled shell is averaged to zero at the nuclear site due to nearly equal contributions from both of the states \( \psi^m_J \) and \( \psi^{-m}_J \) which are opposite in sign. This effect, however, has been observed in second order in \( \text{TmCl}_3 \) at temperatures below 3\(^\circ\)K (25). Comparing \( \text{Tm}_3\text{Al}_2 \) to the \( \text{TmCl}_3 \) results indicate that this is not
the source of relaxation effects observed in the ME spectra. The asymme-
tries which have been observed in the lineshapes of the ME spectra at high
temperatures do indicate a relaxation phenomenon. A similar asymmetry is
not observed in rare-earth salts which may suggest that the conduction
electrons rather than the $4f$ electrons contribute to this phenomenon. It
was mentioned in Chapter I that an exchange interaction exists between $4f$
electrons and the conduction electrons. This idea will be pursued further
here.

The effect of $s$-$f$ exchange will be different at the site of the magne-
tic ion than at the site of the nonmagnetic ion; hence, they will be
treated separately. Since the moments of the thulium ions are coupled by
the conduction electrons in the ordered state, it is reasonable to expect
some residual coupling at higher temperatures. The magnitudes of the in-
ternal fields in the ordered state are large in the rare-earth compounds.
These fields may be strong enough to overcome fast spin-lattice relaxation
effects above the ordering temperature. If this is the case, the nucleus
will then "see" a nonzero magnetic field strong enough to perturb its quad-
rupole levels.

The situation at the aluminum site is different, however. The conduc-
tion electrons will be polarized by their interaction with the $4f$ shell.
This polarization will produce an effective field at the aluminum site
which will shift the resonance observed when the crystal is in an external
magnetic field. The two cases will be considered below following the ideas
of Jaccarino (26).
1. The thulium site

Consider an exchange interaction between a rare-earth nucleus with a
spin $\mathbf{I}$ and the spin $\mathbf{S}$ of its 4f shell of the form

$$H_{\text{ex}} = -J_{\text{ex}} \mathbf{I} \cdot \mathbf{S}. \quad (26)$$

In an effective field formalism, one can write the expression as

$$-g_N \beta_N \mathbf{I} \cdot \mathbf{H}_{\text{eff}} = -J_{\text{ex}} \mathbf{I} \cdot \mathbf{S}$$

or

$$\mathbf{H}_{\text{eff}} = J_{\text{ex}} \mathbf{S}/g_N \beta_N \quad (27)$$

where $\beta_N$ is the nuclear magneton and $g_N$ is the nuclear g-factor. This
effective field interacts with the nucleus to perturb the quadrupole levels.
The effect of this perturbation is to remove the $m$ degeneracy of the quad­
rupole levels of the nucleus. Instead of seeing two distinct energy tran­
sitions as for the pure quadrupole Hamiltonian, five distinct transition
energies will occur. However, they are not readily resolvable so that an
asymmetric two line pattern will be observed experimentally as is shown in
Figure 1.

In the rare-earths, $J \cdot J$ and $J_z$ are good quantum numbers, so the pro­
jection of $\mathbf{S}$ onto $\mathbf{J}$ must be taken. This gives

$$\mathbf{H}_{\text{eff}} = J_{\text{ex}} \mathbf{S}/g_N \beta_N = J_{\text{ex}} \mathbf{S} \cdot \mathbf{J}/g_N \beta_N J(J+1). \quad (28)$$

Actually a Boltzmann average of $\mathbf{J}$ must be taken over all of the crystal
field levels in the spirit of Equation 21. Thus $\mathbf{J}$ is replaced by $\langle \mathbf{J} \rangle$ and
the nucleus "sees" a temperature dependent magnetic field which is proportional to \( \langle J \rangle_T \).

2. The aluminum site

In this case it is desired to calculate the effective field produced by the polarization of the conduction electrons by the spin \( \vec{S} \) of the unfilled 4f shell of the thulium ion. It is this field which acts to shift the NMR of the nonmagnetic nucleus. Since the experiment is carried out in an external magnetic field, \( \vec{H}_0 \) say, the complete expression is written

\[
-g_s \beta \vec{s} \cdot \vec{H} = -J_{\text{ex}} \vec{s} \cdot \vec{S} - g_s \beta \vec{s} \cdot \vec{H}_0 = -g_s \beta \vec{s} \cdot (\vec{H}_{\text{eff}} + \vec{H}_0)
\]

where \( g_s \) is the Lande g-factor for the conduction electrons and \( \beta \) is the Bohr magneton, this makes

\[
\vec{H}_{\text{eff}} = J_{\text{ex}} \vec{s} / g_s = J_{\text{ex}} \langle J \rangle_T < \vec{S} \cdot \vec{J} > / g_s \beta J(J+1)
\]

as above. Again an expression for \( \vec{H}_{\text{eff}} \) is obtained which depends on \( \langle J \rangle_T \). This discussion will be expanded in the next section.

E. The Nucleus in an Applied Magnetic Field

Consider a nucleus with moment \( \vec{I} = \gamma \hbar \vec{I} \) which is in an applied field of strength \( \vec{H}_0 \). The Hamiltonian describing the interaction of the nucleus with this field can be written

\[
\vec{H}_M = \gamma \hbar \vec{H}_0 \cdot \vec{I} = \gamma \hbar \vec{H}_0 \vec{I}_Z
\]

where \( \vec{H}_0 \) is taken to lie along the z-axis of quantization. This Hamiltonian is diagonal, so the eigenvalues are just \( \gamma \hbar \vec{H}_0 m \) where \( m=1, I-1, \ldots -I \). The nuclear level splits into \( 2I+1 \) equally spaced sublevels, the so-called Zeeman effect.
By applying an alternating rf field perpendicular to the static field, transitions can be induced between the adjacent levels, since the levels are equally spaced, all of the transitions will have the same energy

$$\pi \omega = \Delta E = \gamma \mathbf{H}_0 \Delta \mathbf{m} = \gamma \mathbf{H}_0$$

(32)

since $\Delta \mathbf{m} = 1$. A single line will be observed when the resonance condition

$$\omega = \gamma \mathbf{H}_0$$

(33)

is satisfied. There are many good references which treat this subject in much greater detail than has been done here (27,28).

The above forms the basis for NMR experiments. In the remainder of this section two specific aspects of NMR will be discussed: electrostatic quadrupole effects and the Knight shift. A brief review will be given of only those points of interest for the work here.

1. Electrostatic quadrupole effects

A nucleus with a spin greater than 1/2 possesses a quadrupole moment which interacts with the crystal field as discussed above. When the crystal is in an applied field, however, this interaction can be treated as a perturbation on the nuclear Zeeman levels. The external field is taken as the z-axis of quantization by convention. Due to this the principal axis system of the EFG tensor may not align itself with the axis of quantization, i.e., off-diagonal elements may appear in the quadrupole Hamiltonian. The resonance position is then a function of the angles required to describe the orientation of the EFG tensor with respect to the external field. Figure 2 shows an energy diagram for the case in which the EFG tensor is perpendicular to the applied field with the EFG tensor
Figure 2. Energy level diagram showing the effect of a perturbing EFG tensor on the nuclear Zeeman levels.
rotated by 90° about its z-axis. It must be stressed that the separation of these energy levels will change as the orientation of the single crystal is changed in the magnetic field. From the figure it can be seen that the quadrupole interaction changes the transition energies so that additional lines appear in the NMR spectrum. For half-integral spin nuclei the central line is unshifted since the $m = 1/2 \rightarrow -1/2$ transition is unchanged in energy, but 2$I$ satellite lines appear corresponding to the rest of the $\Delta m=1$ transitions which are equally divided on both sides of the central transition. For integral spin nuclei, no central transition appears since there are an even number of transitions.

In the case of metallic compounds, it is usually not feasible to work with single crystals. The rf field inducing the transitions between neighboring levels cannot penetrate much beyond the skin depth of the sample; hence, only a small fraction of the nuclei will be excited, making the resonances difficult to observe. By using powders this problem can be avoided. However, the crystallites in the sample have a spherical distribution, i.e., they "point" uniformly in all directions. This means that the spectrum will consist of many resonances as the field is swept since the transition energies are different for crystallites "pointing" in different directions. If the crystal field is axial, the satellite lineshapes are still rather simple, consisting of a singularity and a step. The effect of a non-axial crystal field is to "split" the singularity into two parts: a singularity which moves toward the step as $\eta$ increases and a shoulder which moves in the opposite direction. In Figures 3 and 4 the unbroadened powder patterns for nuclear spin $5/2$ are shown for $\eta=0.1$ and $\eta=0.5$ respectively. It should be noticed that the singularity and the
Figure 3. Unbroadened satellite powder pattern for $I = 5/2$, $n = 0.01$. 

SATELLITE POWDER PATTERN FOR $\eta = 0.1$ AND $I = 5/2$. THE CENTRAL TRANSITION IS EXCLUDED.
Figure 4. Unbroadened satellite powder pattern for $I = 5/2$, $\eta = 0.05$. 

SATELLITE POWDER PATTERN FOR $\eta = 0.5$ AND $I = 5/2$. THE CENTRAL TRANSITION IS EXCLUDED.
shoulder are difficult to resolve for small \( n \). In these figures \( H_0 \) is the center of the spectrum which depends on the operating frequency \( \nu_0 \).

R. B. Creel discussed these lineshapes in detail in his dissertation (29). The points of interest here are the location of the features of the satellite lines mentioned above. They are given by the expressions

\[
\Delta H_{\text{sing}} = nH_Q(1-n) \\
\Delta H_{\text{shld}} = nH_Q(1+n) \\
\Delta H_{\text{step}} = 2nH_Q
\]

where \( H_Q = 3e^2q_{zz}Q/h \gamma 2I(2I-1) \) and \( n=1 \) for the first satellite pair, \( n=2 \) for the second satellite pair, etc.. Determining the locations of two of these features yields equations in two unknowns which then can be solved for \( q_{zz} \) and \( n \).

The central line also has a distribution of resonant frequencies which are more complex for non-axial crystal fields than axial crystal fields. The central line exhibits second-order effects at low frequencies which cause the line to split into two parts as a function of \( q_{zz} \) and \( n \). Several papers discuss this splitting for both axial (30) and non-axial (31,32) EFG tensors. It is also possible to determine values of \( H_Q \) and \( n \) from the second-order splitting of the central line.

2. The Knight shift

The conduction electrons of a metal become polarized when the metal is placed in a magnetic field. This produces a temperature-independent effective field which shifts the resonance to a lower applied field if the experiment is performed at constant frequency. s-electrons are responsible
for this effect through the Fermi contact term of the dipole-dipole interaction. The magnitude of the shift is given by the expression

\[ K = \frac{(H_R - H_M)}{H_M} \]  (35)

for experiments performed at constant frequency where \( H_R \) is the field at which the resonance occurs in a diamagnetic compound and \( H_M \) is the location of the resonance in the metal.

In some metals the Knight shift has a temperature-dependent part also which may be negative. In rare-earths metallic compounds, this shift is thought to arise from s-f exchange (18,26). This effect can only be viewed indirectly at the site of the nonmagnetic ion in these compounds as the rare-earth resonance cannot be detected. From Equation 30 the origin of this temperature dependence can be seen as due to the temperature average of the angular momentum vector over the levels of the crystal-field multiplet.

Rewrite Equation 30 in the form

\[ \hat{H}_{\text{eff}} = J_{\text{ex}} \langle \hat{J} \cdot \hat{S} \rangle_T \cdot \hat{H}_0 \cdot \frac{\langle \hat{S} \rangle}{\langle \hat{S} \rangle^2} = \hat{H}_0. \]  (36)

The conduction electrons thus "see" a field \( \hat{H} = (1+C)\hat{H}_0 \) due to their interaction with the 4f electrons. If there is no s-f exchange, the interaction Hamiltonian can be written

\[ H_N = -\gamma\hat{H}_0 \cdot \hat{S} + A\hat{\mathbf{T}} \cdot \langle \hat{\mathbf{s}} \rangle \]  (37)

where \( \langle \hat{\mathbf{s}} \rangle \) is the average conduction electron spin density at the nucleus and \( A \) is a constant. Rewriting this equation allows the Knight shift to be expressed in terms of \( \langle \hat{\mathbf{s}} \rangle \). This operator can be related to the Pauli susceptibility as follows.
where $\hat{H}$ is the field "seen" by the conduction electrons. Then

$$H_N = -\gamma \hbar \hat{r} \cdot \hat{H}_0 (1 + A \langle S^z \rangle \cdot \hat{H}_0 / \gamma \hbar H_0^2)$$

$$= -\gamma \hbar \hat{r} \cdot \hat{H}_0 (1 + K)$$

where $K = K_o = A \langle S^z \rangle \cdot \hat{H}_0 / \gamma \hbar H_0^2$. The inclusion of s-f exchange requires that $\hat{H}$ in Equation 38 be replaced by $(1+C)\hat{H}_0$ which makes

$$K = A \langle S^z \rangle \cdot \hat{H}_0 / \gamma \hbar H_0^2 = A(1+C) \chi_s \hat{r} \cdot \hat{H}_0 / \gamma \hbar H_0^2 n_s g_s \beta = K_o (1+C)$$

This relates the Knight shift to the temperature averaged operator $\langle \hat{J} \rangle_T$.

This operator can be related to the 4f electron susceptibility $\chi_f$ similarly to Equation 38 with appropriate change in constants. Bulk susceptibility, $\chi$, measurements as a function of temperature can be made on the sample being studied. In this way a value for $J_{ex}$ can be obtained from a plot of $K$ vs. $\chi$ as a function of temperature since only $\chi_f$ is a function of temperature.
III. EXPERIMENTAL APPARATUS

A. The ME Experiment

1. The spectrometer

A block diagram of the ME spectrometer is shown in Figure 5. The source is mounted on the shaker which is driven by a transducer of the Kankeleit design (33). This transducer is driven by a constant acceleration feedback amplifier modeled after one developed by Cohen et al. (34). A triangle wave generator designed by Cohen (35) provides the reference signal for the feedback amplifier.

The photons emitted by the source pass through the absorber. Those which are not absorbed are then counted by a homemade proportional counter (36) filled with a mixture of 90% argon and 10% methane. The radiation to be counted passes through a 0.02" beryllium window. The resolution of this homemade counter is superior to that of the standard sodium iodide scintillation crystal and photomultiplier tube assembly for energies below 20 keV and comparable to the resolution of commercial proportional counters.

The pulses from the counter are shaped by an ORTEC P35 FET preamplifier and a RIDL DD2 linear amplifier. They then pass through a RIDL model 33-10B single channel analyzer which puts out a ten volt pulse when signals of the desired voltage are received. This pulse is stored in a RIDL 34-12B 400 channel analyzer (MCA).

To provide a proper storage spectrum, the time required to scan through the 400 channels of the MCA is one period of the reference triangle wave. The triangle wave generator supplies a trigger pulse to a time base generator (crystal controlled oscillator) which provides the start pulse for
Figure 5. Block diagram of the ME experimental setup.
the MCA. This time base generator also provides the signal to advance from one channel to the next in the MCA.

Since the source moves with constant acceleration, the entire spectrum is scanned in one pass. This has the advantage over constant velocity drives in that the decay of the source is not a problem. The operating frequency of 12 MHz allows the individual velocity points of the spectrum to be accumulated essentially independent of the half-life of the source.

The constant acceleration drive produces a parabolic effect on the background of the ME spectrum due to the displacement of the source. When the displacement of the source becomes an appreciable fraction of the separation between the source and the detector, the change in solid angle intercepted by the detector becomes large enough to produce a noticeable change in the background counting rate as the spectrum is scanned. A parabolic curve is superposed on the background scanned because of the $1/r^2$ dependence of the solid angle. By counting over the entire period of the driving waveform, two spectra are accumulated: one when the source approaches the absorber, i.e., positive velocity, and one when the source recedes from the absorber, i.e., negative velocity. This technique is acceptable since 200 channels provide sufficient resolution to study the spectra. This allows the two halves of the spectrum to be added together during the data analysis which eliminates the parabola superposed on each half. A typical spectrum as accumulated in the MCA is shown in Figure 6.
Figure 6. ME absorption spectrum as stored in the MCA.
2. The cryostat

The experiments were carried out with the absorber placed in a cryostat (Figure 7). The sample chamber shown in this figure allowed the temperature of the absorber to be varied between 4.2°K and 300°K by the use of a heat-leak chamber. The absorber is mounted on a copper tail and secured by a lead plate with a 0.5" hole to allow the radiation to pass through. Cooling of the absorber is accomplished by means of an exchange gas system between the coolant and the copper tail.

For measurements above the bath temperature, a manganin wire heater was wound about the tail. A servo system senses the temperature from the resistance of a copper wire also wound around the tail. A Wheatstone bridge measures the resistance change and controls the heater. Temperatures could be maintained to within ±0.5°K for 24-36 hours. A copper versus constantan thermocouple is used to measure the absorber temperature above 20.0°K.

3. The source

Early ME experiments performed in this lab involving thulium as the absorber used Er$_2$O$_3$ as the source material (17). The oxide is undesirable as a source since a large quadrupole splitting is observed at room temperature. In order to obtain a single line, the source had to be heated to 400°K. At this temperature the quadrupole splitting is at a minimum. However, the single line obtained has a linewidth 1.79 times as broad as expected.

It was later discovered (12) that Er$_{0.1}$Al$_{0.9}$ would provide a single line source at room temperature. For this absorber the linewidth is roughly 1.41 times as broad as might be expected; hence, the resolution of the
Figure 7. Cryostat used in ME experiments.
spectra were improved by using the Er\textsubscript{0.1}Al\textsubscript{0.9} source. From the phase diagram it appears that this alloy consists of the intermetallic compound ErAl\textsubscript{3} dissolved in an aluminum matrix. This was verified from an x-ray powder pattern made from some of the source material which had been filed. These filings were passed through a 200 mesh sieve before being mounted in the camera. The most intense line of the ErAl\textsubscript{3} spectrum was judged to be about 1/7 of the intensity of the most intense aluminum line. No extraneous lines were observed in the powder pattern when it was compared to the known powder patterns for Al and ErAl\textsubscript{3}. The erbium atom in ErAl\textsubscript{3} occupies a site of cubic symmetry so that no quadrupole splitting of the excited state occurs. This leads to the desirable single line at room temperature.

The source was prepared by arc melting stoichiometric amounts of the constituents in an argon atmosphere. The arc was struck to the component which had the lowest melting point. The molten metal then flowed over the other material. The button was then turned over several times to insure homogeneity of the compound. The button was then cleaved and cold rolled to a thickness of 2 mills. These foils, which weighed 66mg, were then irradiated for use as sources.

The source was irradiated by Idaho Nuclear Corporation at Arco, Idaho for 18 days at a flux of 5\times10^{14} neutrons/cm\textsuperscript{2}sec. At first the foils were insulated thermally from the aluminum can in which they were irradiated. The sources received were damaged through overheating. New foils were prepared which were in thermal contact with their container. This evidently solved the problem. Using the foils as sources offers the advantages of easier preparation and handling than the earlier Er\textsubscript{3}O\textsubscript{2} powder sources.
4. The absorber

The absorber used in the ME experiments was the intermetallic compound Tm$_3$Al$_2$. It was prepared in the same manner as the source. The final button was checked for weight loss. The absence of impurity phases in amounts in excess of five per cent was checked by standard x-ray diffraction analysis.

The compound was crushed in a diamond mortar and sieved to 325 mesh. A quantity of powder to make an absorber with an areal density of 10 mg/cm$^2$ was weighed. This powder was settled onto a beryllium disk 0.02" thick through an acetone slush. The resulting uniform deposition was then covered with a thin layer of spray lacquer which maintained a simple bond between the sample and the beryllium disk even at low temperatures. The remaining powder was cleaned of ferromagnetic particles and placed in a test tube in order to perform the NMR experiments.

5. Spectrometer calibration

Calibration of the drive was performed using the ME spectrum of Armco iron. The source of the calibrations consists of radioactive $^{57}$Co in a copper matrix. It was mounted in a holder identical to that in which the thulium source was mounted. The half life of the Moessbauer gamma decay of $^{169}$Tm is 9.2 days. Hence, a working time of 2-3 weeks was possible with each source. The spectrometer was calibrated at the end of each data taking period.

As many as a dozen iron spectra were obtained over a range of velocities at which the iron hyperfine spectrum could easily be resolved. The double iron spectra were stored in the MCA during each calibration run. A plot of velocity setting versus channel number for each of the four
outside peaks was made for each individual series of calibration runs. A least mean squares fit was made to the points from a given peak. The intercept of each line gives the channel of zero velocity independent of the isomer shift. From the known hyperfine splittings of iron and the slopes of the lines for each peak, the velocity per channel can be calculated for each half of the spectrum. From the plots six different velocities along with four values of the zero of velocity could be obtained for each half of the spectrum. These were averaged to get the calibration used for the run. Due to the small source displacements the geometric effect was not readily observable.

The velocities required for the thulium experiments are much larger than those at which the spectrometer was calibrated. Hence, the velocity used for the thulium experiments was extrapolated from the calibrations assuming that the velocity increased linearly as a function of the amplitude of the input triangle wave. This amplitude is controlled by a ten-turn helipot which is linear to within 0.25%. The linearity was consistent in the low velocity range where the calibrations were obtained. Spectra of Tm\textsubscript{2}O\textsubscript{3} taken with this spectrometer at both 300°K and 77°K were also consistent with similar spectra obtained by constant velocity techniques. It seems that the linearity of the spectrometer is good throughout the velocity range to within one or two percent.

B. NMR Experimental Apparatus

Conventional crossed coil NMR techniques were used to take the NMR data (37). The spectrometer used was designed by D. R. Torgeson (38) and built at the Ames Lab. The frequency range in which the experiments were
conducted was 4-19 MHz. A Varian Model V4320B 4-8 MHz magnesium probe was used throughout this range. The $^{27}$Al resonance can be seen in a standard aluminum probe which adds an undesirable line to the spectrum. For this reason the magnesium probe was modified for the experiments above 8 MHz. This is accomplished by removing the trimmer capacitor from the circuit in the probe well and adding inductors in parallel with both the transmitter and receiver coils. This step in conjunction with shortening the lead cables allowed the spectrometer to be tuned as high as 29 MHz. The experimental arrangement can be seen in Figure 8.

The external field for the NMR experiments was supplied by a Varian Associates Model 43800 fifteen inch electromagnet. This magnet is equipped with the Varian Mark II Fieldial which is used in conjunction with the Varian VF5 2515 External Sweep Adaptor to convert the field sweep to voltage control.

The experiments were performed by sweeping the magnetic field at fixed frequency. The transmitter signal is generated by a crystal oscillator which maintains extremely constant frequencies over long periods of time. The crystal oscillator was built by D. R. Torgeson (38). A computer Measurements 8808 Frequency Counter is used to monitor the oscillator frequency. The magnet power supply is driven by the channel address voltage of a RIDL Model 24-2 400 channel analyzer to generate the field scan.

The spectrum is stored in the MCA taking the signal from a phase sensitive detector (Varian Output Control Unit Model V4270). The dc signal from the phase sensitive detector is converted to a sine wave with a frequency proportional to the magnitude of the input signal by a Vidar Model 241
Figure 8. Block diagram of the NMR experimental setup.
Voltage-to-Frequency Converter. The MCA counts this frequency and stores it in its memory. Since each scan is retained in the memory, the signal can be averaged by making many individual scans. This improves the signal-to-noise ratio which is proportional to $N^{1/2}$ where $N$ is the number of scans through the resonance.

A Varian V4257 Variable Temperature System is used for the temperature work. A gas flow insert dewar tube designed to fit the Varian probes allows the passage of either hot or cold gas over the sample. Warmed nitrogen gas is used to raise the temperature of the sample while cool helium gas is used to lower the temperature of the sample. The temperature is controlled by varying the flow rate of the gas. A temperature could be maintained to within $\pm 1^\circ K$ for about 10 minutes which was ample time to allow a measurable spectrum to be recorded. The temperature is measured with a copper versus constantan thermocouple which is placed in the sample itself.
IV. DATA ANALYSIS AND NUMERICAL TECHNIQUE

Since the data requires considerable numerical analysis, an entire chapter will be devoted to discussing it. The computations were performed on an IBM 360/65 computer using full Fortran IV as the programming language. Two major fitting routines were required: one to fit the lineshape expression and one to fit the expression for the temperature dependence of the quadrupole coupling parameter. The first two sections will be spent developing these expressions. The programming technique will be discussed in the final section of this chapter.

A. The ME Lineshape

As can be seen in Figure 1, the ME spectrum consists of five individual Lorentzian lines of the form of Equation 1. These lines are unsolvable so that only an asymmetric two-line pattern is observed experimentally. This asymmetric pattern has been noted in previous studies (7,12,13,17), but it was still possible to fit the pattern with two Lorentzian lines. However, the Tm$_3$Al$_2$ spectra could not be fit this way since the observed asymmetry is much more pronounced.

Both perturbation techniques (39) and stochastic models (40,41) have been employed to generate expressions for the transition probability which allow for relaxation effects. The perturbation techniques are more rigorous but only give good results for the cases of either fast or slow fluctuation rates of the effective field. On the other hand, stochastic models have been solved for all rates of effective field fluctuation and give results satisfactory with experiment. Following Blume and Tjon (40), an expression for the transition probability will be derived using a
stochastic model. Using standard time-dependent perturbation techniques a general expression for the transition probability may be obtained. A stochastic Hamiltonian is then used to solve this expression in terms of measurable parameters. This procedure is outlined below.

Consider the interaction of a photon with a nucleus bound in a solid. The probability of making a transition from an initial state \( |i> \) to a final state \( |f> \) emitting or absorbing a photon with wave vector \( \vec{k} \) is

\[
W_{if}(\vec{k}) = \frac{1}{2} \frac{|<f|H|i>|^2}{((\omega+E_f-E_i)^2 + \gamma_i^2/4)}
\]

(41)

where \( \gamma_i \) is the inverse of the natural lifetime of the excited state and \( H \) is the Hamiltonian for the entire system. The system will be treated as an emitter here for reasons given below. Here \( \gamma_i \) is considered to be the same for each sublevel of the excited state. If the time dependent operator \( U(t) = \exp(-iHt) \) is defined, then, with suitable manipulation, it can be shown that

\[
W_{if}(\vec{k}) = \frac{2}{\gamma} \text{Re} \int_0^\infty dt \exp(i\omega t - \gamma t/2) <i|H^\dagger|f><f|U(t)HU(t)|i>
\]

(42)

by using the interaction representation. The experimentally observed emission spectrum is found by averaging this equation over all of the possible initial states \( |i> \) and summing over all of the final states \( |f> \) of the emitter. This gives the total transition probability

\[
W(\vec{k}) = \sum_{i,f} p_i W_{if}(\vec{k}) = \frac{2}{\gamma} \text{Re} \int_0^\infty dt \exp(i\omega t - \gamma t/2) <H^\dagger H(t)>
\]

(43)

where \( p_i \) is the probability that \( |i> \) occurs, \( H(t)=U^\dagger(t)HU(t) \), and the average is defined by

\[
<0> = \sum_i p_i <i|0|i>
\]

(44)
At this point the nucleus is considered to be under the effects of explicitly time-dependent forces. These forces may be due physically to the interaction of the nucleus with the electrons of the unfilled 4f shell in the case under study here. This means that the operator $U(t)$ must be replaced by a time-ordered operator

$$U(t) = \exp(-i\int_0^t dt' H(t'))$$ (45)

in Equation 43 where $H(t')$ is a time-dependent Hamiltonian for a given interaction. If such a Hamiltonian is included here, then Equation 44 may be rewritten

$$W(\tilde{g}) = \frac{2}{r} \text{Re} \int_0^\infty dt \exp(i\omega t-\gamma t^2)(\langle H^+H(t) \rangle)_{av}$$ (46)

where $(0)_{av}$ denotes the average over all of the stochastic degrees of freedom of the Hamiltonian.

Consider now the explicitly time-dependent Hamiltonian

$$H(t) = H_0 + Q \left( 3I_z^2-I^2 + \frac{n}{2}(I_+^2+I_-^2) \right) + g\eta\eta' h I_z f(t)$$ (47)

where $f(t) = \pm 1$, at random and $Q$ is a general quadrupole coupling parameter. This is the case of an effective magnetic field, interacting with the nucleus, which fluctuates between $\pm h$ along the z-axis of a non-axial EFG tensor. For a field perpendicular to the z-axis of an axial EFG tensor, the Hamiltonian can be manipulated into this form with $n$ being replaced by -3 and $Q'$ by $-Q'/2$. The lineshape for the case in which the EFG tensor is parallel to $h$ will be different from the lineshape for the case in which the EFG tensor is perpendicular to $h$. Synthesized lineshapes for the two cases are shown in Figure 9. The ME data for Tm$_3$Al$_2$ resembles the lineshape
Figure 9. Synthesized relaxation spectra showing the EFG tensor (a) parallel to and (b) perpendicular to the effective magnetic field.
for the EFG tensor parallel to \( h \). Thus \( h \) and the EFG tensor have been assumed parallel in the data analysis. For other orientations of the field \( h \) and the EFG tensor, cross terms will appear in \( H(t) \). These cross terms complicate the derivation of the lineshape and a different technique must be used than has been here. Recent papers have discussed this problem more thoroughly (41,42).

By substituting Equation 47 into Equation 43, the general expression for the transition probability can be calculated. The problem is complicated due to the fact that the Zeeman term and the quadrupole part of the Hamiltonian no longer commute with each other. The case of interest is that of fast fluctuation rate of the field so that the quadrupole part of the Hamiltonian will dominate in the description of the system. Only the result will be reported here. The reader is referred to Blume and Tjon (40) for the mathematical details. The final expression is

\[
W(k) = \frac{N}{D},
\]

where

\[
N = d(p+ib+2w) + 3Q' \eta^2(p-ib)
\]

\[
D = d[(p+i(\beta-C'_{1}+C_{0})+W)(p+i(\beta+\beta-C'_{1}+C_{0})+W)-w^2]
+3Q'^2\eta^2[(p+i(\beta+C'_{1}-C_{0})+W)(p-i(\beta-C'_{1}+C_{0})+W)
+(p+i(\beta-C_{1}+C_{0})+W)(p-i(\beta+C_{1}-C_{0})+W)+2w^2+3Q'^2\eta^2]
\]

with

\[
d = (p-ib)^2 + (C'_{1}-C_{0})^2 + 2W(p-ib).\]
In the above expression

\[ C_1 = g_1 m_1 \beta N h, \quad C_0 = g_0 m_0 \beta N h, \quad \beta = Q' (3m_1^2 - 15/4) \]

\[ C'_1 = g_1 (m_1^2 + 2) \beta N h, \quad p = -1(\omega - \omega_0) + r/2. \]

where \( g_0 \) (-0.232 nuclear magnetons) and \( g_1 \) (0.59 nuclear magnetons) are the g-factors for the ground state and the excited state respectively of \( ^{169}\text{Tm} \) (43), \( W \) is the fluctuation rate of the magnetic field, and \( m_0 \) and \( m_1 \) are the magnetic quantum numbers of the ground and excited states respectively.

This expression yields reasonable fits to the ME data.

In Figure 10 a fit to the raw Moessbauer spectrum of Figure 6 is shown. Notice that the spectrum resembles that of Figure 9a which indicates that the magnetic field and the EFG tensor are probably parallel. The individual lines which compose this spectrum are also shown. The areas under these individual lines are essentially equal, indicating that only two inequivalent thulium sites contribute to this spectrum, although there are three inequivalent thulium sites in the intermetallic compound \( \text{Tm}_3\text{Al}_2 \).

This point will be discussed further in Chapter V.

B. The Quadrupole Coupling Parameter as a Function of Temperature

An expression for the energy separation between the pure quadrupole levels is given in Equation 25. In earlier work, the ME spectra were fit to Lorentzian lineshapes; therefore, this energy splitting could be measured directly from the two-line quadrupole spectrum. However, here the spectrum is not a simple two-line pattern, due to the effective magnetic field which perturbs the nuclear quadrupole levels as mentioned above.
Figure 10. Raw data as fit to Equation 48 with the two individual lines making up the complex spectrum displayed separately.
Figure 10. (cont.)

One component line of $\text{TM}_3\text{Al}_2$
Spectrum at 85.30 degrees Kelvin

Velocity (cm/sec)
Figure 10. (cont.)
Thus, the energy splitting cannot be directly measured, but rather a value for the quadrupole coupling parameter itself is obtained. This parameter must now be related to the energy separation of the quadrupole levels calculated in Chapter II.

Consider the quadrupole part of the time-dependent Hamiltonian given in Equation 47. It is assumed that the effective field does not affect the crystal-field levels since the energies involved in the Zeeman term are of the order of $10^{-2}$ below the energies of the quadrupole term. The eigenvalue problem for this Hamiltonian was solved to obtain an expression for the energy splitting

$$<E>_T = 6Q'(T)(1+n^2/3)^{1/2}$$ (49)

which was set equal to the energy splitting of Equation 25. The temperature-dependent quadrupole coupling parameter $Q'(T)$ thus obtained is:

$$Q'(T) = (1/6(1+n^2/3)^{1/2})\{[C_0^0C_2^0<\psi^2_0\psi^2_1+4C_2^0C_2^0]^2
+ (1/3)[(3/2)C_2^0C_2^0<\psi^2_0\psi^2_1+4C_2^0C_2^0]^2\}^{1/2}$$ (50)

This function was used to fit the temperature-dependent quadrupole coupling data.

From Equation 49 it can be seen that relatively unimportant the value of $n$ is. The value of $n$ lies between zero and one. With $n = 1$ the energy splitting is changed by only about 20%. In fact, all of the data were relatively insensitive to the value of $n$ assumed, a point which will be discussed further below.
C. Numerical Analysis

In this section the various numerical analysis techniques will be discussed. A listing of the various programs used will be found in the Appendix. Several subroutines used in the minimization programs are available in the SHARE library and hence are not listed.

It is convenient to discuss some of the numerical techniques separately, even though there is some duplication in the logic. Therefore, this section is subdivided into paragraphs, each one dealing with a different phase of the computations. Other programs used will be discussed later when particular results are being discussed.

1. The ME lineshape

An example of the raw spectrum stored in the RIDL MCA is given in Figure 5. An attempt was made to fit this data with the lineshape function given in Equation 48. In order to do this, the data had to be pre-processed.

Data stored in the MCA was punched out on a Tally Tape Punch. It was also read out on an IBM typewriter and plotted on a Mosley X-Y Recorder. The points were read out in ordered pairs consisting of the channel number and the number of counts stored in that channel. The processing of the data consists of adding the two halves of a given spectrum together, converting the channel number to velocity, and finally normalizing and inverting the data so that the peaks are higher than the background. Since the spectrum now resembles an emission spectrum rather than an absorption spectrum, it is fitted with the emission lineshape which was derived in part A.

This processed data was then fit to the lineshape function given by Equation 48 using the variable metric minimization technique of Davidon (44). This is an iterative technique in which a matrix which characterizes the
behavior of the function about the minimum is determined. It is also possible to apply linear constants upon the variables by a suitable choice of initial parameters.

The following parameters can be treated as variables or held constant as desired by the user: the linewidth $\Gamma$, the asymmetry parameter $\eta$, the quadrupole coupling parameter $Q'$, the effective magnetic field $h$, the fluctuation rate of the effective field $W$, and a normalizing factor $I$. It is possible to fit up to three individual superposed lines in the case of a complex spectrum such as exists for Tm$_3$Al$_2$. No correlation is allowed between the variables of one line and those of another line during the fitting process.

A serious problem which had to be contended with was the exact choice of the function to be minimized. Rather than using Equation 48 directly, the actual function fitted to the data was

$$F = \sum_i (Y_C(i) - Y_D(i))^2BG/(N-NVAR)(1-Y_D(i)) \quad (51)$$

where $Y_C(i)$ is the calculated point using Equation 48, $Y_D(i)$ is the data point, $N$ is the number of data points, $NVAR$ is the number of variables, and $BG$ is the background. This function is nothing more than the square of the standard deviation divided by the number of counts per channel. It will be 1.0 for a perfect fit. Certain computation advantages are obtained for this function choice, although it is not understood why other function choices did not fare as well. It is suspected, however, that the calculated change in the parameter values in a given iteration during the minimization process is rather sensitive to the way in which the function is defined.
The program requires initial parameters in order to start the minimization process. An estimate of Q could be obtained from the spectrum itself. None of the other parameters could be estimated in this manner, however. Spectra were synthesized using different parameters in order to determine the effect they had on the lineshape. It was possible to estimate the magnitudes of these parameters from the synthesized spectra in order to obtain reasonable starting points for the fitting routine. Various starting points were used to see what effect this would have on the final fit. Tables 1 and 2 show the final parameters obtained from the fits of the raw data.

The large number of parameters required in the fitting routine also presents a problem in that various "fits" could be obtained with different parameters. Therefore, runs were made for each temperature point starting with different parameters. These various runs were then compared for "goodness of fit" which was based on the final value of the fitted function and the repeatability of certain parameters. An example of the raw data shown in Figure 6 is shown in Figure 9 after being processed and fit to Equation 57. The two lines composing the spectrum are also shown.

2. The quadrupole data

The parameters which were most valuable were the quadrupole coupling parameters. These parameters could be obtained with reasonable repetition relatively independent of the starting point of the fitting routine. This is not surprising due to the fact the quadrupole term is the most important in the time-dependent Hamiltonian with the Zeeman term only perturbing the quadrupole levels. It is felt, therefore, that these results are probably quite reliable.
<table>
<thead>
<tr>
<th>Temperature (°K)</th>
<th>Linewidth (cm/sec)</th>
<th>Quadrupole coupling parameter (cm/sec)</th>
<th>Magnetic field (cm/sec)</th>
<th>Fluctuation rate (sec)⁻¹</th>
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</table>

*See pp. 61-62 for the crystallographic details*
Table 2. Fitted parameters from the ME data for a thulium ion at the c₁ site

<table>
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<th>Temperature (°K)</th>
<th>Linewidth (cm/sec)</th>
<th>Quadrupole coupling parameter (cm/sec)</th>
<th>Magnetic field (cm/sec)</th>
<th>Fluctuation rate (sec)^{-1}</th>
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<td>33.6</td>
<td>1468.9</td>
</tr>
</tbody>
</table>

\(^a\)See pp. 61-62 for the crystallographic details
These quadrupole coupling parameters were fit to the expression given in Equation 50. The variable metric minimization technique was used here also. In order to solve this equation, the eigenvalue problem for the crystal-field interaction with the free ion has to be solved. Using a numerical diagonalization routine, the eigenvalues and eigenfunctions of the ground state multiplet were calculated. The 13X13 matrix thus obtained for the \( ^3H_6 \) thulium ground state could be reduced to a 6X6 and a 7X7 due to the absence of the odd N terms in the potential expansion. Since it is impossible to find solutions of any equation higher than fourth order in terms of the coefficients of that equation, numerical diagonalization techniques are required. Unfortunately, the derivatives of the energy eigenvalues as a function of the \( C_N \)'s are required for the minimization process, and since these eigenvalues could not be obtained analytically, a perturbation solution of the crystal-field Hamiltonian was made. The off-diagonal coefficients are small with the exception of \( C_2 \). Because of this, this procedure gives reasonable approximations for the gradients. This source of error, moreover, is probably small compared to other possible sources, but it is not certain how it directly affects the minimization process.

The number of nonzero crystal-field parameters for \( \text{Tm}_3\text{Al}_2 \) is 14 as can be seen from Equation 10. Added to these are the dimensionless parameters \( \rho_1 \) and \( \rho_2 \). In an effort to reduce this large number of variables, parameters with the same N value were assumed to remain in the ratio given by the crystal-field calculations with the exception of the N=2 terms. This reduces the number of variables to six. This approximation is valid
as long as there is little non-linear antishielding (11) which probably is the case here. Hutchings and Wolf (11) employed a similar argument in their work on Yb$^{+++}$ and obtained good results.

Initial parameters were also required for this routine. Initial values for the crystal-field parameters were based on the results of the point-ion lattice calculations. Different combinations of these parameters were used in different runs. The $C_N$'s were then evaluated using the values for $<r^N>_4f$ given by Freeman and Watson (45), viz.,

$$<r^2>_4f = 0.81 \times 10^{-16} \text{ cm}^2, <r^4>_4f = 0.084 \times 10^{-32} \text{ cm}^4, <r^6>_4f = 0.080 \times 10^{-48} \text{ cm}^6.$$

Estimates of $\rho_1$ and $\rho_2$ could be obtained by using the high and low temperature limits of the quadrupole coupling parameter respectively, i.e.,

$$Q'(T) = \frac{2}{3} \rho_1^0 \rho_2^0 \quad T \gg 500^\circ K$$

$$Q'(T) = \frac{1}{6}(1+n^2/3)^{1/2} \left[ \frac{C_2^0}{C_2^0} \langle 1 | 3J_z^2-J^2 | 1 \rangle^2 + 4C_2^0 \rho_2^0 \right]^2$$

$$\left( \frac{1}{3} \right) \left[ 4C_2^0 \rho_2^0 \right]^{1/2} \quad T \gg 0^\circ K \quad (52)$$

where $\langle 1 | 3J_z^2-J^2 | 1 \rangle$ is the contribution to the EFG from the lowest lying crystal-field level.

This routine also finds many minima depending on the input. The routine was started from many different points to insure a "best" fit. Different final results were compared to determine the final acceptable values. The results of the different sites were also checked for internal consistency.
3. The crystal-field calculations

The coefficients of the crystal-field expansion of the potential given in Equation 6 were calculated using a direct-sum approach. The program allowed a variable radius for the sphere in which the ions included in the sum are located. The conduction electrons were assumed to be uniformly distributed for the purposes of this calculation, since the contribution of a uniform spherical distribution of charge to the EFG tensor is zero. The program also allowed the calculations to be carried out in the principal axis system of the EFG tensor by a suitable rotation of the crystalline axis system.

Lattice sums were carried out at all five inequivalent sites in the Tm₃Al₂ lattice (see Section A, Chapter V). The initial calculation was made with the thulium valence set at +3.0 and the aluminum valence set at +1.0 in the axis system of the crystal. The second-order coefficients were then used to calculate the EFG tensor with the thulium and aluminum contributions calculated separately. The total EFG at each site was then calculated for charges on the aluminum site from +3.0 to -4.5 in 0.1 steps. These matrices were diagonalized to find the principal axis system of the EFG for each individual aluminum charge. The full potential could then be calculated for various aluminum valences using the eigenfunctions as the similarity transformation. The final results were consistent with the diagonalized results. The summations were normally carried out to six lattice spacings, at which the convergence is probably better than 5%.
V. EXPERIMENTAL RESULTS

A. Crystal Structure

A search of the literature yielded no specific crystallographic data on Tm$_3$Al$_2$. However, Buschow (46) has reported crystallographic studies on several rare-earth aluminides of the form R$_3$Al$_2$. These intermetallics were shown to have the same structure as Gd$_3$Al$_2$ and Dy$_3$Al$_2$ studied earlier by Baenziger and Hegenbarth (47). The structure of the latter compounds was determined by single-crystal x-ray diffraction techniques, and reported to be P4$_2$nm -- C$_4^4$ with 4 formula units per unit cell.

An x-ray powder pattern was taken of the Tm$_3$Al$_2$ sample using copper radiation. This pattern was successfully indexed to the Gd$_3$Al$_2$ structure. The indexing was compared with that reported for Er$_3$Al$_2$ and found to be in good agreement. The lattice constants were then obtained using a lattice-constant refinement program (LCR-2) developed by D. Williams (48) using 43 measurable lines from the powder pattern. These lattice constants were found to be $a=8.0895\pm0.0021$ and $c=7.4765\pm0.0054$. These values are consistent with values previously obtained for other R$_3$Al$_2$ intermetallics (46) as shown in Table 3.

The atomic positions used are those of Baenziger and Hegenbarth for Gd$_3$Al$_2$ (47):

4 Tm(1) in (c):

\[
x, x, z; \quad \bar{x}, \bar{x}, z; \quad \frac{1}{2} + x, \frac{1}{2} - x, \frac{1}{2} + z; \quad \frac{1}{2} - x, \frac{1}{2} + x, \frac{1}{2} + z
\]

with $x = 0.152$ and $z = 0.268$

4 Tm(2) in (c):

\[
\text{with } x = 0.205 \text{ and } z = 0.742
\]
4 Tm(3) in (b):

\(0, \frac{1}{2}, z; \frac{1}{2}, 0, z; 0, \frac{1}{2}, \frac{1}{2} + z; \frac{1}{2}, 0, \frac{1}{2} + z\)

with \(z = 0.517\)

4 Al(1) in (c):

with \(x = 0.377\) and \(z = 0.048\)

4 Al(2) in (c):

with \(x = 0.396, z = 0.456\)

Table 3. Lattice constants for various \(R_3Al_2\) intermetallics\(^a\)

<table>
<thead>
<tr>
<th>Compound</th>
<th>(a)</th>
<th>(c)</th>
<th>(c/a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Gd_3Al_2)</td>
<td>8.329</td>
<td>7.578</td>
<td>0.91</td>
</tr>
<tr>
<td>(Tb_3Al_2)</td>
<td>8.255</td>
<td>7.568</td>
<td>0.92</td>
</tr>
<tr>
<td>(Dy_3Al_2)</td>
<td>8.170</td>
<td>7.523</td>
<td>0.92</td>
</tr>
<tr>
<td>(Ho_3Al_2)</td>
<td>8.182</td>
<td>7.525</td>
<td>0.92</td>
</tr>
<tr>
<td>(Er_3Al_2)</td>
<td>8.123</td>
<td>7.484</td>
<td>0.92</td>
</tr>
<tr>
<td>(Tm_3Al_2)</td>
<td>8.090</td>
<td>7.477</td>
<td>0.92</td>
</tr>
</tbody>
</table>

\(^a\)All but \(Tm_3Al_2\) taken from reference 46

In the following discussions these inequivalent sites will be referred to as the \(c_1, c_2, b\) thulium sites and the \(c_1, c_2\) aluminum sites respectively. These positions were used to calculate the potential coefficients using the point-ion approximation.
The point symmetry of the (c) sites is \( \text{m} \) -- \( \text{C}_s \) as mentioned above. Although the (b) site is a site of axial symmetry by itself, it is reduced to the lower non-axial point symmetry by the presence of the other charges in the crystal. Effectively, then, the crystal contains five inequivalent sites of non-axial point symmetry.

B. NMR Measurements of the Field Gradient \( q_{zz} \) and the Asymmetry Parameter \( \eta \)

A very real problem exists in the point-ion model potential calculations, viz., the value of the valence to assign to the aluminum ion. The thulium ion was always chosen to be tripositive. Although aluminum is often tripositive in the rare-earth aluminides, evidence exists which indicates that it may effectively not be tripositive in the rare-earth aluminides. In Table 4 are shown some measured values of quadrupole coupling parameter \( |e^2 q_{zz} Q/h| \) for some \( \text{RAI}_2 \) compounds. Taking \( Q(^{27}\text{Al}) = 0.149 \times 10^{-24} \text{ cm}^2 \) (49), a value for \( q_{zz} \) can be calculated. Using the relationship

\[
q_{zz} = (1-\gamma_\infty)A_2^0 Z_{\text{Al}}
\]

a value for the valence can be obtained using the point-ion value for \( A_2^0 \) for a unit charge. Some uncertainty will exist in this procedure due to lack of precise theoretical calculations for \(-\gamma_\infty\) and the error in calculating \( A_2^0 \). It is also impossible to determine the sign of \( q_{zz} \) in NMR experiments except at very low temperatures. In the rare-earth aluminides, the resonance disappears due to broadening before sufficiently low temperatures can be reached to detect the sign of \( q_{zz} \). Calculations to obtain
$Z_{Al}$ have been performed for both positive and negative $q_{zz}$ and are shown in Table 4 using $-\gamma_{\infty}(Al^{+++}) = 2.36^4$ and $-\gamma_{\infty}(Al^+) = 1.13$ (50). It is interesting to note that White et al. (51) concluded that the aluminum site carries a negative charge on the basis of susceptibility measurements on CeAl$_2$. A minus charge is obtained if $q_{zz}$ is negative as is shown in Table 4. Furthermore, de Wijn et al. (20) have measured a large quadrupole coupling parameter, 7-8 MHz, in the cubic compounds RAl$_3$, where R=Er,Tm,Yb, which have the structure AuCu$_3$. These are much larger than those measured for other rare-earth aluminides even though the crystal field is smaller. The EFG at the aluminum site in these compounds is dependent on the value of the charges assigned to the different ions, and it is zero if the charges are equal. Using $-\gamma_{\infty} = 2.36$ de Wijn et al. calculated a charge difference of 3.7 electrons and thereby assigned a valence of roughly -1.0 to the aluminum site. The validity of this treatment, of course, depends on the value of $-\gamma_{\infty}$ chosen and a value of 1.13 gives a physically unrealistic result, viz., a non-neutral compound. The other compounds of the form RAl$_3$ have hexagonal crystal structures with measured quadrupole coupling parameters of about 0.7 MHz (19). The large measured quadrupole coupling parameter for RAl$_3$ seems puzzling in light of the small quadrupole coupling parameter calculated from the point-ion model.

It can be seen from Table 4 that the valence of the aluminum ion varies between 2.0 and 2.5 for positive $q_{zz}$, and -0.35 and 0.45 for negative $q_{zz}$. A question should be raised regarding the precision of the Sternheimer anti-shielding factors employed since they might differ from those calculated for aluminum valences of +3.0 and +1.0. More important, probably, is the
| Compound | $|e^2 q_{zz} Q/P|/\text{MHz}$ | $Z_{\text{AL}}(q_{zz}<0)$ | $Z_{\text{AL}}(q_{zz}<0)$ |
|----------|-----------------|-----------------|-----------------|
|          |                 | $-\gamma_{\infty} = +2.36(4)^a$ | $-\gamma_{\infty} = 1.13(50)$ |
| LaAl$_2$ | 4.5(52)         | 2.47             | -0.29           |
|          | 4.63(18)        | 2.50             | -0.34           |
| CeAl$_2$ | 4.5(52)         | 2.43             | -0.24           |
|          | 4.54(18)        | 2.44             | -0.25           |
| PrAl$_2$ | 4.54(18)        | 2.43             | -0.24           |
|          | 4.56$^b$(30)    | 2.43             | -0.24           |
|          | 4.50$^c$(30)    | 2.40             | -0.22           |
| NdAl$_2$ | 4.52$^d$        | 2.54             | -0.34           |
| SmAl$_2$ | 4.20$^d$        | 2.44             | -0.18           |
| GdAl$_2$ | 4.27(53)        | 2.32             | -0.06           |
| ErAl$_2$ | 3.66$^d$        | 2.26             | 0.10            |
| TmAl$_2$ | 3.05$^d$        | 2.03             | 0.40            |
| YbAl$_2$ | 2.30$^d$(18)    | 1.42             | 0.15            |
|          | 2.58$^{d,e}$    | 1.48             | 0.06            |
| LuAl$_2$ | 2.85$^d$        | 2.05             | 0.45            |

$^a$Reference numbers appear in parentheses  
$^b$Derived from first-order quadrupole coupling  
$^c$Derived from second-order quadrupole coupling  
$^d$T. P. Graham, unpublished data  
$^e$Yb taken to be $4f^{14}$ ion, i.e., valence is +2
exact nature of the role of the conduction electrons and whether or not they are bound to the aluminum ion. At any rate, the above data indicate that the conduction electrons are probably not uniformly distributed throughout the crystal as assumed in the point-ion calculations. The so-called effective charge on the aluminum site may just reflect this non-uniform charge density and serve as a convenient means for introducing a conduction electron contribution to the EFG at the nuclear sites.

Two NMR experiments were performed in an effort to measure the field-gradient and asymmetry parameter at the aluminum sites: the entire satellite spectrum was scanned at 19 MHz, and the central line was observed as a function of frequency. The results of these experiments will be presented here.

1. First-order effects -- the satellite lines

Since the symmetry of the two inequivalent spin 5/2 aluminum sites is non-axial, the four satellite transitions for each site should show both singularities and shoulders. Also, there is some overlapping of the two spectra since the environments of the different aluminum ions seem to be magnetically similar. Hence, sorting out the features may be quite complex.

A scan of 2500 Oe was required to obtain the full spectrum. Due to spectrometer drift for magnetic field scans of this width, the spectrum was taken in two overlapping parts, scanning in each direction from the central line. This technique is acceptable due to the field consistency in the Mark II Fi/eldia1. The position of the central line shifted only 5 Oe in the two runs and the calibration remained unchanged.
Figure 11 shows the experimental spectrum. Three satellite peaks are observed on either side of the central transition. Peak a is clearly a singularity due to the base line crossing. Peak b is probably a combination of singularities and shoulders from both sites since it is too intense to be due to just one site. Peak c is probably a combined shoulder and singularity due to its width. Judging the exact location of the various peaks is difficult due to the lack of resolution of the individual lines.

One other feature observed in this spectrum is the shift of the satellite pattern with respect to the central transition. This effect is due to an anisotropy of the Knight shift tensor. The spectrum is shifted uniformly in first order and thus the splitting between the satellites is unchanged. This effect will not be considered further at this time.

The program used by R. B. Creel (29) was modified for the case of spin 5/2. This adds a satellite pair to the spectrum for spin 3/2. The program generates the satellite lineshape and then adds in the other three lines with proper normalization factors; then a Gaussian central transition is included. The derivative of this spectrum is then taken to compare with the experimental lineshape. The derivative of the line is obtained experimentally due to the lock-in amplifier in the experimental apparatus.

Various values of n and H_Q were tried by picking different parts of the experimental spectrum as the location of the various features and applying Equations 34.

From the point-ion calculations, site c_2 has a larger quadrupole coupling than site c_1. Peak c in Figure 11 is probably the second singularity and shoulder and first step for site c_2. Peak b would then correspond to
Figure 11. Experimentally obtained NMR spectrum of $^{27}$Al at 19 MHz.
the first singularity and shoulder. The lack of resolution of these peaks indicates that the asymmetry parameter for this site is small. Peak a is probably associated with site \( c_1 \). There are two possible interpretations for this peak: Peak a could be the second singularity and peak b contain the second shoulder. For this case, the asymmetry parameter would be about 0.5. Alternatively, peak a could be the first singularity and shoulder and peak b contain the second singularity, second shoulder, and first step. Here the asymmetry parameter would be small and the singularities and shoulders unresolved. Interestingly enough, \( H_Q \) is about the same value for each of these cases. Figures 12 and 13 show various synthesized spectra for different combinations of \( H_Q \) and \( n \).

2. Second-order effects -- the central transition

For large field gradients, second-order effects become important in determining the shape of the central transition. The line splits apart as a function of frequency with the splitting increasing as the frequency is decreased. In Figure 14 the second-order powder patterns are shown for non-zero asymmetry parameter as taken from Baugher et al. (32). It is the position of the singularities as a function of frequency which is useful in determining values for \( n \) and \( H_Q \). Unfortunately, the splitting is given as a function of both parameters and another measurement is required to determine either one.

Figures 15-17 show the central line at various frequencies. The most salient features of these lines are the presence of an unsplit line which apparently has a second line superposed on it. At 15 MHz the second line has clearly split apart and is gradually disappearing. At 5 MHz, the
Figure 12. Synthesized NMR spectra for the $c_1^{27}$Al site showing the satellite transitions only.
SYNTHESIZED SATELLITE SPECTRA FOR $^{27}$Al AT 19 MHZ

$\nu = 0.03$

$H_0 = 866.7$ Oe

$\nu = 0.07$

$H_0 = 868.7$ Oe

$\nu = 0.11$

$H_0 = 907.8$ Oe

Figure 13. Synthesized NMR spectra for the $c_2$ $^{27}$Al site showing the satellite transitions only.
Figure 14. Unbroadened central line powder pattern in second order.
Figure 15. Experimental $^{27}\text{Al}$ central transition at 15 MHz in $\text{Tm}_3\text{Al}_2$. 

Central transition of $^{27}\text{Al}$ in $\text{Tm}_3\text{Al}_2$ at 15.00855 MHz.
Figure 16. Experimental $^{27}\text{Al}$ central transition at 10 MHz in Tm$_3$Al$_2$. 
Figure 17. Experimental $^{27}\text{Al}$ central transition at 5 MHz in Tm$_3$Al$_2$. 
second line is unobservable and the first line is beginning to show evidence of splitting. It is interesting that the splitting of the first line decreases as a function of decreasing frequency contrary to expectations. Apparently the combination of the two superposed spectra gave a false linewidth for this line until the singularities of the second line have split far enough apart.

An attempt was made to measure the linewidth of the two inequivalent aluminum sites as a function of frequency. The line due to the aluminum ions at the c_{2} site appears as shoulders on the central transition of the c site, (Figures 15 and 16). Hence, only an estimate of the peaks could be obtained. The measured values are shown in Table 5. The uncertainty in the measurements is pointed up in the variation of the Knight shift which is independent of frequency, hence, it should be constant. A plot of \( \Delta \nu v_0 \) versus \( \nu_0^2 \) was made where \( \nu_0 \) is the operating frequency and \( \Delta \nu \) is the linewidth expressed in units of frequency. The plot is a straight line as is shown in Figure 18. A least mean squares fit was made to determine the slope of the line and its intercept. These values were compared to the expression

\[
\Delta \nu v_0 = \frac{\nu_0^2}{18} (25-22n+n^2) + \left[ \frac{(5+n)K_3+2(2+n)K_2 - K_2}{3(3+n)} \right] \nu_0^2
\]

for \( n<1/3 \) where \( \nu_Q = \gamma H_Q \) and the K's are the diagonal components of the Knight shift tensor. This expression is derived by Baugher et al. (32) for powders with a non-axial EFG tensor. Here the extrapolation to \( \nu_0^2 = 0 \) gives an expression containing both \( \nu_Q \) and \( n \) which can be compared to satellite data.
Figure 18. Least mean squares fit of central line splitting of $^{27}$Al resonance at $c_1$ sites in Tm$_3$Al$_2$. 

$\nu_0 \Delta \nu = 0.00195 \nu_0^2 + 0.9133$
Since the magnesium probe could not go below 4.0 MHz, it was not possible to get very much data from the splitting of the $^{27}$Al resonance due to the $c_1$ site since the line does not begin to split until about 5.0 MHz. The data obtained indicates that a plot of $v_0 \Delta v$ vs. $v_0^2$ would yield a line with a negative slope as opposed to the similar plot for the $c_2$ site. A quadrupole coupling parameter about one half that of the $c_2$ site is indicated from this plot.

Table 5. Linewidth and Knight shift of the $c_2$ site as a function of frequency

<table>
<thead>
<tr>
<th>Frequency (MHz)</th>
<th>Resonance position (kOe)</th>
<th>Gyromagnetic ratio</th>
<th>Linewidth (Oe)</th>
<th>Knight shift (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.00134</td>
<td>8.2028</td>
<td>1.0974</td>
<td>105.7</td>
<td>-1.086</td>
</tr>
<tr>
<td>10.00137</td>
<td>9.1047</td>
<td>1.0985</td>
<td>101.3</td>
<td>-0.984</td>
</tr>
<tr>
<td>11.00150</td>
<td>10.0182</td>
<td>1.0981</td>
<td>93.7</td>
<td>-1.014</td>
</tr>
<tr>
<td>12.00781</td>
<td>10.9430</td>
<td>1.0973</td>
<td>91.0</td>
<td>-1.090</td>
</tr>
<tr>
<td>13.00691</td>
<td>11.8451</td>
<td>1.0981</td>
<td>87.3</td>
<td>-1.020</td>
</tr>
<tr>
<td>15.00855</td>
<td>13.6538</td>
<td>1.0992</td>
<td>83.9</td>
<td>-0.918</td>
</tr>
<tr>
<td>17.00543</td>
<td>15.4761</td>
<td>1.0988</td>
<td>76.8</td>
<td>-0.982</td>
</tr>
</tbody>
</table>

3. Results of the NMR experiments

Values of $H_Q$ and $n$ were determined from the satellite data. A value of $H_Q$ was also obtained from the central line data using the value of $n$ obtained from the satellite data. The ambiguity over the value of $n$ at the
c₁ site was resolved in favor of the small asymmetry parameter. In Figure 13 it can be seen that the pattern for \( n = 0.51 \) is too weak to justify its selection. The values of \( H_q \) and \( n \) determined from the data are shown in Table 6.

Table 6. Values of \( H_q \) and \( n \) determined experimentally from \(^{27}\text{Al} \) NMR data

| Effect                  | Site | \( H_q \) (Oe) | \( n \)       | Ratio | \( |e^{2}q_{zz}Q/h| \) (MHz) |
|-------------------------|------|----------------|--------------|-------|------------------|
| First-order (satellite) | \( c_1 \) | 449.7±10.0     | 0.01±0.03    |       | 3.29             |
|                         | \( c_2 \) | 868.7±10.0     | 0.07±0.02    | 1.932 | 6.36             |
| Second-order (central line) | \( c_1 \) | 485.5±10.0     | 0.10         |       | 3.55             |
|                         | \( c_2 \) | 762.2±15.0     | 0.07         | 1.570 | 5.58             |

The values for \( H_q \) are quite uncertain due to the lack of precision in determining the peak positions in both the central line data and the satellite data. This is clearly visible in the disparity between the values from the separate experiments. The values calculated from the central line are probably more suspect since it was almost impossible to locate the exact position of the singularities. Its usefulness lies mainly in the fact that it gives numbers which agree reasonably well with the satellite data.

The experimental values were then compared to those calculated from the point-ion lattice. Ratios of the calculated values were taken and
those that agreed with the experimental ratios were used. This seemed more appropriate than comparing magnitudes of $H_Q$ and $n$ since no values could be found which agreed in both of these respects. It is reasonable to assume that the experimental ratios would probably agree with the theoretical ratios since the ions are the same and react similarly with the lattice. Table 7 shows these results.

Table 7. Comparison of calculated and experimental values for $H_Q$ and $n$

<table>
<thead>
<tr>
<th>Ratio</th>
<th>Site</th>
<th>$H_Q$ (exp.)</th>
<th>$H_Q$ (cal.)</th>
<th>$n$ (exp.)</th>
<th>$n$ (cal.)</th>
<th>$Z_{AL}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.932</td>
<td>$c_1$</td>
<td>449.7</td>
<td>316.8</td>
<td>0.10</td>
<td>0.64</td>
<td>0.11</td>
</tr>
<tr>
<td></td>
<td>$c_2$</td>
<td>868.7</td>
<td>613.0</td>
<td>0.07</td>
<td>0.12</td>
<td></td>
</tr>
<tr>
<td>1.570</td>
<td>$c_1$</td>
<td>485.5</td>
<td>392.7</td>
<td>0.10</td>
<td>0.62</td>
<td>-0.24</td>
</tr>
<tr>
<td></td>
<td>$c_2$</td>
<td>762.2</td>
<td>616.3</td>
<td>0.07</td>
<td>0.18</td>
<td></td>
</tr>
</tbody>
</table>

The values of the $H_Q$ were calculated using $-\gamma_\infty = 2.36$. If $-\gamma_\infty = 1.13$ were used, the calculated values would be about a factor of 2/3 smaller. It is slightly disturbing that the results don't agree any better than they do. Also, the $-\gamma_\infty$ used is for $Al^{+++}$ rather than $Al^+$ as was the case for $TmAl_3$ (20).

The results here contribute a little more to the confusion concerning the location of the conduction electrons in the crystal. If the assumptions here are correct, apparently they contribute greatly to the EFG at the
nuclear site. Since this contribution is not included in the point-ion calculations it is not surprising that there is some disagreement. It is reasonable, also, to suppose that the aluminum actually contributes three electrons to the conduction band. This would imply that the crystal field at the aluminum site would be "seen" by an Al$^{+++}$ ion rather than a nearly neutral one. If, however, the conduction electrons were localized in the neighborhood of the aluminum ion, the other ions might "appear" to be neutral. This "effective valence" of the aluminum ion then is merely an artifice in which to include a contribution from the conduction electrons to the crystal field.

Das and Ray (54) concluded, from theoretical calculations, that the conduction electrons enhance the EFG at the nuclear site in rare-earths. They based their original calculations on a uniform distribution of the conduction electrons similar to what has been done here. The results of their calculations are too small when compared with experimental results, and hence conduction electron antishielding is assigned to the EFG. The results here are somewhat consistent with these ideas.

Covalancy and overlap effects are not considered here. The aluminum nucleus is larger than that of the rare-earth ion and may interact more strongly with its neighbors; the first nearest neighbor being an aluminum ion for both inequivalent aluminum sites. Also, the valence band is not buried in the Fermi sea of electrons, but occurs near the Fermi surface. Hence, lack of agreement with point-ion calculations surely is not surprising and might almost be expected. Notice the seemingly large disparity in the values of $\eta$ for the $c_1$ site. This suggests that the field is not
being enhanced isotropically. This also is not too unreasonable since the crystal symmetry is quite low. This might possibly be attributed to some type of bonding mechanism.

It should also be noted that the method of calculating the "effective charge" is different here than for other cases mentioned above. Since there are two sites, a ratio of the fields seen at the nucleus can be taken. However, this is not true in the other calculations. There the "effective charge" is calculated assuming that the point-ion calculations are correct. If that were done here, the effective charge would be about 2.0 in agreement with the RAl₃₂ calculations. If an "effective valence" closer to zero were taken for TmAl₃, then the calculated coupling parameter would be smaller than the measured one consistent with the Tm₃Al₂ results. However, this statement would not apply to the RAl₂ compounds since the contributions to the EFG from the different ion types have opposite signs.

Before leaving this discussion, one last point should be made. Earlier crystal field work on TmMn₂ seemed to indicate that the manganese ion, normally divalent, was essentially neutral (13). Neutron diffraction experiments by Felcher et al. indicated that there was no moment at the manganese site (55). This observation would be consistent with the idea of a localized band yielding no net spin density at the manganese site. It is possible that a similar situation exists in the rare-earth aluminides.
C. ME Measurements of the Crystal-Field Parameters $C_j^M$ and the Shielding Parameters $\sigma_N$.

In Figure 9 a two line fit to the raw data is shown. This is somewhat surprising since there are three inequivalent thulium sites in Tm$_3$Al$_2$. Each site has four equivalent ions so that three equally intense lines might be expected. It can be seen from Figure 9 that the two lines which make up the pattern have essentially the same area, indicating that only two lines compose the spectrum. Similar three line fits failed to yield three lines of equal area. From the crystal-field calculations, moreover, a third line would probably be resolved. It has been assumed that the two lines observed are due to the thulium ions at the two c sites since the calculated crystal-field parameters are much larger than at the b site. It is not understood why the latter line is not seen. If the principal axis system of the EFG tensor for the c$_2$ sites is defined in the usual way, $S^M_N$-terms with odd M appear in the crystal-field calculation while $S^M_N$-terms with even M are zero. By a suitable rotation of the axis system, the odd M terms disappear and the even M terms reappear. This procedure leads to a value of $\eta$ which is greater than one. This was done in order that the proper expansion coefficients would appear in the potential and thus the calculations could be kept relatively simple.

The crystal-field parameters for $Z_{AL}$ equal to both 0.11 and -0.24 were calculated from the point-ion model as described in Chapter IV. These were then used as initial values in the quadrupole splitting fitting routine. Initial values for $\rho_1'$ and $\rho_2'$ were calculated using Equations 52. The crystal-field parameters for $Z_{AL}=0.11$ were used as the point-ion values.
This was done since the satellite data is more reliable than the central line data and since these calculated values are more consistent with the thulium data. The parameters for $Z_{AL} = -0.24$ were about 15 to 20% larger and probably are more consistent with a three line fit since the parameters for the b site are also larger.

The initial parameters, as well as those giving the best fit to the data, are displayed in Tables 8 and 9. Figures 19 and 20 show the fitted data for the $c_1$ and $c_2$ sites respectively. The energy levels and the eigenfunctions of the crystal-field levels are given in Figures 21 and 22.

It is clear from the computer fits that the second-order crystal-field parameters are smaller than the predicted point-ion values. This is usually attributed to shielding of the crystal field by the inner filled electron shells. It is standard practice to define shielding parameters of the form

\[ C_N^{0'} = (1 - \sigma_N) C_N^0 \]  

where $\sigma_N$ represents this shielding mentioned above (7). This parameter is most important here for the second-order term, but parameters are calculated for all of the terms. By comparing the fitted parameters to the point-ion calculations, values for these shielding parameters can be calculated. These are given in Table 10.

From the fitted values for $\rho_1'$ and $\rho_2'$, the shielding parameters $R_Q$ and the conduction electron contribution to the EFG tensor can be calculated using Equations 24. Certain theoretical and experimental values are required for these calculations, viz., the quadrupole moment of the excited state of
Table 8. Crystal-field parameters for the $C_1$ thulium sites

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Point-ion calculation</th>
<th>Full parameter fit</th>
<th>$C^0_C^2$ only fit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C^0_2$</td>
<td>-682.38 cm$^{-1}$</td>
<td>-285.39 cm$^{-1}$</td>
<td>-285.39 cm$^{-1}$</td>
</tr>
<tr>
<td>$C^2_2$</td>
<td>-231.09 cm$^{-1}$</td>
<td>-58.55 cm$^{-1}$</td>
<td>-58.49 cm$^{-1}$</td>
</tr>
<tr>
<td>$C^0_4$</td>
<td>0.08 cm$^{-1}$</td>
<td>0.0796 cm$^{-1}$</td>
<td>0.0</td>
</tr>
<tr>
<td>$C^2_4$</td>
<td>-8.83 cm$^{-1}$</td>
<td>-8.78 cm$^{-1}$</td>
<td>0.0</td>
</tr>
<tr>
<td>$S^2_4$</td>
<td>1.13 cm$^{-1}$</td>
<td>1.12 cm$^{-1}$</td>
<td>0.0</td>
</tr>
<tr>
<td>$C^4_4$</td>
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<td>41.58 cm$^{-1}$</td>
<td>0.0</td>
</tr>
<tr>
<td>$S^4_4$</td>
<td>28.94 cm$^{-1}$</td>
<td>28.79 cm$^{-1}$</td>
<td>0.0</td>
</tr>
<tr>
<td>$C^6_6$</td>
<td>0.59 cm$^{-1}$</td>
<td>0.59 cm$^{-1}$</td>
<td>0.0</td>
</tr>
<tr>
<td>$C^2_6$</td>
<td>-0.40 cm$^{-1}$</td>
<td>-0.40 cm$^{-1}$</td>
<td>0.0</td>
</tr>
<tr>
<td>$S^2_6$</td>
<td>-0.48 cm$^{-1}$</td>
<td>-0.48 cm$^{-1}$</td>
<td>0.0</td>
</tr>
<tr>
<td>$C^4_6$</td>
<td>2.57 cm$^{-1}$</td>
<td>2.57 cm$^{-1}$</td>
<td>0.0</td>
</tr>
<tr>
<td>$S^4_6$</td>
<td>-1.88 cm$^{-1}$</td>
<td>-1.88 cm$^{-1}$</td>
<td>0.0</td>
</tr>
<tr>
<td>$C^6_6$</td>
<td>-0.39 cm$^{-1}$</td>
<td>-0.39 cm$^{-1}$</td>
<td>0.0</td>
</tr>
<tr>
<td>$S^6_6$</td>
<td>-1.23 cm$^{-1}$</td>
<td>-1.23 cm$^{-1}$</td>
<td>0.0</td>
</tr>
<tr>
<td>$p_1$</td>
<td>-0.039(10$^{-5}$)</td>
<td>-0.170(10$^{-5}$)</td>
<td>-0.171(10$^{-5}$)</td>
</tr>
<tr>
<td>$p_2$</td>
<td>-0.257(10$^{-5}$)</td>
<td>0.411(10$^{-5}$)</td>
<td>0.417(10$^{-5}$)</td>
</tr>
<tr>
<td>$n$</td>
<td>0.305</td>
<td>0.205</td>
<td>0.204</td>
</tr>
</tbody>
</table>
Table 9. Crystal-field parameters for the $c_2$ thulium sites

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Point-ion calculation</th>
<th>Full parameter fit</th>
<th>$c_2^0$ only fit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_2^0$</td>
<td>-802.44 cm$^{-1}$</td>
<td>-284.99 cm$^{-1}$</td>
<td>-276.92 cm$^{-1}$</td>
</tr>
<tr>
<td>$C_2^2$</td>
<td>-975.75 cm$^{-1}$</td>
<td>-40.26 cm$^{-1}$</td>
<td>-28.15 cm$^{-1}$</td>
</tr>
<tr>
<td>$C_4^0$</td>
<td>1.77 cm$^{-1}$</td>
<td>1.76 cm$^{-1}$</td>
<td>0.0</td>
</tr>
<tr>
<td>$C_4^2$</td>
<td>-36.35 cm$^{-1}$</td>
<td>-36.23 cm$^{-1}$</td>
<td>0.0</td>
</tr>
<tr>
<td>$S_4^2$</td>
<td>18.11 cm$^{-1}$</td>
<td>18.05 cm$^{-1}$</td>
<td>0.0</td>
</tr>
<tr>
<td>$C_4^4$</td>
<td>-48.02 cm$^{-1}$</td>
<td>-47.86 cm$^{-1}$</td>
<td>0.0</td>
</tr>
<tr>
<td>$S_4^4$</td>
<td>17.98 cm$^{-1}$</td>
<td>17.92 cm$^{-1}$</td>
<td>0.0</td>
</tr>
<tr>
<td>$C_6^0$</td>
<td>0.23 cm$^{-1}$</td>
<td>0.227 cm$^{-1}$</td>
<td>0.0</td>
</tr>
<tr>
<td>$C_6^2$</td>
<td>-5.72 cm$^{-1}$</td>
<td>-5.65 cm$^{-1}$</td>
<td>0.0</td>
</tr>
<tr>
<td>$S_6^2$</td>
<td>2.37 cm$^{-1}$</td>
<td>2.34 cm$^{-1}$</td>
<td>0.0</td>
</tr>
<tr>
<td>$C_6^4$</td>
<td>-0.83 cm$^{-1}$</td>
<td>-0.82 cm$^{-1}$</td>
<td>0.0</td>
</tr>
<tr>
<td>$S_6^4$</td>
<td>1.18 cm$^{-1}$</td>
<td>1.17 cm$^{-1}$</td>
<td>0.0</td>
</tr>
<tr>
<td>$C_6^6$</td>
<td>-0.96 cm$^{-1}$</td>
<td>-0.95 cm$^{-1}$</td>
<td>0.0</td>
</tr>
<tr>
<td>$S_6^6$</td>
<td>-0.769 cm$^{-1}$</td>
<td>-0.78 cm$^{-1}$</td>
<td>0.0</td>
</tr>
<tr>
<td>$\rho_1$</td>
<td>$-0.039(10^{-5})$</td>
<td>-0.121(10^{-5})</td>
<td>-0.121(10^{-5})</td>
</tr>
<tr>
<td>$\rho_2$</td>
<td>$0.131(10^{-5})$</td>
<td>0.670(10^{-5})</td>
<td>0.653(10^{-5})</td>
</tr>
<tr>
<td>$n$</td>
<td>1.216</td>
<td>0.141</td>
<td>0.102</td>
</tr>
<tr>
<td>Energy (cm$^{-1}$)</td>
<td>$</td>
<td>+6&gt;$</td>
<td>$</td>
</tr>
<tr>
<td>------------------</td>
<td>-------</td>
<td>-------</td>
<td>-------</td>
</tr>
<tr>
<td>0.0</td>
<td>0.049+.699i</td>
<td>-0.024-.012i</td>
<td>0.001+.005i</td>
</tr>
<tr>
<td>0.0</td>
<td>0.708-.0001i</td>
<td>-0.021-.017i</td>
<td>-0.055-.001i</td>
</tr>
<tr>
<td>171.94</td>
<td>0.026-.100i</td>
<td>0.570-.407i</td>
<td>-0.086-.042i</td>
</tr>
<tr>
<td>172.73</td>
<td>0.001+.026i</td>
<td>0.639+.288i</td>
<td>-0.041-.081i</td>
</tr>
<tr>
<td>267.28</td>
<td>0.007+.003i</td>
<td>0.068-.042i</td>
<td>0.557+.371i</td>
</tr>
<tr>
<td>283.78</td>
<td>-0.004-.007i</td>
<td>0.075+.028i</td>
<td>0.363+.563i</td>
</tr>
<tr>
<td>318.71</td>
<td>0.067-.007i</td>
<td>0.208+.211i</td>
<td>0.669+.670i</td>
</tr>
</tbody>
</table>

| $|+5>$ | $|+3>$ | $|+1>$ | $|-1>$ | $|-3>$ | $|-5>$ |
|-------|-------|-------|-------|-------|-------|
| 96.55 | -0.696+.110i | -0.051 | 0.008+.007i | 0.002+.005i | -0.031-.035i | -1.10-.696i |
| 96.55 | 0.036+.705i | -0.035+.036i | -0.008+.007i | 0.002+.005i | 0.047+.007i | 0.705-.036i |
| 228.95 | 0.001-.047i | 0.511+.451i | -0.055-.039i | 0.175+.030i | 0.693-.125i | 0.047+.001i |
| 233.44 | -0.046+.009i | 0.679+.055i | 0.056-.038i | -0.174-.033i | 0.485+.510i | -0.009-.046i |
| 297.78 | -0.004+.007i | 0.180+.031i | -0.703-.040i | 0.683+.050i | 0.026+.039i | 0.007-.003i |
| 315.89 | 0.005-.011i | 0.148+.108i | 0.702+.048i | 0.682+.059i | -0.047 | 0.011+.005i |

Figure 19. Energy levels and eigenfunctions for the ground state crystal-field multiplet of $^{169}$Tm at $c_1$ sites in $\text{Tm}_3\text{Al}_2$. 
| Energy (cm⁻¹) | |+6> | |+4> | |+2> | |0> | |-2> | |-4> | |-6> |
|---|---|---|---|---|---|---|---|---|---|---|
| 0.0 | 0.518 - 0.500i | -0.015 + 0.035i | -0.003 + 0.001i | 0.001 | -0.003 + 0.001i | 0.029 - 0.024i | 0.508 + 0.514i |
| 0.0 | -0.563 - 0.402i | -0.037 - 0.007i | 0.003 + 0.001i | 0.002 | -0.003 - 0.001i | -0.030 - 0.024i | 0.407 - 0.556i |
| 168.96 | 0.034 - 0.017i | 0.455 - 0.533i | -0.058 + 0.023i | -0.029 + 0.018i | -0.072 + 0.024i | -0.654 + 0.259i | 0.018 + 0.034i |
| 169.56 | -0.035 - 0.011i | 0.696 - 0.082i | 0.058 + 0.024i | -0.030 - 0.017i | -0.072 - 0.026i | 0.656 + 0.254i | 0.012 - 0.035i |
| 268.70 | -0.006 - 0.002i | 0.069 - 0.020i | -0.690 - 0.109i | -0.087 + 0.079i | 0.689 + 0.117i | 0.061 + 0.012i | 0.002 - 0.006i |
| 282.93 | 0.006 - 0.003i | 0.055 - 0.047i | 0.692 - 0.093i | -0.089 - 0.077i | 0.692 - 0.104i | -0.061 + 0.013i | 0.003 + 0.006i |
| 313.17 | 0.052 - 0.028i | 0.002 - 0.129i | 0.985 - 0.013i | 0.100 + 0.001i | | 0.004i |
| | | | | | | | |
| | | | | | | | |
| | | | | | | | |

| |+5> | |+3> | |+1> | |-1> | |-3> | |-5> |
|---|---|---|---|---|---|---|---|---|
| 92.28 | 0.113 - 0.695i | -0.058 - 0.026i | -0.003 - 0.009i | 0.009 - 0.003i | 0.021 - 0.055i | -0.695 - 0.113i |
| 92.28 | 0.704 - 0.040i | -0.050 - 0.036i | -0.009 - 0.002i | -0.002 - 0.009i | -0.059 + 0.008i | -0.039 - 0.704i |
| 228.93 | 0.025 - 0.055i | 0.678 - 0.115i | -0.103 - 0.049i | 0.049 - 0.103i | -0.412 + 0.571i | -0.055 - 0.025i |
| 231.61 | 0.058 - 0.019i | 0.636 + 0.262i | -0.096 - 0.062i | 0.062 - 0.096i | 0.650 - 0.270i | -0.019 - 0.058i |
| 301.06 | 0.010 - 0.016i | 0.152 + 0.001i | 0.275 + 0.641i | -0.641 + 0.275i | -0.010 + 0.023i | -0.016 - 0.010i |
| 301.06 | 0.017 - 0.008i | 0.148 + 0.032i | 0.690 - 1.071i | + 0.107 + 0.690i | 0.025 - 0.004i | -0.008 - 0.017i |

Figure 20. Energy levels and eigenfunctions for the ground state crystal-field multiplet of $^{169}$Tm at $c_2$ sites in Tm$_3$Al$_2$. 
Figure 21. Computer fit of the temperature dependence of the quadrupole coupling parameter for $^{159}\text{Tm}$ at $c_1$ sites in Tm$_3$Al$_2$. 
Figure 22. Computer fit of the temperature dependence of the quadrupole coupling parameter for $^{169}\text{Tm}$ at $c_2$ sites in $\text{Tm}_3\text{Al}_2$. 
thalium was taken to be 1.5 barns (56), $\sigma_{4f}^{-3}$ was taken to be $86.766(10^{24}) \text{cm}^{-3}$ (45), and $-\gamma_{\infty}$ was taken to be -75.3 (4). These values are also tabulated in Table 10.

Table 10. Experimentally determined shielding parameters compared with theoretically calculated shielding parameters

<table>
<thead>
<tr>
<th>Thulium site</th>
<th>$\sigma_2$</th>
<th>$\sigma_4$</th>
<th>$\sigma_6$</th>
<th>$R_Q$</th>
<th>$q_{zz}^{ce}$ ($10^{24}\text{cm}^{-3}$)</th>
<th>$(1-\gamma_{\infty}) q_{zz}^{lat}$ ($10^{24}\text{cm}^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c_2$</td>
<td>.58</td>
<td>.01</td>
<td>0.0</td>
<td>.77</td>
<td>0.247</td>
<td>2.46</td>
</tr>
<tr>
<td>$c_1$</td>
<td>.64</td>
<td>.01</td>
<td>0.0</td>
<td>.68</td>
<td>-1.45</td>
<td>2.91</td>
</tr>
<tr>
<td>Theory</td>
<td>.545$^a$</td>
<td>.088</td>
<td>-.043</td>
<td></td>
<td>0.24$^b$</td>
<td></td>
</tr>
</tbody>
</table>

$^a\sigma_2$, $\sigma_4$, $\sigma_6$ calculated in reference (10)

$^b$Data of reference (57)

The value calculated here for $\sigma_2$ compares reasonably well with the calculated values of Sternheimer et al. (10). The experimental values are slightly higher than the theoretical values, and they agree very well with previous experimental values determined by Uhrich et al. (13), for TmRu$_2$ ($\sigma_2=0.57$), TmRe$_2$ ($\sigma_2=0.58$), and TmMn$_2$ ($\sigma_2=0.64$ with $Z_{MN}=0$). The values determined for $R_Q$ are larger than those determined for the compounds above by a factor of about 15 - 20%.
The calculations for $c_4$ and $c_6$ yield roughly zero. This is not too surprising since the function being fitted is rather insensitive to these parameters. Fits were attempted with the $N=4,6$ terms of the potential expansion set to zero. The rest of the parameters were essentially unchanged in the fit as can be seen in Tables 8 and 9. Fits were also attempted with the two sets of quadrupole data interchanged. In this case the $N=4$ parameter was considerably more active. In each case it moved toward the values given in Tables 8 and 9. Hence, it is felt that the sites have been assigned properly.

One other aspect of the data is the large discrepancy between the conduction electron contributions for the different sites. Not only are they different in sign, but they are different by an order of magnitude. This seems to indicate that there is some difference in the electronic environment of the two sites. This might be further borne out by the varying discrepancy between the point-ion value of $n$ for each site and the fitted value. Further discussion of this point will be left to Chapter VI.

The conduction electron contribution and the lattice contribution to the EFG tensor differ in sign for the $c_1$ sites, but not for the $c_2$ sites. The sign difference for the $c_1$ sites is consistent with the TmX$_2$ intermetallic data (13); however, in thulium metal these contributions were found to have the same sign.

Calculations based on the fitted parameters indicate that the line at the $c_1$ site should be split at room temperature. This was not observed. However, the splitting is essentially zero at the $c_2$ sites. The room temperature spectrum was very broad which indicates that the unsplit $c_2$ line
line covers up the splitting of the $c_1$ line. This suggests that going to higher temperatures would not be too fruitful.

D. Magnetic Hyperfine Interactions

Some indication of the effective magnetic field seen by the magnetic thulium nucleus is given by the ME lineshape data. This data, however, is not too reliable as will be remarked below. Coupled with the Knight shift data, some attempt will be made to indicate a general trend only. Some further experimentation is required in order to definitely specify the strength of the effective field in the paramagnetic state as a function of temperature. This point will be discussed briefly after the Knight shift data is presented.

The Knight shift of the aluminum resonance was measured as a function of temperature between 180°K and 400°K at 15 MHz with respect to AlCl$_3$ in a water solution. Data below 180°K was not obtainable since the central line became too broad to be readily observable. The shift to higher fields seen in other studies of the rare-earth alummines (18,19) was observed here. The resonance broadened as the temperature decreased indicating that the compound would eventually order. An attempt to see the resonance at 77.00°K failed.

The data seemed to be less reliable at high temperatures, i.e., more scatter was observed. Maintaining a constant flow of warm gas during the time for one pass, about 12 minutes, was not too easy at high temperatures; hence, there was more drift in the temperature. The weak signal required the long scan time and hence the uncertainty in the temperature. The
results of the runs are displayed in Table 11. Notice the change in line-width as a function of temperature.

A plot of the inverse Knight shift versus temperature was made (Figure 23). A least mean squares fit was made which gives a reasonable fit to the data except at higher temperatures. Extrapolating to infinite Knight shift (1/K=0) yields an ordering temperature of roughly 1.5°K. This compares with about 3.0°K given by Barbara et al. (58). The straight line indicates that the Knight shift follows a Curie-Weiss law as a function of temperature.

No susceptibility data is available as a function of temperature for Tm₃Al₂. Using the eigenvalues and the eigenfunctions of Figures 21 and 22, the temperature average of Jₓ was calculated. Using the temperature as a parameter, K was plotted versus <Jₓ>ᵣ as shown in Figures 24 and 25. A straight line was expected from Equation 40. A least mean squares fit was performed which yielded a value for the temperature independent Knight shift, Kₒ, of 0.576% for the c₁ site and .615% for the c₂ site. Surprisingly enough, the values of the slope of the two plots are opposite in sign. Using the slopes of the lines, values for Jₑₓ can be calculated. They are -0.286 eV and 0.458 eV for the c₁ and c₂ sites respectively. These values compare with Jₑₓ=-0.25 calculated for TmAl₂ (19). Values for Jₑₓ have been calculated for other rare-earth aluminides and usually are between -0.1 and -1.0 eV (19).

The eigenfunctions and eigenvalues of Tables 8 and 9 were also used to fit the effective magnetic hyperfine field at the thulium sites to the following equation:
Table 11. Temperature dependent Knight shift data of $^{27}$Al in Tm$_3$Al$_2$

<table>
<thead>
<tr>
<th>Temperature °K</th>
<th>$H_M$ kOe</th>
<th>$K$ %</th>
<th>$\Delta H$ Oe</th>
</tr>
</thead>
<tbody>
<tr>
<td>179.1±0.2</td>
<td>13.7577</td>
<td>-1.677</td>
<td>104.0</td>
</tr>
<tr>
<td>185.0±0.1</td>
<td>13.7430</td>
<td>-1.614</td>
<td>93.6</td>
</tr>
<tr>
<td>195.0±0.6</td>
<td>13.7292</td>
<td>-1.576</td>
<td>86.4</td>
</tr>
<tr>
<td>211.5±0.1</td>
<td>13.7196</td>
<td>-1.447</td>
<td>84.4</td>
</tr>
<tr>
<td>240.4±1.1</td>
<td>13.6968</td>
<td>-1.283</td>
<td>60.7</td>
</tr>
<tr>
<td>299.1</td>
<td>13.6610</td>
<td>-1.021</td>
<td>57.6</td>
</tr>
<tr>
<td>299.6</td>
<td>13.6604</td>
<td>-1.020</td>
<td>57.0</td>
</tr>
<tr>
<td>304.3±3.5</td>
<td>13.6587</td>
<td>-0.996</td>
<td>58.7</td>
</tr>
<tr>
<td>336.1±1.2</td>
<td>13.6431</td>
<td>-0.889</td>
<td>52.9</td>
</tr>
<tr>
<td>362.5±2.1</td>
<td>13.6365</td>
<td>-0.844</td>
<td>49.3</td>
</tr>
<tr>
<td>366.3±1.0</td>
<td>13.6317</td>
<td>-0.809</td>
<td>47.9</td>
</tr>
<tr>
<td>373.2±1.35</td>
<td>13.6307</td>
<td>-0.802</td>
<td>47.1</td>
</tr>
<tr>
<td>398.9±1.3</td>
<td>13.6255</td>
<td>-0.764</td>
<td>45.0</td>
</tr>
<tr>
<td>404.1±2.4</td>
<td>13.6219</td>
<td>-0.738</td>
<td>45.5</td>
</tr>
</tbody>
</table>
\[ H_{\text{eff}} = c \langle 0 \rangle_T \]

where \( \langle 0 \rangle_T \) is a temperature averaged angular momentum operator. Several different operators were employed. A similar problem arose as with the Knight shift data in that the parameter \( c \) was positive for one site and negative for the other. \( J_z \) gave the best fit, but as can be seen in Figure 26 the data has considerable scatter. Calculations here for \( J_{ex}^1 \) using Equation 28 yielded values of \( 0.568 \) eV for the \( c_1 \) site and \( -0.450 \) eV for the \( c_2 \) site. These are probably reasonable values, but it is not clear what significance they have.

It should be remarked that these values for \( J_{ex} \) and \( J_{ex}^1 \) are very sensitive to the eigenfunctions calculated from the quadrupole coupling parameter fitting routine. The eigenfunctions generated from the \( C_2^0, C_2^2 \) only fit yielded values very much different from above. This suggests that the higher order terms perhaps are important in determining the magnetic properties of intermetallic compounds.
Figure 23. Least mean squares fit of the inverse Knight shift of the $^{27}$Al resonance in Tm$_3$Al$_2$ versus temperature.
Figure 24. Least mean squares fit of the Knight shift of the $^{27}\text{Al}$ resonance in $\text{Tm}_3\text{Al}_2$ versus $<J_z>_T$ for the ground state crystal-field multiplet for $^{169}\text{Tm}$ at $c_1$ sites in $\text{Tm}_3\text{Al}_2$. 
Figure 25. Least mean squares fit of the Knight shift of the $^{27}$Al resonance in $\text{Tm}_3\text{Al}_2$ versus $<J_z>_T$ for the ground state crystal-field multiplet for $^{169}\text{Tm}$ at $c_2$ sites in $\text{Tm}_3\text{Al}_2$. 
Figure 26. Computer fits of the magnetic hyperfine interaction at $^{169}$Tm nucleus for $c_1$ and $c_2$ sites in Tm$_3$Al$_2$ versus temperature.
Figure 26. (cont.)
VI. REMARKS

A. The ME Data

The parameters obtained from the ME data are given in Tables 1 and 2. Due to the large number of parameters, fits could be easily obtained, especially if the data was not too well resolved. Deciding what the actual parameters are, then, becomes a serious problem as there is no way of estimating the value of the different parameters with the exception of the quadrupole coupling parameter. At this time several pertinent remarks are in order.

The most useful parameter for the purposes here is the quadrupole coupling parameter. Fortunately, this parameter is determined by the position of the peaks in the ME spectrum, hence, a reliable estimate of this parameter can be made from the raw data. Throughout the computer fits, this parameter remained essentially constant for each individual temperature when the other parameters were varied. The fluctuation rate will have some effect on the positions of the peaks, but this is negligible at the fluctuation rates employed here.

The lineshape parameter displayed an interesting temperature dependence. This can probably be attributed to the quality of the data which was more resolved at the ends of the temperature range than in the middle. Since the temperature dependence of the observed linewidth, as normally measured, is accounted for by the changing magnetic field and fluctuation rate, it might be expected that the linewidth would remain relatively constant. The broadening of the spectrum as temperature decreases is due to the spreading of the five line pattern of Figure 1. This is caused by either an increase
in the value of the magnetic field or a decrease in the fluctuation rate, and it is not an actual broadening of the spectrum.

The two parameters which are the most troublesome, and, therefore, the least reliable, are the magnetic field and the fluctuation rate. As was implied above, these parameters are strongly correlated with a decrease in the fluctuation rate having a similar affect on the lineshape as an increase in the magnetic field. Therefore, changing one parameter would cause the other parameter to change in a like manner to compensate; thus the data could be fit with different parameters. Thus without any independent measurements to specify one of these parameters, they cannot be independently determined from the ME data.

It would be useful to observe the ME spectrum in the ordered state. Unfortunately, the spectrometer for this investigation is only capable of a maximum velocity in the neighborhood of ±15 cm/sec. This is far too low to observe the magnetic hyperfine splitting in thulium compounds as it is larger than 100 cm/sec. Earlier attempts to see any kind of magnetic hyperfine spectrum for thulium in this lab have failed. Also, in order to observe the hyperfine interaction, temperatures below 3°K would probably be required.

Measurements of the internal magnetic hyperfine interaction in thulium metal indicate that its strength is roughly 150 cm/sec (59). Barbara et al. have measured the thulium moment in Tm$_3$Al$_2$ to be 7.8 Bohr magnetons compared with 7.0 Bohr magnetons in thulium metal. This is consistent with the more pronounced asymmetry in the Tm$_3$Al$_2$ ME spectrum which indicates a larger magnetic interaction. However, it is rather difficult to say exactly
what values this field should assume at these temperatures. Varying the fluctuation rate, using the experimental line collected at 77.15°K, between $100 \text{(sec)}^{-1}$ and $1500 \text{(sec)}^{-1}$ varies the magnetic hyperfine interaction strength between 100 cm/sec and 225 cm/sec, and between 50 cm/sec and 100 cm/sec for the $c_1$ and $c_2$ thulium sites, respectively. It should be emphasized that the quadrupole coupling parameter changed less than 1% throughout this range.

The fitted fluctuation rates indicate a relaxation time between 0.5 msec and 5 msec. These times are probably appropriate for a metallic compound. Since this is a multilevel system, several relaxation rates will occur with different ones dominating as a function of temperature. Thus, it is difficult to say just how the fluctuation rate should vary as a function of temperature. Here the fluctuation rate remains relatively constant over the temperature range of the experiments. Unfortunately, relaxation time measurements in Tm$_3$Al$_2$ are difficult to perform and hence there is little hope of making an independent measurement to obtain a value for the relaxation time to compare with the fitted values.

The ME spectra of Er$_3$Al$_2$ has been observed by R. A. Reese (unpublished data) from 4°K to 30°K. Here two values of the internal field are observed, apparently corresponding to the same two inequivalent sites observed in the Tm$_3$Al$_2$ data. The difference in these fields is about 15% compared to about a 50% difference for the two sites in the paramagnetic state of Tm$_3$Al$_2$. It would be interesting to see if this ratio would be maintained into the ordered state. These fields remained roughly in the same ratio throughout the variation of the fluctuation rate for the 77.15°K spectrum.
B. The Crystalline Electric Field

The main thrust of this investigation has been directed toward an understanding of the role of the conduction electrons in rare-earth intermetallics. In comparing this data with previous data it was noted that the crystal-field splitting is much larger than previously found for rare-earth metallic compounds (12,13), but still smaller than those of rare-earth salts (7). Some covalency effects may be present since the fitted asymmetry parameter does not agree with that calculated using the point-ion model.

The noticeable difference in the asymmetry parameter for the $c_1$ sites was puzzling. The point-ion calculations indicated a value of roughly 1.25 whereas the fitted value is roughly 0.151. This seems to indicate that the point-ion model may not be totally valid for discussing the crystal field.

It is useful to compare the nearest neighbors of the two thulium sites:

$\text{Tm}(c_1)$ has

1 $\text{Al}(c_1)$ at 3.14, 2 $\text{Al}(c_1)$ at 3.15, 1 $\text{Al}(c_2)$ at 3.22, 1 $\text{Al}(c_2)$ at 3.23, 1 $\text{Tm}(c_1)$ at 3.58, and 1 $\text{Tm}(c_2)$ at 3.69 Å.

$\text{Tm}(c_2)$ has

1 $\text{Al}(c_1)$ at 3.10, 1 $\text{Al}(c_2)$ at 3.14, 2 $\text{Tm}(b)$ at 3.46, 2 $\text{Tm}(b)$ at 3.66, and 1 $\text{Tm}(c_1)$ = 3.69 Å.

If conduction electrons are localized about the aluminum ions as suggested in Chapter V, then it is reasonable that the site with aluminum nearest neighbors would have a larger conduction electron contribution to the EFG tensor. This can be compared to the much smaller conduction electron contribution observed at the $c_2$ sites which have only two aluminum nearest-
neighbors and the five thulium nearest neighbors. These nearest aluminum ions should be larger in spatial extent than the thulium ions and, therefore, they may overlap the outer 5s5p shells of the thulium ion. This might cause some variance in the value of the calculated asymmetry parameter with that measured experimentally. It also may be responsible for the similarity in the values of the $C^0_2$ parameter at the two sites, although the calculated values are more disparate. The point-ion model may need to be modified for this effect.

It should be remarked that the fitting routine is far from ideal. Since a perturbation solution of the crystal-field Hamiltonian is required, the off-diagonal elements of the energy matrix should be small. This is not the case since the $C^2_2$ parameters are comparable to the diagonal $C^0_2$ parameters. This means that the gradients calculated for the minimization are probably incorrect, and hence the routine does not function properly. Fortunately, this has no bearing on the values of the parameters which fit the data, but only means that the program will have a very difficult time finding a proper minimum. Coupled with this problem was the difficulty in getting some of the parameters to change, notably $C^0_4$, $C^0_6$ and $n$. This was overcome by adjusting the initial values of the metric which seemed to weigh the parameters in importance. What effect this procedure has on the final fit is hard to say, but the results were much more satisfactory in that the program had an easier time finding a good minimum. At any rate, the data given in Tables 8 and 9 does give a set of values which fits the quadrupole coupling parameter data.
An attempt was made to fit the N=2 terms only in the manner of Uhrich et al. (13). Fits were obtained with the parameters not constrained to zero remaining roughly the same. This indicates that the $C_4^0$ and $C_6^0$ parameters are not as important in the fitting as the $C_2^0$, $\rho_1^0$ and $\rho_2^0$; however, they do seem to affect the fitting procedure somewhat. It is possible to get fits with different values for these parameters, therefore, not much can be concluded about their values or the shielding parameters associated with them. This particular experiment is not too sensitive to the higher-order terms in the expansion as they are small compared to the N=2 terms, either in absolute magnitude, or in the energy matrix through the much smaller reduced matrix elements for the N=4 and N=6 terms.

It seems, however, that the N=4,6 terms are important for the calculation of the eigenfunctions. This becomes important in calculating the $\langle J_z \rangle_T$ terms as a function of temperature. The problem encountered with the slope of the $1/K$ vs. $\langle J_z \rangle_T$ plot being positive may result from not having proper values for $C_4^0$ and $C_6^0$. It would be useful to have an independent measurement of the crystal-field parameters to compare with the values listed in Tables 8 and 9. Probably the only feasible type of such an alternative measurement is a neutron scattering experiment of the sort which has been employed recently in the study of some other rare-earth intermetallics by Turberfield et al. (60).

In conclusion it can be said that there is a definite indication that shielding effects are important for the $C_4^0$ and $C_6^0$ terms in the crystal-field expansion. This experiment is not sensitive enough to draw definite conclusions regarding the higher-order shielding parameters. The disparity
between the asymmetry parameter values as calculated from the point-ion model and determined experimentally indicates that the point-ion model is only approximate. The value of \( n \) for the \( c_1 \) site is definitely much less than 1.0 since fits were impossible to obtain with values of \( n \) this large. Since the nearest neighbors of the \( c_1 \) site are aluminum ions, the possibility of some sort of covalency or overlap is probably good. In fact, this might be partially responsible for the large crystal-field effects observed in \( \text{Tm}_3\text{Al}_2 \).

The NMR data indicates that there are narrow conduction bands localized about the aluminum ion. There is also some indirect evidence in the relative magnitudes of the conduction electron contributions to the EFG tensors at the two thulium sites. The linearity of the Knight shift \( \langle J_z \rangle_T \) plot describes the polarization of the conduction electrons by the 4f shell in the thulium ion. This exchange interaction probably has some effect on the thulium nucleus, i.e., an indirect exchange interaction in the paramagnetic state. At any rate, there definitely is a relaxation effect distorting the quadrupole spectrum. It is this effect which caused the low-temperature broadening and asymmetries in the earlier work on thulium intermetallics. That it is caused by conduction electrons seems certain since this same effect is not observable in salts. Unfortunately, the data is a little too inconclusive on this point due to the lack of agreement between the theory and experiment along with lack of knowledge of the proper values for the fluctuation rate or the magnetic field.
C. Summary of the Experimental Results

It is felt that this investigation has produced a good set of crystal-field levels for two of the three inequivalent sites in Tm$_3$Al$_2$. The values calculated for $\sigma_2$, the second-order shielding parameter, and the conduction electron contribution to the EFG are quite acceptable. Due to the insensitivity of this experiment to the higher order terms, nothing conclusive can be said about $\sigma_4$ and $\sigma_6$. The question of the importance of shielding for these terms remains unanswered from the results of this investigation.

The value of the s-f exchange parameter estimated from the temperature dependence of the Knight shift is of the right order of magnitude, although the one positive value obtained is unexplained at present. The rate of fluctuation and the strength of the magnetic field interacting with the nucleus which was determined from the ME lineshape are also of the right order of magnitude. Unfortunately, they cannot be determined independently by the techniques employed in this work. This investigation does emphasize, however, that the conduction electrons play an important role in the magnetic properties of thulium intermetallics, and consequently rare-earth intermetallics, and that the nucleus is influenced by large internal fields at temperatures far above the ordering temperature.
VII. LITERATURE CITED


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IX. APPENDIX

The computations involved in the analysis of the experimental data presented in this paper were carried out with the aid of an IBM 360/65 computer. In this section the listing of the Fortran computer programs used to fit the raw Moessbauer data is given. Some of the programs used are available in the SHARE library and are not included here.

The required decks are:

1. MAIN
2. FCN
3. VMIN
4. READY
5. AIM
6. FIRE
7. DRESS
8. MATMPY

The listings of decks 1-2 follows:
SOURCE DECK FOR VMMIN FITTING ROUTINE TO FIT RELAXATION SPECTRA TO THULIUM DATA. SEE BLUME AND TJON, PHYS. REV., 165, 446 (1968).

This is the main calling program for subroutine VMMIN. The random step check for minimum has been removed from the subroutine since output contains graph. The purpose of the main routine is to read in the data and prepare it for processing to be fit with subroutine VMMIN.

DESCRIPTION OF PARAMETERS:

BG - Background (automatically calculated if BG = 0).
E - Minimization epsilon.
EG - Parameter used in calculation of error matrix if NH = 0.
GO - G-factor of ground state.
G1 - G-factor of excited state.
IDD - Number of data sets being fitted.
IR - Number of channels on either side of zero considered.
IX10 - Velocity zero of first half of the spectrum.
IX20 - Velocity zero of second half of the spectrum.
LIMIT - Maximum number of iterations desired (set to 40 if zero).
N1 - Number of sets of lines in spectrum (1, 2, or 3).
ND - Parameter containing 10(5) and 10(6) added counts.
VC - Velocity calibration.

DIMENSION H(18,18), YDATA(400), S3(200), TITLE(57),
1 G(18), X(18), GA(7), HA(7), A(6), GLB1(5), GLB2(5), XLB(5), YLB(5)
COMMON /M10/ XD(400), YD(400), FFF(400), YC(400), A1(18), IND(18),
C ITB(18), PG0, G1, N1, NDP, NVAR1, NVAR2, FSAVE(3, 200)
COMMON /M20/ NVAR10, NVAR20, N10
DATA XLB/", VE", 'LOCI', 'TY(C', 'M/SE', 'C') '/", YLB/", ' IN', 'TE CNS', 'ITY ', '/'
L = 0
1 M = 1 + 19 * L
L = L + 1
M1 = M + 18

READ STOPPER, TITLE CARD(S)
READ(5,105) ISTOP,(TITLE(I),I=M1,M1)
IF(ISTOP) 2,4,1
2 WRITE(6,106) (TITLE(I),I=1,M1)
STOP
4 READ (5,107) IR,IX10,IX20,IMAX,N1,ND,LIMIT,IDD,NV,IP,NDS,NH,BG,
C E,EG
IF (IP .EQ. 1) GO TO 6
IF (IR .EQ. 0) IR=399-IX20
IF (LIMIT .EQ. 0) LIMIT=50
NDP=2*IR+1
GO TO 7
6 NDP=IMAX
7 READ (5,112) GO,G1
WRITE(6,110) (TITLE(I),I=1,M1)
C
C PREPROCESS DATA IF IP EQUAL TO 0.
IF (IP .EQ. 1) GO TO 393
C
C ADD GA*10(5) AND HA*10(6) COUNTS TO DATA SET IF ND UNEQUAL TO ZERO.
16 IDD=IDD+1
IF(ND) 17,18,17
17 READ(5,111) (GA(I),HA(I),I=1,IDD)
GO TO 20
18 DO 19 I=1,IDD
GA(I)=0.0
19 HA(I)=0.0
20 TH=1.0E+05
TM1=1.0E+06
C
C PREPROCESS DATA: CENTER ABOUT ZERO OF VELOCITY, ADD TWO SPECTRA TOGETHER, AND CONVERT CHANNEL NUMBER TO VELOCITY.
DO 23 I=1,400
23 YD(I)=0.0
DO 24 J=1,IDD
READ(5,148) (XD(I),YDATA(I),I=1,400)
C SUM IDD SETS OF DATA.

DO 24 I=1,400

24 YD(I)=YD(I)+YDATA(I)+GA(J)*TH+TM1*HA(J)

IF(IX10-200) 26,25,25

25 IA=IX10-IR-200+1
    IB=IX10+IR-200+1
    GO TO 27

26 IA=IX10-IR+1
    IB=IX10+IR+1

C INVERT SECOND HALF OF DATA AND ADD TO FIRST HALF.

27 IF(IX20) 31,31,28

28 CONTINUE

DO 30 J=IA,IB

L=IX10+IX20-J+2

30 YD(J)=YD(J)+YD(L)

C CONVERT TO VELOCITY

31 READ(5,13)VC,XNW,(A(I),I=1,6)

X10=IX10

DO 34 I=IA,IB

S3(I)=XD(I)-X10

IF(XNW) 32,33,32

32 XD(I)=VC*XNW*SIN(S3(I)/XNW)

GO TO 34

33 XD(I)=VC*S3(I)*(1.0+A(1)*S3(I)+A(2)*S3(I)*S3(I)+A(3)*S3(I)**3+A(4)*S3(I)**4+A(5)*S3(I)**5+A(6)*S3(I)**6)

34 CONTINUE

C INVERT DATA POINTS IF VC IS NEGATIVE.

IF (VC) 340,343,343

340 DO 341 I=IA,IB

J=IA+IB-I

YDATA(I)=YD(J)

341 YC(I)=XD(J)

DO 342 I=IA,IB

YD(I)=YDATA(I)
WRITE TABLE OF RESULTS.

WRITE(6,114) IR,VC,IX10,IX20,(S3(I),XD(I),YD(I),I=IA,IB)
DO 35 I=IA,NDP
  J=I+IA-1
  XD(I)=XD(J)
  YD(I)=YD(J)
35 CONTINUE

CALCULATE BACKGROUND FROM DATA IF NBG EQUALS ZERO.

IF (BG) 385,37,385
37 BG=0.0
DO 38 J=1,5
  L=NDP+1-J
38 BG=BG+YD(J)+YD(L)
BG=BG/10.0
385 CONTINUE
DO 39 I=1,NDP
39 YD(I)=1.0-YD(I)/BG
GO TO 405

READ IN PREPROCESSED DATA FOR 400 CHANNELS IF IP=1.

READ (5,149) (XD(I),YD(I),I=1,400)
IF (IMAX .EQ. 400) GO TO 396
DO 394 I=1,IMAX
  J=399-IMAX+I
  XD(I)=XD(J)
394 YD(I)=YD(J)
396 WRITE (6,150) (XD(I),YD(I),I=1,IMAX)

CALCULATE INITIAL ERROR MATRIX.

IF (EG .EQ. 0.0) EG=0.03
N2=6*N1

READ IN INITIAL VARIABLE PARAMETERS.
READ (5,108) (AI(I),I=1,N2)
READ (5,109) (IND(I),I=1,N2)
READ (5,142) GLB1,GLB2
NVAR=0
DO 5 I=1,N2
IF (I .EQ. 6) NVAR1=NVAR
IF (I .EQ. 12) NVAR2=NVAR
IF (IND(I) .EQ. 0) GO TO 5
NVAR=NVAR+1
IF (I .EQ. 6) NVAR1=NVAR
IF (I .EQ. 12) NVAR2=NVAR
X(NVAR)=A1(I)
ITB(NVAR)=I
5 CONTINUE
DO 407 I=1,NVAR
DO 407 J=1,NVAR
407 H(I,J)=0.0
IF (NH . EQ. 0) GO TO 408
READ (5,152) (H(I,I),I=1,NVAR)
GO TO 415
408 DO 41 J=1,NVAR
41 H(J,J)=EG*EG*X(J)*X(J)
415 WRITE(6,116)
WRITE(6,147) (TITLE(I),I=1,M1)
WRITE (6,117) NVAR,NDP
C CWRITE INITIAL PARAMETERS.
IF (IP .NE. 0) GO TO 42
WRITE (6,118) BG
42 WRITE (6,119) (A1(I),IND(I),I=1,N2)
C CWRITE INITIAL ERROR MATRIX.
WRITE (6,123) (H(I,I),I=1,NVAR)
NVAR10=NVAR1
NVAR20=NVAR2
N10=NVAR
L=0
CALL VMMIN(NVAR,X,H,0,E,IER,G,F,GS,NV,LIMIT)
GO TO (50,51,101,50),IER
51 WRITE (6,125)
50 WRITE (6,124)
   DO 56 I = 1, NVAR
   DO 56 J = 1, NVAR
56 H(I,J) = 2.0*H(I,J)
   WRITE (6,127)
   DO 59 I = 1, NVAR
59 WRITE (6,128) I, H(I,J), J = 1, NVAR
   WRITE (6,133) (G(I), I = 1, NVAR)
   WRITE (6,134) F, GS
   WRITE (6,120) (X(I), I = 1, NVAR)
   L = 0
   WRITE (6,135)
C
C GENERATE PLOT
   XSF = (XD(NDP) - XD(1))/20.
   CALL GRAPH(NDP, XD, YD, 2, 7, 20., 9., XSF, XD(1), 0., 0., XLB, YLB, GLB1, GLB2)
   CALL GRAPH(NDP, XD, YC, 0, 2, 0., 0., 0., 0., 0., 0., 0., 0., 0., 0.)
100 L = 0
   IF (NDS .EQ. 0) GO TO 1015
C
C GRAPH THE INDIVIDUAL SPECTRA COMPOSING THE COMPLEX
C LINESHAPE IF NDS=1.
   DO 1006 I = 1, N1
      DO 1005 K = 1, NDP
1005 FFF(K) = FSAVE(I,K)
      CALL GRAPH(NDP, XD, FFF, 0, 2, 20., 9., XSF, XD(1), 0., 0., XLB, YLB, GLB1, GLB2)
1006 CONTINUE
   GO TO 1015
101 L = 0
   WRITE (6,120) (X(I), I = 1, NVAR)
1015 READ (5,151) N1
   IF (N1 .EQ. 0) GO TO 1
   GO TO 405
C
105 FORMAT (I4,19A4)
106 FORMAT(1H019A4) 2230
107 FORMAT(414,6I2,3E15.7) 2240
108 FORMAT(12F6.0) 2250
109 FORMAT(18I4) 2260
110 FORMAT(1H1,19A4/1X,19A4/1X,19A4) 2270
111 FORMAT(14F5.0) 2280
112 FORMAT(2F10.0) 2290
113 FORMAT(8F8.4) 2300
114 FORMAT(1H0,24HRESULTS OF PREPROCESSING) 2310
115 FORMAT(4H0IR=I3,4X,3HVC=F8.5,4X,6HX(10)=I3,4X,6HX(20)=I3//6X,6HX-X 2320
1(0),12X,1HV,11X,1HY//(1H ,6X,F4.0,5X,F12.4,3X,E12.6)) 2330
116 FORMAT(1H1,50HLINE SHAPE FITTING BY VARIABLE METRIC MINIMIZATION) 2340
117 FORMAT(20HNO. OF VARIABLES ISI3,18H NO. OF POINTS ISI4) 2350
118 FORMAT(11H0BACKGROUND,1PE14.5//11H+PARAMETERS) 2360
119 FORMAT(1H0E15.5,I2,2X,E15.5,I2,2X,E15.5,I2,2X,E15.5,I2,2X,E15.5,I2 2370
1,2X,E15.5,I2,2X) 2380
120 FORMAT(1H0PARAMETERS/(1P6E15.5)) 2390
123 FORMAT(34H0DIAGONAL ELEMENTS OF ERROR MATRIX//1P6E15.5)) 2400
124 FORMAT(13H0FINAL VALUES) 2410
125 FORMAT(20H0PROCESS INTERRUPTED/21H0PRESENT VALUES * * *) 2420
127 FORMAT(13H0ERROR MATRIX) 2430
128 FORMAT(1H0I2/(5X,1P6E15.5)) 2440
133 FORMAT(9H0GRADIENT/(1P6E15.5)) 2450
134 FORMAT(3H0F=1PE14.5,5H GS=E14.5) 2460
135 FORMAT(20H0END OF MINIMIZATION) 2470
142 FORMAT(10A4) 2480
147 FORMAT(1H0,19A4/1X,19A4/1X,19A4) 2490
148 FORMAT(5(F4.1,F9.3)) 2500
149 FORMAT(3(2E13.6)) 2510
150 FORMAT(1H0,24X,1HV,11X,1HY//(1H ,17X,F12.4,3X,E12.6)) 2520
151 FORMAT(12) 2530
152 FORMAT(12F6.0) 2540

END
SUBROUTINE FCN(NVAR,VAL,X,GRAD)

C FUNCTION EVALUATION. THIS ROUTINE CALCULATES THE FUNCTION TO
C BE MINIMIZED AS WELL AS ITS FIRST DERIVATIVE. THE FUNCTION IS
C CHOSEN SO THAT THE DIAGONAL ELEMENTS OF THE H-MATRIX ARE THE
C EXPECTATION VALUES OF THE ERROR IN THE CALCULATED PARAMETERS.

PARAMETERS:

A(1) - LINELWIDTH OF EXCITED STATE.
A(2) - ASSYMMETRY PARAMETER.
A(3) - ELECTRIC QUADRUPOLE INTERACTION PARAMETER.
A(4) - MAGNETIC INTERACTION PARAMETER.
A(5) - RATE OF FIELD FLUCTUATION.
A(6) - INTENSITY NORMALIZATION FACTOR.

REMARKS:
I - THIS PROGRAM WAS WRITTEN TO HANDLE THREE INEQUIVALENT
SITES IN THE LATTICE UNDER CONSIDERATION.
II - ONLY M1 TRANSITIONS FROM SPIN 3/2 TO 1/2 STATES
CAN BE DONE HERE. THIS INCLUDES IRON AND THULIUM.

IMPLICIT REAL*4(M)
DIMENSION ME(2,4),FUNC(400),F(400),G(18),GRAD(18),X(18),M1(4),
C DD(3),E1(3),E2(3),E3(3),P1(3)
COMMON /M10/ XD(400),YD(400),FFF(400),YC(400),A(18),IND(18),
C ITB(18),BG,GO,G1,N1,N,NVAR1,NVAR2,FSAVE(3,200)
DATA M0/0.5,-0.5/,M1/1.5,0.5,-0.5,-1.5/,ME/1.0,0.0,0.0,6666667,
C 1.0,3333333,0.3333333,0.6666667,0.0,1.0/

DO 5 I=1,NVAR
5 A(ITB(I))=X(I)
DO 10 I=1,18
10 GRAD(I)=0.0
DO 12 I=1,N
12 YC(I) = 0.0
   VAL = 0.0
   DO 13 I1 = 1, N1
   I2 = (I1 - 1) * 6
   P1(I1) = A(I2 + 1) / 2
   C2(I1) = 3. * A(I2 + 3) * A(I2 + 2) * A(I2 + 2)
   C3(I1) = P1(I1) + 2. * A(I2 + 5)
13 C8(I1) = P1(I1) + A(I2 + 5)
   IER = 0
   IERG = 0

C
   EVALUATE FUNCTION AT EACH DATA POINT FOR N1 SETS OF LINES.
   DO 75 K = 1, N
   DO 14 I = 1, 18
14 G(I) = 0.0
   P2 = -X0(K)
   DO 68 I1 = 1, N1
   F(K) = 0.0
   I2 = 6 * (I1 - 1)
   L1 = I1 * 6
   L2 = I1 * 6

C
   SUM OVER MO AND M1.
   DO 60 I = 1, 2
   C0(I1) = G0 * M0(I) * A(I2 + 4)
   DO 60 J = 1, 4
   IF (ME(I, J) .EQ. 0.) GO TO 60
   IF (M1(J) .GE. 0.) GO TO 15
   C11(I1) = G1 * (M1(J) + 2.) * A(I2 + 4)
   GO TO 20
15 C11(I1) = G1 * (M1(J) - 2.) * A(I2 + 4)
   20 C11(I1) = G1 * M1(J) * A(I2 + 4)
   C4(I1) = P2 + BETA(I1)
   C5(I1) = P2 - BETA(I1)
   C6(I1) = C1(I1) - C0(I1)
   C7(I1) = C11(I1) - CO(I1)
A1(I1)=P1(I1)*C3(I1)-C4(I1)*C4(I1)+C6(I1)*C6(I1)
A2(I1)=2.*C2(I1)*(P1(I1)*C3(I1)-P2*P2+BETA(I1)*BETA(I1)
C +2.*A(I2+5)*A(I2+5)-C6(I1)*C7(I1)+C2(I1)/2.1)
A3(I1)=2.*C4(I1)*C8(I1)
A4(I1)=4.*P2*C8(I1)*C2(I1)
D1(I1)=P1(I1)*C3(I1)-C5(I1)*C5(I1)+C7(I1)*C7(I1)
D2(I1)=2.*C8(I1)*C5(I1)
B1(I1)=D1(I1)*C3(I1)-D2(I1)*C4(I1)+C2(I1)*P1(I1)
B2(I1)=D1(I1)*C4(I1)+D2(I1)*C3(I1)+C2(I1)*C5(I1)
E1(I1)=D1(I1)*A1(I1)+A2(I1)-D2(I1)*A3(I1)
E2(I1)=D2(I1)*A1(I1)+A4(I1)+D1(I1)*A3(I1)
E3(I1)=B1(I1)*E1(I1)+B2(I1)*E2(I1)
D(I1)=E1(I1)*E1(I1)+E2(I1)*E2(I1)
F(K)=F(K)+ME(I,J)*E3(I1)/DD(I1)

C
CALCULATE GRADIENTS.
K1=0
IF (I1 .EQ. 2) K1=NVAR1
IF (I1 .EQ. 3) K1=NVAR2
K1SAVE=K1+1
K2SAVE=NVAR1
IF (I1 .EQ. 2) K2SAVE=NVAR2
IF (I1 .EQ. 3) K2SAVE=NVAR

C
CALCULATE PARTIAL DERIVATIVES OF THE LINESHAP WITH RESPECT
TO THE PARAMETERS.
DO 55 L=1,2
IF (IND(L) .EQ. 0) GO TO 55
K1=K1+1
GO TO 25,30,35,40,45,48,25,30,35,40,45,48,25,30,35,40,45,48)
L = (25,30,35,40,45,48,25,30,35,40,45,48,25,30,35,40,45,48)
LER=1
D61=2.*(C3(I1)*C8(I1)-C5(I1)*C4(I1))+D1(I1)+C2(I1)
D62=2.*(C8(I1)*C4(I1)+C5(I1)*C3(I1))+D2(I1)
DE1=2.*(C8(I1)*(D1(I1)+A1(I1)+2.*C2(I1)))-C4(I1)*D2(I1)
C -C5(I1)*A3(I1)
D62=2.*(C8(I1)*(D2(I1)+A3(I1)))+C5(I1)*A1(I1)+C4(I1)*D1(I1)+2.*P2
C *C2(I1))
DA = 0.5
GO TO 50
30 IF (A(I2+2) * E0. 0.) GO TO 32
DB1 = 2.*C2(I1)*P1(I1)/A(I2+2) 3720
DB2 = 2.*C2(I1)*C5(I1)/A(I2+2) 3730
DE1 = 2.* (A2(I1)+C2(I1)*C5(I1))/A(I2+2) 3740
DE2 = 2.*A4(I1)/A(I2+2) 3750
DA = 1.0
GO TO 50
32 DB1 = 0.0
DB2 = 0.0
DE1 = 0.0
DE2 = 0.0
GO TO 50
35 DB1 = 2.*(C5(I1)*C3(I1)+C8(I1)*C4(I1)+C2(I1)*P1(I1)/BETA(I1))-D2(I1) 3830
DB2 = 2.*(C5(I1)*C4(I1)-C8(I1)*C3(I1)+D1(I1)-C2(I1) 3840
C + 2.*C2(I1)*C5(I1)/BETA(I1)
DE1 = 2.*(C8(I1)*A3(I1)-D2(I1)) + C5(I1)*A1(I1)-C4(I1)*D1(I1) 3860
C + (C2(I1)*C2(I1)+2.*A2(I1))/BETA(I1)-2.*BETA(I1)
DE2 = 2.*(C4(I1)*D2(I1)+C5(I1)*A3(I1)+C8(I1)*D1(I1)-A1(I1)) 3880
C +A4(I1)/BETA(I1)
DA = BETA(I1)/A(I2+3)
GO TO 50
40 DB1 = 2.*C7(I1)*C3(I1)+C8(I1)*C4(I1)*A(I2+4) 3920
DB2 = 2.*C7(I1)*C7(I1)+C4(I1)/A(I2+4) 3930
DE1 = 2.*(C6(I1)*(C6(I1)*D1(I1)-2.*C2(I1)*C7(I1)) 3940
C +C7(I1)*C7(I1)*A1(I1))/A(I2+4)
DE2 = 2.*(C6(I1)*C6(I1)*D2(I1)+C7(I1)*C7(I1)*A3(I1))/A(I2+4) 3960
DA = 1.0
GO TO 50
45 DB1 = 2.*(P1(I1)*C3(I1)+D1(I1)-C5(I1)*C4(I1)) 3990
DB2 = 2.*(P1(I1)*C4(I1)+C5(I1)*C3(I1)+D2(I1)) 4000
DE1 = 2.*(P1(I1)+(D1(I1)+A1(I1))-C4(I1)*D2(I1)-C5(I1)*A3(I1) 4010
C +C2(I1)*C3(I1))
DE2 = 2.*(P1(I1)*(D2(I1)+A3(I1))+C5(I1)*A1(I1)+C4(I1)*D1(I1) 4030
C +2.*P2*C2(I1))
DA = 1.0
GO TO 50
48 K3SAVE=K2SAVE
   K2SAVE=K2SAVE-1
   IERG=1
   GO TO 55
50 DE3=DB1*E1(I1)+DE1*B1(I1)+DB2*E2(I1)+DE2*B2(I1)
   DDD=2.*(E1(I1)*DE1+E2(I1)*DE2)
   G(K1)=G(K1)+ME(I,J)*(DE3-E3(I1)*DDD/DD(I1))/DD(I1)*DA
   IF (IER .EQ. 0) GO TO 55
   G(K1)=G(K1)-ME(I,J)*E3(I1)/(DD(I1)*A(I2+4))
   IER=0
55 CONTINUE
60 CONTINUE
   F(K1)=F(K)*0.25*A(I2+6)/P1(I1)
   DO 65 K2=K1SAVE,K2SAVE
65 G(K2)=G(K2)*0.25*A(I2+6)/P1(I1)
   FSAVE(I1,K)=F(K)
   YC(K)=YC(K)+F(K)
   IF (IERG .EQ. 0) GO TO 68
   G(K3SAVE)=F(K)/A(I2+6)
   K2SAVE=K2SAVE+1
   IERG=0
68 CONTINUE
   CALCULATE FUNCTION VALUE.
   FUNC(K)=(YD(K)-YC(K))
   FFF(K)=FUNC(K)/((N-NVAR)*(1.-YD(K)))
   VAL=VAL+FUNC(K)*FFF(K)
   DO 70 K1=1,NVAR
70 GRAD(K1)=GRAD(K1)-2.*G(K1)*FFF(K)
   DO 80 I=1,NVAR
80 GRAD(I)=BG*GRAD(I)
   VAL=BG*VAL
   RETURN
END