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MASTER

A STUDY OF CRYSTALLINE ELECTRIC FIELDS IN
SOME THULIUM ALUMINUM COMPOUNDS

Ph. D. Thesis Submitted to Iowa State University, August 1971

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A study of crystalline electric fields in
some thulium aluminum compounds

by

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A study of crystalline electric fields in
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ABSTRACT

The crystal field in Tm_3Al_2 was investigated by measuring the temperature dependence of the nuclear quadrupole splitting of the 8.42 keV gamma transition in ^{169}Tm and by NMR measurements of the quadrupole coupling parameter of ^{27}Al . The Moessbauer effect study was carried out between 77°K and 300°K. The observed asymmetric lineshape was fit to a theoretical relaxation lineshape by computer using several variable parameters. Crystal-field parameters for the $m \rightarrow C_s$ point symmetry in Tm_3Al_2 were determined by a best fit to the temperature dependence of the quadrupole interaction. Overall crystal-field splittings were found to be roughly 300 cm^{-1} for two of the three inequivalent thulium sites. Values for the crystal-field shielding parameters and for the conduction electron contributions to the EFG tensor were derived from the data.

The asymmetry observed in the Moessbauer lineshape was attributed to an indirect s-f exchange interaction between thulium ions in the paramagnetic state. In addition, the polarization of the conduction electrons brought about by this interaction causes a negative Knight shift of the ^{27}Al NMR spectrum. The s-f exchange parameters for the two thulium sites

were approximately -0.25 eV and $+0.45$ eV, as inferred from the measured temperature dependence of the ^{27}Al Knight shift in the range $180 - 400^\circ\text{K}$. The significance of the positive exchange parameter is not understood.

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 $3.9(10^{-9})$ sec. By employing the uncertainty principle, one obtains a corresponding linewidth of about $1.2(10^{-7})$ eV. This linewidth is smaller than the energy splitting due to the interaction of nuclei with their crystalline 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

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

where E_0 is the nuclear transition energy, Γ 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, α 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 Moessbauer 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 $5s^2 5p^6$ 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_3Al_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_3Al_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 inter-band transitions between the conduction band and the highly localized 4f band are responsible for the negative exchange parameter.

Tm_3Al_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 RAI_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 tripositive. It is assumed for these calculations that the rare-earth ion has a tripositive 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, α, β . The potential at some point r, θ, ϕ , ($r < R$) is given by the expression

$$V = Ze \sum_{N+1} (r^N/R^{N+1}) P_N(\cos\gamma) \quad (2)$$

where P_N are Legendre polynomials. To get the total potential at the point r, θ, ϕ ; 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

$$V = \sum_i Z_i e \sum_{N=0}^{\infty} (r^N / R^{N+1}) [P_N(\cos \alpha_i) P_N(\cos \theta) + 2 \sum_{M=1}^N \frac{(N-M)!}{(N+M)!} P_N^M(\cos \alpha_i) P_N^M(\cos \theta) (\cos M\phi \sin M\beta_i + \sin M\phi \sin M\beta_i)] \quad (3)$$

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 Θ_N^M such that

$$\Theta_N^M = \left[\frac{2N+1}{2} \frac{(N-M)!}{(N+M)!} \right]^{1/2} P_N^M(\cos \theta). \quad (4)$$

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:

$$V_N^{-M} = \Theta_N^M \sin M\phi/\pi^{1/2}; \quad V_N^0 = \Theta_N^0/(2\pi)^{1/2}; \quad V_N^M = \Theta_N^M \cos M\phi/\pi^{1/2} \quad (5)$$

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

$$V = (1/e) \sum_{N=0}^{\infty} r^N \sum_{M=-N}^N A_N^M V_N^M$$

where

$$A_N^M = \frac{4\pi e^2}{2N+1} \sum_i (Z_i/R_i^{N+1}) V_N^M(\alpha_i, \beta_i) \quad (6)$$

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:

$$V_N^M = a_N^M V_N^M \quad \text{with} \quad A_N^M = a_N^M A_N^M \quad (7)$$

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

$$V = (1/e) \sum_{N=0}^{\infty} r^N \sum_{M=-N}^N A_N^M V_N^M. \quad (8)$$

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 , 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

$$\int \chi^\dagger V_N^M(\vec{x}) \chi d\vec{x} = - \int \chi^\dagger V_N^M(\vec{x}) \chi d\vec{x} = 0 \quad (9)$$

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 $m \rightarrow C_s$ point symmetry, the situation for all of the sites for Tm_3Al_2 , the relevant terms are $N=2,4,6$ and $M=\pm 2, \pm 4, \pm 6$.

The explicit form of the potential for C_s symmetry is

$$\begin{aligned} eV_{C_s} = & A_2^0(2z^2 - x^2 - y^2) + A_2^2(x^2 - y^2) + A_4^0(35z^4 - 30r^2z^2 + 3r^4) \\ & + A_4^2(6z^2 - x^2 - y^2)(x^2 - y^2) + A_4^{-2}(6z^2 - x^2 - y^2)2xy + A_4^4(x^4 - 6x^2y^2 + y^4) \\ & + A_4^{-4}4xy(x^2 - y^2) + A_6^0(231z^6 - 315r^2z^4 + 105r^4z^2 - 5r^6) \\ & + (A_6^2(x^2 - y^2) + A_6^{-2}2xy)(33z^4 - 18r^2z^2 + r^4) + (A_6^4(x^4 - 6x^2y^2 + y^4) \\ & + A_6^{-4}(4x^3y - 4xy^3))(10z^2 - x^2 - y^2) + A_6^6(x^6 - 15x^4y^2 + 15x^2y^4 - y^6) \\ & + A_6^{-6}(3x^2 - y^2)(x^2 - 3y^2)2xy \end{aligned} \quad (10)$$

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

$$H_{\text{CEF}} = -e \sum_k V(r_k, \theta_k, \phi_k) = -\sum_k \sum_{N=0}^6 r_k^N \sum_{M=-N}^N A_N^M V_N^M(\theta_k, \phi_k) \quad (11)$$

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

$$H_{\text{CEF}} = -\sum_{N,M} A_N^M \langle r^N \rangle_{4f} \langle J \| \Theta_N \| J \rangle \langle J, m_J | O_N^M(J_x, J_y, J_z) | J, m_J \rangle \quad (12)$$

where $\langle r^N \rangle_{4f} = \langle U_{4f} | r^N | U_{4f} \rangle$ 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 $O_N^M(J_x, J_y, J_z)$ are the operator equivalents. The expressions $\langle J \| \Theta_N \| J \rangle$ are reduced matrix elements and are found in the literature (22).

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

$$C_N^M = -A_N^M \langle r^N \rangle_{4f} \quad (13)$$

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

$$\psi_i = U(r) \sum_{m_J} c_i^{m_J} \psi_J^{m_J} \quad (14)$$

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 $\vec{J}$ 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 eq^{4f} at the nucleus.
- (2) The ions situated at the lattice sites produce a direct EFG eq^{lat} at the nucleus. This EFG is usually negligible compared with eq^{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 $-\gamma_{\infty}eq^{lat}$ to the EFG at the nucleus. The proportionality constant $-\gamma_{\infty}$ 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 $-R_Qeq^{4f}$ at the nucleus. $-R_Q$ also represents a scalar shielding or antishielding factor.
- (5) The electrons in the conduction band also produce an EFG 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

$$eq_{ij} = (1-\gamma_{\infty})eq_{ij}^{lat} + (1-R_Q)eq_{ij}^{4f} + eq_{ij}^{ce} \quad (15)$$

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

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

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 $\eta = (q_{xx} - q_{yy})/q_{zz}$, the asymmetry parameter.

Using the value for eq_{ij} in Equation 15, the following relation for the crystal field Hamiltonian can be written

$$H_Q = \frac{e^2Q}{4I(2I-1)}\{[(1-\gamma_{\infty})q_{zz}^{lat} + (1-R_Q)q_{zz}^{4f} + q_{zz}^{ce}](3I_z^2 - I^2)\}$$

$$+ \frac{1}{2}[(1-\gamma_{\infty})n^{lat}_{q_{zz}} + (1-R_Q)n^{4f}_{q_{zz}} + n^{ce}_{q_{zz}}](I_+^2 + I_-^2) \quad (17)$$

In general, the EFG tensor is defined by the relation

$$eq_{ij} = d^2V(r, \theta, \phi)/dx_i dx_j |_{r=0} \quad (18)$$

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

$$e^2_{q_{zz}}^{lat} = 4A_2^0; \quad e^2_n^{lat}_{q_{zz}} = 4A_2^2. \quad (19)$$

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

$$\begin{aligned} q_{zz}^{4f} &= \sum_k d^2(-1/r_k)/d^2z = -\sum_k (3z_k^2 - r_k^2)/r_k^5 \\ &= -\langle J||\alpha||J \rangle \langle r^{-3} \rangle_{4f} (3J_z^2 - J^2) \\ n^{4f}_{q_{zz}} &= \sum_k [d^2(-1/r_k)/d^2x - d^2(-1/r_k)/d^2y] \\ &= -\sum_k 3(x_k^2 - y_k^2)/r_k^5 = -(3/2) \langle J||\alpha||J \rangle \langle r^{-3} \rangle_{4f} (J_+^2 + J_-^2) \end{aligned} \quad (20)$$

The summation k is 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, viz.,

$$q_{ii}^{4f} = \sum_{v=1}^{2J+1} \langle v | q_{ii}^{4f} | v \rangle e^{-E_v/kT} / \sum_{v=1}^{2J+1} e^{-E_v/kT} \quad (21)$$

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

$$H_Q(T) = \frac{e^2 Q}{4I(2I-1)} [\langle q_{zz} \rangle_T (3I_z^2 - I^2) + \frac{1}{2} \langle nq_{zz} \rangle_T (I_+^2 - I_-^2)]$$

where $\langle q_{zz} \rangle_T = -\langle J \| \alpha \| J \rangle (1-R_Q) \langle r^{-3} \rangle_{4f} \langle 3J_z^2 - J^2 \rangle_T$

$$- 4C_2^0(1-\gamma_\infty)/e^2 \langle r^2 \rangle_{4f} + q_{zz}^{ce}$$

$$\langle nq_{zz} \rangle_T = -(3/2) \langle J \| \alpha \| J \rangle (1-R_Q) \langle r^{-3} \rangle_{4f} \langle J_+^2 + J_-^2 \rangle_T$$

$$- 4C_2^2(1-\gamma_\infty)/e^2 \langle r^2 \rangle_{4f} + n q_{zz}^{ce} \quad (22)$$

Here the term $\langle \dots \rangle_T$ indicates the operator used in the Boltzmann average of Equation 21. The temperature dependence of q_{ii}^{lat} and q_{ii}^{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 $\pm 3/2$ and the other by the numbers $\pm 1/2$. 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 straight forward manner. The resultant energy splitting is

$$\langle \Delta E \rangle_T = e^2 Q \left[\langle q_{zz} \rangle_T^2 + (1/3) \langle n q_{zz} \rangle_T^2 \right]^{1/2} \quad (23)$$

This splitting, however, is not measured directly in the experiments when Tm_3Al_2 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

$$\begin{aligned} \rho_1' &= e^2 Q \langle J \| a \| J \rangle (1 - R_Q) \langle r^{-3} \rangle_{4f} / C_2^0 \\ \rho_2' &= Q(1 - \gamma_\infty) / \langle r^2 \rangle_{4f} - e^2 Q q_{zz}^{ce} / 4 C_2^0. \end{aligned} \quad (24)$$

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

$$\begin{aligned} \langle \Delta E \rangle_T = & \frac{1}{2} [\rho_1^0 C_2^0 \langle 3J_z^2 - J^2 \rangle_T + 4C_2^0 \rho_2^1]^2 \\ & + (1/3) [(3/2) \rho_1^0 C_2^0 \langle J_+^2 + J_-^2 \rangle_T + 4C_2^0 \rho_2^1 \eta^{\text{lat}}]^2 \}^{1/2}. \end{aligned} \quad (25)$$

where η^{ce} has been assumed to equal η^{lat} and $C_2^2 = \eta^{\text{lat}} C_2^0$. 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 ψ_J^m and ψ_J^{-m} which are opposite in sign. This effect, however, has been observed in second order in TmCl_3 at temperatures below 3°K (25). Comparing Tm_3Al_2 to the TmCl_3 results indicate that this is not

the source of relaxation effects observed in the ME spectra. The asymmetries 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 magnetic 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 internal 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 quadrupole levels.

The situation at the aluminum site is different, however. The conduction 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 $\vec{I}$ and the spin $\vec{S}$ of its 4f shell of the form

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

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

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

or

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

where β_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 quadrupole levels of the nucleus. Instead of seeing two distinct energy transitions 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, $\vec{J} \cdot \vec{J}$ and J_z are good quantum numbers, so the projection of $\vec{S}$ onto $\vec{J}$ must be taken. This gives

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

Actually a Boltzmann average of $\vec{J}$ must be taken over all of the crystal field levels in the spirit of Equation 21. Thus $\vec{J}$ is replaced by $\langle \vec{J} \rangle_T$ and

the nucleus "sees" a temperature dependent magnetic field which is proportional to $\langle \vec{J} \rangle_T$.

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

$$-g_s \beta \vec{S} \cdot \vec{H} = -J_{ex} \vec{S} \cdot \vec{S} - g_s \beta \vec{S} \cdot \vec{H}_0 = -g_s \beta \vec{S} \cdot (\vec{H}_{eff} + \vec{H}_0) \quad (29)$$

where g_s is the Lande g-factor for the conduction electrons and β is the Bohr magneton, this makes

$$\vec{H}_{eff} = J_{ex} \vec{S} / g_s = J_{ex} \langle \vec{J} \rangle_T \langle \vec{S} \cdot \vec{J} \rangle / g_s \beta J(J+1) \quad (30)$$

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

E. The Nucleus in an Applied Magnetic Field

Consider a nucleus with moment $\vec{\mu} = \gamma \hbar \vec{I}$ 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

$$H_M = \gamma \hbar \vec{H}_0 \cdot \vec{I} = \gamma \hbar H_0 I_z \quad (31)$$

where $\vec{H}_0$ is taken to lie along the z-axis of quantization. This Hamiltonian is diagonal, so the eigenvalues are just $\gamma \hbar H_0 m$ where $m = I, I-1, \dots, -I$. 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

$$\hbar\omega = \Delta E = \gamma\hbar H_0 \Delta m = \gamma\hbar H_0 \quad (32)$$

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

$$\omega = \gamma H_0 \quad (33)$$

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 experimnts. 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 allign 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 $2I$ 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 η 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 $I = 5/2$, $\eta = 0.01$.

Figure 4. Unbroadened satellite powder pattern for $I = 5/2$, $\eta = 0.05$.

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 ν_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

$$\Delta H_{\text{sing}} = nH_0(1-n)$$

$$\Delta H_{\text{shld}} = nH_0(1+n)$$

$$\Delta H_{\text{step}} = 2nH_0 \quad (34)$$

where $H_0 = 3e^2q_{zz}Q/h\gamma 2I(2I-1)$ 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_0 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

$$K = (H_R - H_M)/H_M \quad (35)$$

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

$$\vec{H}_{\text{eff}} = J_{\text{ex}} \langle \vec{J} \rangle_T \cdot \vec{H}_0 \langle \vec{S} \cdot \vec{J} \rangle / g_S \beta H_0^2 J(J+1) = C \vec{H}_0. \quad (36)$$

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

$$H_N = -\gamma \hbar \vec{I} \cdot \vec{H}_0 - A \vec{I} \cdot \langle \vec{S} \rangle \quad (37)$$

where $\langle \vec{S} \rangle$ 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 $\langle \vec{S} \rangle$. This operator can be related to the Pauli susceptibility as follows

$$\vec{M}_S = \chi_S \vec{H} = n_S \langle \vec{\mu}_S \rangle_T = n_S g_S \beta \langle \vec{S} \rangle \quad (38)$$

where $\vec{H}$ is the field "seen" by the conduction electrons. Then

$$\begin{aligned} H_N &= -\gamma \hbar \vec{I} \cdot \vec{H}_0 (1 + A \langle \vec{S} \rangle \cdot \vec{H}_0 / \gamma \hbar H_0^2) \\ &= -\gamma \hbar \vec{I} \cdot \vec{H}_0 (1 + K) \end{aligned} \quad (39)$$

where $K = K_0 = A \langle \vec{S} \rangle \cdot \vec{H}_0 / \gamma \hbar H_0^2$. The inclusion of s-f exchange requires that $\vec{H}$ in Equation 38 be replaced by $(1+C)\vec{H}_0$ which makes

$$K = A \langle \vec{S} \rangle \cdot \vec{H}_0 / \gamma \hbar H_0^2 = A(1+C) \chi_S \vec{H}_0 \cdot \vec{H}_0 / \gamma \hbar H_0^2 n_S g_S \beta = K_0(1+C) \quad (40)$$

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

This operator can be related to the 4f electron susceptibility χ_f similarly to Equation 38 with appropriate change in constants. Bulk susceptibility, χ , 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. χ as a function of temperature since only χ_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 $\pm 0.5^\circ\text{K}$ 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_2O_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 $\text{Er}_{0.1}\text{Al}_{0.9}$ 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 $\text{Er}_{0.1}\text{Al}_{0.9}$ source. From the phase diagram it appears that this alloy consists of the intermetallic compound ErAl_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_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_3 . The erbium atom in ErAl_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 5×10^{14} neutrons/cm²sec. 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_3O_2 powder sources.

4. The absorber

The absorber used in the ME experiments was the intermetallic compound Tm_3Al_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_2O_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 880B 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 $\pm 1^\circ\text{K}$ 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 unresolvable 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_3Al_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 $|i\rangle$ to a final state $|f\rangle$ emitting or absorbing a photon with wave vector $\vec{k}$ is

$$W_{if}(\vec{k}) = |\langle f|H|i\rangle|^2 / ((\omega + E_f - E_i)^2 + \Gamma_i^2/4) \quad (41)$$

where Γ_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 Γ_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

$$W_{if}(\vec{k}) = (2/\Gamma) \text{Re} \int_0^\infty dt \exp(i\omega t - \Gamma t/2) \langle i|H^\dagger|f\rangle \langle f|U^\dagger(t)HU(t)|i\rangle \quad (42)$$

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

$$W(\vec{k}) = \sum_{i,f} p_i W_{if}(\vec{k}) = (2/\Gamma) \text{Re} \int_0^\infty dt \exp(i\omega t - \Gamma t/2) \langle H^\dagger H(t) \rangle \quad (43)$$

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

$$\langle 0 \rangle = \sum_i p_i \langle i|0|i\rangle \quad (44)$$

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

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

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

$$W(\vec{k}) = (2/\Gamma) \text{Re} \int_0^\infty dt \exp(i\omega t - \Gamma t/2) (\langle H^\dagger H(t) \rangle)_{av} \quad (46)$$

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

Consider now the explicitly time-dependent Hamiltonian

$$H(t) = H_0 + Q' (3I_z^2 - I^2 + (n/2)(I_+^2 + I_-^2)) + g_N \beta_N h I_z f(t) \quad (47)$$

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_3Al_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

$$W(k) = N/D,$$

where $N = d(p+i\beta+2W) + 3Q_n'^2(p-i\beta)$

$$\begin{aligned} D = & d[(p+i(\beta-C_1+C_0)+W)(p+i(\beta+C_1-C_0)+W)-W^2] \\ & + 3Q_n'^2[(p+i(\beta+C_1-C_0)+W)(p-i(\beta-C_1+C_0)+W) \\ & + (p+i(\beta-C_1+C_0)+W)(p-i(\beta+C_1-C_0)+W)+2W^2+3Q_n'^2] \end{aligned}$$

with $d = (p-i\beta)^2 + (C_1-C_0)^2 + 2W(p-i\beta).$

In the above expression

$$\begin{aligned} C_1 &= g_1 m_1 \beta_N h, & C_0 &= g_0 m_0 \beta_N h, & \beta &= Q' (3m_1^2 - 15/4) \\ C_1' &= g_1 (m_1 \pm 2) \beta_N h, & p &= -1(\omega - \omega_0) + \tau/2, \end{aligned} \quad (48)$$

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}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 Tm_3Al_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.

51a

Figure 10. Raw data as fit to Equation 48 with the two individual lines making up the complex spectrum displayed separately.

Figure 10. (cont.)

51c

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

$$\langle E \rangle_T = 6Q'(T)(1+n^2/3)^{1/2} \quad (49)$$

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

$$\begin{aligned} Q'(T) = & (1/6(1+n^2/3)^{1/2}) \{ [C_{2\rho 1}^0 \langle 3J_z^2 - J^2 \rangle_T + 4C_{2\rho 2}^0]^2 \\ & + (1/3)[(3/2)C_{2\rho 1}^0 \langle J_+^2 + J_-^2 \rangle_T + 4C_{2\rho 2}^0]^2 \}^{1/2} \end{aligned} \quad (50)$$

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

From Equation 49 it can be seen how 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 Γ , the asymmetry parameter η , 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_3Al_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

$$F = \sum_I (YC(I) - YD(I))^2 BG / ((N - NVAR)(1 - YD(I))) \quad (51)$$

where $YC(I)$ is the calculated point using Equation 48, $YD(I)$ 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 1. Fitted parameters from the ME data for a thulium ion at the c_2 site^a

Temperature °K	Linewidth (cm/sec)	Quadrupole coupling parameter (cm/sec)	Magnetic field (cm/sec)	Fluctuation rate (sec) ⁻¹
77.15	1.76	1.71	180.2	1099.2
85.30	1.96	1.64	168.7	1119.6
90.77	1.96	1.58	186.6	940.5
90.90	1.82	1.64	190.3	1068.3
105.83	1.79	1.46	140.7	1149.8
110.12	1.84	1.37	148.9	1275.6
114.49	2.19	1.30	144.3	1157.6
120.16	2.17	1.24	135.6	1164.0
129.71	2.16	1.28	133.8	1166.3
139.72	1.73	1.16	127.2	1378.5
140.81	1.95	1.17	127.7	1255.0
149.60	2.09	1.08	126.0	1208.9
153.06	1.73	1.06	121.4	1229.0
157.37	1.78	1.04	108.4	1258.7
194.24	2.00	.753	82.1	1488.4

^aSee pp. 61-62 for the crystallographic details

Table 2. Fitted parameters from the ME data for a thulium ion at the c_1 site^a

Temperature °K	Linewidth (cm/sec)	Quadrupole coupling parameter (cm/sec)	Magnetic field (cm/sec)	Fluctuation rate (sec) ⁻¹
77.15	1.81	.866	84.1	1071.2
85.30	1.97	.834	82.7	1120.8
90.77	2.21	.829	71.4	1060.2
90.90	1.93	.845	93.6	1077.8
105.83	2.07	.647	68.8	1194.3
110.12	2.11	.644	77.9	1218.0
114.49	2.04	.596	82.9	1289.6
120.16	2.44	.564	68.0	1243.3
129.71	2.28	.566	65.0	1229.8
139.72	2.15	.474	53.6	1265.5
140.81	2.40	.487	58.1	1195.1
149.61	2.21	.432	52.5	1268.3
153.06	1.94	.446	55.5	1306.3
157.37	2.04	.418	55.9	1242.8
194.24	2.25	.219	33.6	1468.9

^aSee 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^M '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_2^2 . 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 Tm_3Al_2 is 14 as can be seen from Equation 10. Added to these are the dimensionless parameters ρ_1 and ρ_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^M 's were then evaluated using the values for $\langle r^N \rangle_{4f}$ given by Freeman and Watson (45), viz.,

$$\langle r^2 \rangle_{4f} = 0.81 \times 10^{-16} \text{ cm}^2, \quad \langle r^4 \rangle_{4f} = 0.084 \times 10^{-32} \text{ cm}^4, \quad \langle r^6 \rangle_{4f} = 0.080 \times 10^{-48} \text{ cm}^6.$$

Estimates of ρ_1' and ρ_2' could be obtained by using the high and low temperature limits of the quadrupole coupling parameter respectively, i.e.,

$$\begin{aligned} Q'(T) &= (2/3) C_{2\rho_2}^{0'} & T \gg 500^\circ\text{K} \\ Q'(T) &= (1/6(1+n^2/3))^{\frac{1}{2}} \{ [C_{2\rho_1}^{0'} \langle 1|3J_z^2 - J^2|1 \rangle + 4C_{2\rho_2}^{0'}]^2 \\ &\quad (1/3)[4C_{2\rho_2}^{0'}]^2 \}^{\frac{1}{2}} & T \approx 0^\circ\text{K} \end{aligned} \quad (52)$$

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 Tm_3Al_2 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_3Al_2 . However, Buschow (46) has reported crystallographic studies on several rare-earth aluminides of the form R_3Al_2 . These intermetallics were shown to have the same structure as Gd_3Al_2 and Dy_3Al_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 $\text{P4}_2\text{nm} \rightarrow \text{C}_{4v}^4$ with 4 formula units per unit cell.

An x-ray powder pattern was taken of the Tm_3Al_2 sample using copper radiation. This pattern was successfully indexed to the Gd_3Al_2 structure. The indexing was compared with that reported for Er_3Al_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_3Al_2 intermetallics (46) as shown in Table 3.

The atomic positions used are those of Baenziger and Hegenbarth for Gd_3Al_2 (47):

4 Tm(1) in (c):

$$x, x, z; \bar{x}, \bar{x}, z; \frac{1}{2} + x, \frac{1}{2} - x, \frac{1}{2} + z; \frac{1}{2} - x, \frac{1}{2} + x, \frac{1}{2} + z$$

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

4 Tm(2) in (c):

with $x = 0.205$ and $z = 0.742$

4 Tm(3) in (b):

$$0, \frac{1}{2}, z; \quad \frac{1}{2}, 0, z; \quad 0, \frac{1}{2}, \frac{1}{2} + z; \quad \frac{1}{2}, 0, \frac{1}{2} + z$$

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

Compound	a	c	c/a
Gd ₃ Al ₂	8.329	7.578	0.91
Tb ₃ Al ₂	8.255	7.568	0.92
Dy ₃ Al ₂	8.170	7.523	0.92
Ho ₃ Al ₂	8.182	7.525	0.92
Er ₃ Al ₂	8.123	7.484	0.92
Tm ₃ Al ₂	8.090	7.477	0.92

^aAll but Tm₃Al₂ 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 $m \rightarrow C_s$ 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 η

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 RAI_2 compounds. Taking $Q(^{27}Al) = 0.149 (10^{-24}) \text{ cm}^2 (49)$, a value for q_{zz} can be calculated. Using the relationship

$$q_{zz} = (1 - \gamma_\infty) A_{2Z}^0 \text{AL} \quad (53)$$

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 RAI_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 RAI_3 have hexagonal crystal structures with measured quadrupole coupling parameters of about 0.7 MHz (19). The large measured quadrupole coupling parameter for RAI_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

Table 4. Nuclear quadrupole coupling constants of the Al nucleus in RAI_2 intermetallics

Compound	$ e^2 q_{zz} Q/h $ MHz	$Z_{AL}(q_{zz} < 0)$ $-\gamma_\infty = +2.36(4)^a$	$Z_{AL}(q_{zz} < 0)$ $-\gamma_\infty = 1.13(50)$
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

^aReference numbers appear in parentheses

^bDerived from first-order quadrupole coupling

^cDerived from second-order quadrupole coupling

^dT. P. Graham, unpublished data

^eYb taken to be 4f¹⁴ 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 Fieldial. 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_0 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 η .

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 η 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.

Figure 13. Synthesized NMR spectra for the c_2 ^{27}Al site showing the satellite transitions only.

Figure 14. Unbroadered central line powder pattern in second order.

Figure 15. Experimental ^{27}Al central transition at 15 MHz in Tm_3Al_2 .

Figure 16. Experimental ^{27}Al central transition at 10 MHz in Tm_3Al_2 .

Figure 17. Experimental ^{27}Al central transition at 5 MHz in Tm_3Al_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 $\Delta\nu\nu_0$ versus ν_0^2 was made where ν_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

$$\Delta\nu\nu_0 = \frac{\nu_0^2}{18} (25 - 22\eta + \eta^2) + \left[\frac{(5+\eta)K_3 + 2(2+\eta)K_2}{3(3+\eta)} - K_2 \right] \nu_0^2 \quad (54)$$

for $\eta < 1/3$ 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 ν_Q and η 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_3Al_2 .

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 $\nu_0 \Delta\nu$ vs. ν_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

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

3. Results of the NMR experiments

Values of H_Q and η were determined from the satellite data. A value of H_Q was also obtained from the central line data using the value of η obtained from the satellite data. The ambiguity over the value of η at the

c_1 site was resolved in favor of the small asymmetry parameter. In Figure 13 it can be seen that the pattern for $\eta = 0.51$ is too weak to justify its selection. The values of H_Q and η determined from the data are shown in Table 6.

Table 6. Values of H_Q and η determined experimentally from ^{27}Al NMR data

Effect	Site	H_Q (Oe)	η	Ratio	$ e^2q_{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

Ratio	Site	H_Q (exp.)	H_Q (cal.)	n (exp.)	n (cal.)	Z_{Al}
1.932	c_1	449.7	316.8	0.10	0.64	0.11
	c_2	868.7	613.0	0.07	0.12	
1.570	c_1	485.5	392.7	0.10	0.62	-0.24
	c_2	762.2	616.3	0.07	0.18	

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.

Covalency 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 n 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 RAI_2 calculations. If an "effective valence" closer to zero were taken for $TmAl_3$, then the calculated coupling parameter would be smaller than the measured one consistent with the Tm_3Al_2 results. However, this statement would not apply to the RAI_2 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 $TmMn_2$ 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_N^M and the Shielding Parameters σ_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_3Al_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_N^M -terms with odd M appear in the crystal-field calculation while S_N^M -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 η 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 ρ_1 and ρ_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

$$C_N^{0'} = (1 - \sigma_N) C_N^0 \quad (55)$$

where σ_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 ρ_1' and ρ_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

Parameter	Point-ion calculation	Full parameter fit	C_2^0, C_2^2 only fit
C_2^0	-682.38 cm^{-1}	-285.39 cm^{-1}	-285.39 cm^{-1}
C_2^2	-231.09 cm^{-1}	-58.55 cm^{-1}	-58.49 cm^{-1}
C_4^0	0.08 cm^{-1}	0.0796 cm^{-1}	0.0
C_4^2	-8.83 cm^{-1}	-8.78 cm^{-1}	0.0
S_4^2	1.13 cm^{-1}	1.12 cm^{-1}	0.0
C_4^4	-41.79 cm^{-1}	41.58 cm^{-1}	0.0
S_4^4	28.94 cm^{-1}	28.79 cm^{-1}	0.0
C_6^6	0.59 cm^{-1}	0.59 cm^{-1}	0.0
C_6^2	-0.40 cm^{-1}	-0.40 cm^{-1}	0.0
S_6^2	-0.48 cm^{-1}	-0.48 cm^{-1}	0.0
C_6^4	2.57 cm^{-1}	2.57 cm^{-1}	0.0
S_6^4	-1.88 cm^{-1}	-1.88 cm^{-1}	0.0
C_6^6	-0.39 cm^{-1}	-0.39 cm^{-1}	0.0
S_6^6	-1.23 cm^{-1}	-1.23 cm^{-1}	0.0
ρ_1'	$-0.039(10^{-5})$	$-0.170(10^{-5})$	$-0.171(10^{-5})$
ρ_2'	$-0.257(10^{-5})$	$0.411(10^{-5})$	$0.417(10^{-5})$
n	0.305	0.205	0.204

Table 9. Crystal-field parameters for the c_2 thulium sites

Parameter	Point-ion calculation	Full parameter fit	c_2^0, c_2^2 only fit
C_2^0	-802.44 cm^{-1}	-284.99 cm^{-1}	-276.92 cm^{-1}
C_2^2	-975.75 cm^{-1}	-40.26 cm^{-1}	-28.15 cm^{-1}
C_4^0	1.77 cm^{-1}	1.76 cm^{-1}	0.0
C_4^2	-36.35 cm^{-1}	-36.23 cm^{-1}	0.0
S_4^2	18.11 cm^{-1}	18.05 cm^{-1}	0.0
C_4^4	-48.02 cm^{-1}	-47.86 cm^{-1}	0.0
S_4^4	17.98 cm^{-1}	17.92 cm^{-1}	0.0
C_6^0	0.23 cm^{-1}	0.227 cm^{-1}	0.0
C_6^2	-5.72 cm^{-1}	-5.65 cm^{-1}	0.0
S_6^2	2.37 cm^{-1}	2.34 cm^{-1}	0.0
C_6^4	-0.83 cm^{-1}	-0.82 cm^{-1}	0.0
S_6^4	1.18 cm^{-1}	1.17 cm^{-1}	0.0
C_6^6	-0.96 cm^{-1}	-0.95 cm^{-1}	0.0
S_6^6	-0.769 cm^{-1}	-0.78 cm^{-1}	0.0
ρ_1	-0.039(10^{-5})	-0.121(10^{-5})	-0.121(10^{-5})
ρ_2	0.131(10^{-5})	0.670(10^{-5})	0.653(10^{-5})
η	1.216	0.141	0.102

Energy (cm ⁻¹)	Eigenfunctions						
	+6>	+4>	+2>	0>	-2>	-4>	-6>
0.0	.049-.699i	-.024-.012i	.001-.005i	.001+.002i	-.004+.005i	-.026+.0041i	.707+.002i
0.0	.708-.082i	-.021-.017i	-.005-.001i	.002+.001i	.004-.005i	.008-.026i	-.087-.699i
171.94	.026-.110i	.570-.407i	-.080-.042i	-.026+.006i	.061-.015i	-.230+.665i	-.003+.026i
172.73	.001-.026i	.639+.288i	-.041-.081i	.006-.026i	-.061-.015i	.069-.137i	.026+.001i
267.28	.007+.003i	.068-.042i	.557+.371i	-.135-.181i	-.689-.123i	-.021+.061i	.003-.008i
283.78	-.004-.007i	.075+.028i	.363+.563i	-.181-.135i	.690+.117i	.063-.012i	.007-.004i
318.71		.067-.007i	.208+.211i	.669+.670i	.107i		.001-.001i
	+5>	+3>	+1>	-1>	-3>	-5>	
96.55	-.696+.110i	-.051	.008+.007i	.002+.005i	-.031-.035i	-.110-.696i	
96.55	-.036-.705i	-.035+.036i	-.008+.007i	-.002+.005i	.047+.007i	.705-.036i	
228.95	-.001-.047i	.511-.451i	-.055-.039i	-.175+.030i	-.693-.125i	.047-.001i	
233.44	-.046+.009i	.679-.055i	.056-.038i	-.174-.033i	.485+.510i	-.009-.046i	
297.78	-.004+.007i	.180-.031i	-.703-.040i	.683-.050i	.026+.039i	-.007-.009i	
315.89	.005-.011i	.148-.108i	.702+.048i	.682+.059i	-.047	.011+.005i	

Figure 19. Energy levels and eigenfunctions for the ground state crystal-field multiplet of ¹⁶⁹Tm at c₁ sites in Tm₃Al₂.

Energy (cm ⁻¹)	Eigenfunctions						
	+6>	+4>	+2>	0>	-2>	-4>	-6>
0.0	.518-.500i	-.015+.035i	-.003+.001i	.001	-.003+.001i	.029-.024i	.508+.514i
0.0	-.563-.402i	-.037-.007i	.003+.001i	.002	-.003-.001i	-.030-.024i	.407-.556i
168.96	.034-.017i	.455-.533i	-.058+.023i	-.029+.018i	-.072+.024i	-.654+.259i	.018+.034i
169.56	-.035-.011i	.696-.082i	.058+.024i	-.030-.017i	-.072-.026i	.656+.254i	.012-.035i
268.70	-.006-.002i	.069-.020i	-.690-.109i	-.087+.079i	.689+.117i	.061+.012i	.002-.006i
282.93	.006-.003i	.055-.047i	.692-.093i	-.089-.077i	.692-.104i	-.061+.013i	.003+.006i
313.17		.052-.028i	.002-.129i	.985-.013i	.100+.001i	.004i	
	+5>	+3>	+1>	-1>	-3>	-5>	
92.28	.113-.695i	-.058+.026i	-.003-.009i	.009-.003i	.021-.055i	-.695-.113i	
92.28	.704-.040i	-.050-.038i	-.009+.002i	-.002-.009i	-.059+.008i	-.039-.704i	
228.93	.025-.055i	.678-.115i	-.103-.049i	.049-.103i	-.412+.571i	-.055-.025i	
231.61	.058-.019i	.636+.262i	-.096-.062i	.062-.096i	.650-.270i	-.019-.058i	
301.06	.010-.016i	.152+.001i	.275+.641i	-.641+.275i	-.010+.023i	-.016-.010i	
301.06	.017-.008i	.148+.032i	.690-.107i	+.107+.690i	.025-.004i	-.008-.017i	

Figure 20. Energy levels and eigenfunctions for the ground state crystal-field multiplet of ¹⁶⁹Tm at c₂ sites in Tm₃Al₂.

Figure 21. Computer fit of the temperature dependence of the quadrupole coupling parameter for ^{169}Tm at c_1 sites in Tm_3Al_2 .

Figure 22. Computer fit of the temperature dependence of the quadrupole coupling parameter for ^{169}Tm at c_2 sites in Tm_3Al_2 .

thulium was taken to be 1.5 barns (56), $\langle r^{-3} \rangle_{4f}$ 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

Thulium site	σ_2	σ_4	σ_6	R_Q	q_{zz}^{ce} (10^{24}) cm^{-3}	$(1-\gamma_\infty)q_{zz}^{\text{lat}}$ (10^{24}) cm^{-3}
c_2	.58	.01	0.0	.77	0.247	2.46
c_1	.64	.01	0.0	.68	-1.45	2.91
Theory	.545 ^a	.088	-.043	0.24 ^b		

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

^bData of reference (57)

The value calculated here for σ_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 $Z_{\text{MN}}=0$). 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 σ_4 and σ_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 η 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 aluminides (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 Tm_3Al_2 . Using the eigenvalues and the eigenfunctions of Figures 21 and 22, the temperature average of J_z was calculated. Using the temperature as a parameter, K was plotted versus $\langle J_z \rangle_T$ 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, K_0 , of 0.576% for the c_1 site and .615% for the c_2 site. Surprisingly enough, the values of the slope of the two plots are opposite in sign. Using the slopes of the lines, values for J_{ex} can be calculated. They are -0.286 eV and 0.458 eV for the c_1 and c_2 sites respectively. These values compare with $J_{\text{ex}} = -0.25$ calculated for TmAl_2 (19). Values for J_{ex} 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_3Al_2

Temperature °K	H_M kOe	K %	ΔH Oe
179.1±0.2	13.7577	-1.677	104.0
185.0±0.1	13.7430	-1.614	93.6
195.0±0.6	13.7292	-1.576	86.4
211.5±0.1	13.7196	-1.447	84.4
240.4±1.1	13.6968	-1.283	60.7
299.1	13.6610	-1.021	57.6
299.6	13.6604	-1.020	57.0
304.3±3.5	13.6587	-0.996	58.7
336.1±1.2	13.6431	-0.889	52.9
362.5±2.1	13.6365	-0.844	49.3
366.3±1.0	13.6317	-0.809	47.9
373.2±1.35	13.6307	-0.802	47.1
398.9±1.3	13.6255	-0.764	45.0
404.1±2.4	13.6219	-0.738	45.5

$$H_{\text{eff}} = c \langle O \rangle_T$$

where $\langle O \rangle_T$ 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} using Equation 28 yielded values of .568 eV for the c_1 site and -.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} 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_3Al_2 versus temperature.

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Figure 24. Least mean squares fit of the Knight shift of the ^{27}Al resonance in Tm_3Al_2 versus $\langle J_Z \rangle_T$ for the ground state crystal-field multiplet for ^{169}Tm at c_1 sites in Tm_3Al_2 .

Figure 25. Least mean squares fit of the Knight shift of the ^{27}Al resonance in Tm_3Al_2 versus $\langle J_Z \rangle_T$ for the ground state crystal-field multiplet for ^{169}Tm at c_2 sites in Tm_3Al_2 .

100a

Figure 26. Computer fits of the magnetic hyperfine interaction at ^{169}Tm nucleus for c_1 and c_2 sites in Tm_3Al_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_3Al_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_3Al_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 (sec)^{-1} and 1500 (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_3Al_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_3Al_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_3Al_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_3Al_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 inter-metallics. 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:

$Tm(c_1)$ has

1 Al(c_1) at 3.14, 2 Al(c_1) at 3.15, 1 Al(c_2) at 3.22, 1 Al(c_2) at 3.23, 1 Tm(c_1) at 3.58, and 1 Tm(c_2) at 3.69 Å.

$Tm(c_2)$ has

1 Al(c_1) at 3.10, 1 Al(c_2) at 3.14, 2 Tm(b) at 3.46, 2 Tm(b) at 3.66, and 1 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_2^0 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_2^0 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_4^0 , C_6^0 and η . 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 , ρ_1 and ρ_2 ; 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_2^0 and C_2^2 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 η for the c_1 site is definitely much less than 1.0 since fits were impossible to obtain with values of η 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 Tm_3Al_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 versus $\langle J_z \rangle_T$ 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_3Al_2 . The values calculated for σ_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 σ_4 and σ_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.

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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. VMMIN
4. READY
5. AIM
6. FIRE
7. DRESS
9. MATMPY

See SHARE No. 980
ZO ANFZ013

The listings of decks 1-2 follows:

C	SOURCE DECK FOR VMMIN FITTING ROUTINE TO FIT RELAXATION SPECTRA	0010
C	TO THULIUM DATA. SEE BLUME AND TJON, PHYS. REV., 165,446(1968).	0020
C	THIS IS MAIN CALLING PROGRAM FOR SUBROUTINE VMMIN. THE RANDOM	0030
C	STEP CHECK FOR MINIMUM HAS BEEN REMOVED FROM THE SUBROUTINE	0040
C	SINCE OUTPUT CONTAINS GRAPH. THE PURPOSE OF THE MAIN ROUTINE	0050
C	IS TO READ IN THE DATA AND PREPARE IT FOR PROCESSING TO BE FIT	0060
C	WITH SUBROUTINE VMMIN.	0070
C		0080
C	DESCRIPTION OF PARAMETERS:	0090
C	BG - BACKGROUND(AUTOMATICALLY CALCULATED IF BG = 0.).	0100
C	E - MINIMIZATION EPSILON.	0110
C	EG - PARAMETER USED IN CALCULATION OF ERROR MATRIX IF NH =0.	0120
C	GO - G-FACTOR OF GROUND STATE.	0130
C	G1 - G-FACTOR OF EXCITED STATE.	0140
C	IDD - NUMBER OF DATA SETS BEING FITTED.	0150
C	IR - NUMBER OF CHANNELS ON EITHER SIDE OF ZERO CONSIDERED.	0160
C	IX10 - VELOCITY ZERO OF FIRST HALF OF THE SPECTRUM.	0170
C	IX20 - VELOCITY ZERO OF SECOND HALF OF THE SPECTRUM.	0180
C	LIMIT - MAXIMUM NUMBER OF ITERATIONS DESIRED(SET TO 40 IF ZERO).	0190
C	N1 - NUMBER OF SETS OF LINES IN SPECTRUM(1, 2, OR 3).	0200
C	ND - PARAMETER CONTAINING 10(5) AND 10(6) ADDED COUNTS.	0210
C	VC - VELOCITY CALIBRATION.	0220
C		0230
	DIMENSION H(18,18),YDATA(400),S3(200),TITLE(57),	0240
	1 G(18),X(18),GA(7),HA(7),A(6),GLB1(5),GLB2(5),XLB(5),YLB(5)	0250
	COMMON /M10/ XD(400),YD(400),FFF(400),YC(400),A1(18),IND(18),	0260
	C ITB(18),BG,GO,G1,N1,NDP,NVAR1,NVAR2,FSAVE(3,200)	0270
	COMMON /M20/ NVAR10,NVAR20,N10	0280
	DATA XLB/' VE','LOCI','TY(C','M/SE','C) '/,YLB/' ',' IN','TE	0290
	CNS','ITY ',' ' /	0300
C		0310
	L=0	0320
	1 M=1+19*L	0330
	L=L+1	0340
	M1=M+18	0350
C		0360
C	READ STOPPER, TITLE CARD(S)	0370

READ(5,105) ISTOP,(TITLE(I),I=M,M1)	0380
IF(ISTOP) 2,4,1	0390
2 WRITE(6,106) (TITLE(I),I=1,M1)	0400
STOP	0410
4 READ (5,107) IR,IX10,IX20,IMAX,N1,ND,LIMIT,IDD,NV,IP,NDS,NH,BG,	0420
C E,EG	0430
IF (IP .EQ. 1) GO TO 6	0440
IF (IR .EQ. 0) IR=399-IX20	0450
IF (LIMIT .EQ. 0) LIMIT=50	0460
NDP=2*IR+1	0470
GO TO 7	0480
6 NDP=IMAX	0490
7 READ (5,112) GO,G1	0500
WRITE(6,110) (TITLE(I),I=1,M1)	0510
C	0520
C PREPROCESS DATA IF IP EQUAL TO 0.	0530
IF (IP .EQ. 1) GO TO 393	0540
C	0550
C ADD GA*10(5) AND HA*10(6) COUNTS TO DATA SET IF ND UNEQUAL TO	0560
C ZERO.	0570
16 IDD=IDD+1	0580
IF(ND) 17,18,17	0590
17 READ(5,111) (GA(I),HA(I),I=1,IDD)	0600
GO TO 20	0610
18 DO 19 I=1,IDD	0620
GA(I)=0.0	0630
19 HA(I)=0.0	0640
20 TH=1.0E+05	0650
TM1=1.0E+06	0660
C	0670
C PREPROCESS DATA: CENTER ABOUT ZERO OF VELOCITY, ADD TWO SPECTRA	0680
C TOGETHER, AND CONVERT CHANNEL NUMBER TO VELOCITY.	0690
DO 23 I=1,400	0700
23 YD(I)=0.0	0710
DO 24 J=1,IDD	0720
READ(5,148) (XD(I),YDATA(I),I=1,400)	0730
C	0740

C	SUM IDD SETS OF DATA.	0750
	DO 24 I=1,400	0760
24	YD(I)=YD(I)+YDATA(I)+GA(J)*TH+TM1*HA(J)	0770
	IF(IX10-200) 26,25,25	0780
25	IA=IX10-IR-200+1	0790
	IB=IX10+IR-200+1	0800
	GO TO 27	0810
26	IA=IX10-IR+1	0820
	IB=IX10+IR+1	0830
C		0840
C	INVERT SECOND HALF OF DATA AND ADD TO FIRST HALF.	0850
27	IF(IX20) 31,31,28	0860
28	CONTINUE	0870
	DO 30 J=IA,IB	0880
	L=IX10+IX20-J+2	0890
30	YD(J)=YD(J)+YD(L)	0900
C		0910
C	CONVERT TO VELOCITY	0920
31	READ(5,113)VC,XNW,(A(I),I=1,6)	0930
	X10=IX10	0940
	DO 34 I=IA,IB	0950
	S3(I)=XD(I)-X10	0960
	IF(XNW) 32,33,32	0970
32	XD(I)=VC*XNW*SIN(S3(I)/XNW)	0980
	GO TO 34	0990
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)	1000
	1*S3(I)**4+A(5)*S3(I)**5+A(6)*S3(I)**6)	1010
34	CONTINUE	1020
C		1030
C	INVERT DATA POINTS IF VC IS NEGATIVE.	1040
	IF (VC) 340,343,343	1050
340	DO 341 I=IA,IB	1060
	J=IA+IB-I	1070
	YDATA(I)=YD(J)	1080
341	YC(I)=XD(J)	1090
	DO 342 I=IA,IB	1100
	YD(I)=YDATA(I)	1110

342	XD(I)=YC(I)	1120
C		1130
C	WRITE TABLE OF RESULTS.	1140
343	WRITE(6,114)	1150
	WRITE(6,115)IR,VC,IX10,IX20,(S3(I),XD(I),YD(I),I=IA,IB)	1160
	DO 35 I=1,NDP	1170
	J=I+IA-1	1180
	XD(I)=XD(J)	1190
35	YD(I)=YD(J)	1200
C		1210
C	CALCULATE BACKGROUND FROM DATA IF NBG EQUALS ZERO.	1220
36	IF (BG) 385,37,385	1230
37	BG=0.0	1240
	DO 38 J=1,5	1250
	L=NDP+1-J	1260
38	BG=BG+YD(J)+YD(L)	1270
	BG=BG/10.0	1280
385	CONTINUE	1290
	DO 39 I=1,NDP	1300
39	YD(I)=1.0-YD(I)/BG	1310
	GO TO 405	1320
C		1330
C	READ IN PREPROCESSED DATA FOR 400 CHANNELS IF IP=1.	1340
393	READ (5,149) (XD(I),YD(I),I=1,400)	1350
	IF (IMAX .EQ. 400) GO TO 396	1360
	DO 394 I=1,IMAX	1370
	J=399-IMAX+I	1380
	XD(I)=XD(J)	1390
394	YD(I)=YD(J)	1400
396	WRITE (6,150) (XD(I),YD(I),I=1,IMAX)	1410
C		1420
C	CALCULATE INITIAL ERROR MATRIX.	1430
405	IF (EG .EQ. 0.) EG=0.03	1440
	N2=6*N1	1450
C		1460
C	READ IN INITIAL VARIABLE PARAMETERS.	1470
	READ (5,108) (A1(I),I=1,N2)	1480

READ (5,109) (IND(I),I=1,N2)	1490
READ (5,142) GLB1,GLB2	1500
NVAR=0	1510
DO 5 I=1,N2	1520
IF (I .EQ. 6) NVAR1=NVAR	1530
IF (I .EQ. 12) NVAR2=NVAR	1540
IF (IND(I) .EQ. 0) GO TO 5	1550
NVAR=NVAR+1	1560
IF (I .EQ. 6) NVAR1=NVAR	1570
IF (I .EQ. 12) NVAR2=NVAR	1580
X(NVAR)=A1(I)	1590
ITB(NVAR)=I	1600
5 CONTINUE	1610
DO 407 I=1,NVAR	1620
DO 407 J=1,NVAR	1630
407 H(I,J)=0.0	1640
IF (IH .EQ. 0) GO TO 408	1650
READ (5,152) (H(I,I),I=1,NVAR)	1660
GO TO 415	1670
408 DO 41 J=1,NVAR	1680
41 H(J,J)=EG*EG*X(J)*X(J)	1690
415 WRITE(6,116)	1700
WRITE(6,147) (TITLE(I),I=1,M1)	1710
WRITE (6,117) NVAR,NDP	1720
C	1730
C WRITE INITIAL PARAMETERS.	1740
IF (IP .NE. 0) GO TO 42	1750
WRITE (6,118) BG	1760
42 WRITE (6,119) (A1(I),IND(I),I=1,N2)	1770
C	1780
C WRITE INITIAL ERROR MATRIX.	1790
WRITE (6,123) (H(I,I),I=1,NVAR)	1800
NVAR10=NVAR1	1810
NVAR20=NVAR2	1820
N10=NVAR	1830
L=0	1840
CALL VMMIN(NVAR,X,H,0,E,IER,G,F,GS,NV,LIMIT)	1850

GO TO (50,51,101,50),IER	1860
51 WRITE (6,125)	1870
50 WRITE(6,124)	1880
DO 56 I=1,NVAR	1890
DO 56 J=1,NVAR	1900
56 H(I,J)=2.0*H(I,J)	1910
WRITE(6,127)	1920
DO 59 I=1,NVAR	1930
59 WRITE (6,128) I,(H(I,J),J=1,NVAR)	1940
WRITE (6,133) (G(I),I=1,NVAR)	1950
WRITE(6,134) F,GS	1960
WRITE (6,120) (X(I),I=1,NVAR)	1970
L=0	1980
WRITE (6,135)	1990
C	2000
C GENERATE PLOT	2010
XSF=(XD(NDP)-XD(1))/20.	2020
CALL GRAPH(NDP,XD,YD,3,7,20.,9.,XSF,XD(1),0.,0.,XLB,YLB,GLB1,GLB2)	2030
CALL GRAPH(NDP,XD,YC,0,2,0.,0.,0.,0.,0.,0.,0.,0.,0.)	2040
100 L=0	2050
IF (NDS .EQ. 0) GO TO 1015	2060
C	2070
C GRAPH THE INDIVIDUAL SPECTRA COMPOSING THE COMPLEX	2080
C LINESHAPE IF NDS=1.	2090
DO 1006 I=1,N1	2100
DO 1005 K=1,NDP	2110
1005 FFF(K)=FSAVE(I,K)	2120
CALL GRAPH(NDP,XD,FFF,0,2,20.,9.,XSF,XD(1),0,0.,XLB,YLB,GLB1,GLB2)	2130
1006 CONTINUE	2140
GO TO 1015	2150
101 L=0	2160
WRITE (6,120) (X(I),I=1,NVAR)	2170
1015 READ (5,151) N1	2180
IF (N1 .EQ. 0) GO TO 1	2190
GO TO 405	2200
C	2210
105 FORMAT(I4,19A4)	2220

106	FORMAT(1H019A4)	2230
107	FORMAT(4I4,8I2,3E15.7)	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 1(0),12X,1HV,11X,1HY/(1H ,6X,F4.0,5X,F12.4,3X,E12.6))	2320 2330
116	FORMAT(1H1,50HLINE SHAPE FITTING BY VARIABLE METRIC MINIMIZATION)	2340
117	FORMAT(20HOND. 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 1,2X,E15.5,I2,2X)	2370 2380
120	FORMAT(11HOPARAMETERS/(1P6E15.5))	2390
123	FORMAT(34HODIAGONAL ELEMENTS OF ERROR MATRIX//(1P6E15.5))	2400
124	FORMAT(13H1FINAL VALUES)	2410
125	FORMAT(20HOPROCESS INTERRUPTED/21HOPRESENT 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(I2)	2530
152	FORMAT(12F6.0)	2540
C		2550
	END	2560
C		2570

C	SUBROUTINE FCN(NVAR,VAL,X,GRAD)	2580
C		2590
C	FUNCTION EVALUATION. THIS ROUTINE CALCULATES THE FUNCTION TO	2600
C	BE MINIMIZED AS WELL AS ITS FIRST DERIVATIVE. THE FUNCTION IS	2610
C	CHOSEN SO THAT THE DIAGONAL ELEMENTS OF THE H-MATRIX ARE THE	2620
C	EXPECTATION VALUES OF THE ERROR IN THE CALCULATED PARAMETERS.	2630
C		2640
C	PARAMETERS:	2650
C		2660
C	A(1) - LINEWIDTH OF EXCITED STATE.	2670
C	A(2) - ASSYMMETRY PARAMETER.	2680
C	A(3) - ELECTRIC QUADRUPOLE INTERACTION PARAMETER.	2690
C	A(4) - MAGNETIC INTERACTION PARAMETER.	2700
C	A(5) - RATE OF FIELD FLUCTUATION.	2710
C	A(6) - INTENSITY NORMALIZATION FACTOR.	2720
C		2730
C	REMARKS:	2740
C	I - THIS PROGRAM WAS WRITTEN TO HANDLE THREE INEQUIVALENT	2750
C	SITES IN THE LATTICE UNDER CONSIDERATION.	2760
C	II - ONLY M1 TRANSITIONS FROM SPIN 3/2 TO 1/2 STATES	2770
C	CAN BE DONE HERE. THIS INCLUDES IRON AND THULIUM.	2780
C		2790
	IMPLICIT REAL*4(M)	2800
	DIMENSION ME(2,4),FUNC(400),F(400),G(18),GRAD(18),X(18),M1(4),	2810
C	MO(2),A1(3),A2(3),A3(3),A4(3),B1(3),B2(3),BETA(3),CO(3),C1(3),	2820
C	C2(3),C3(3),C4(3),C5(3),C6(3),C7(3),C8(3),C11(3),D1(3),D2(3),	2830
C	DD(3),E1(3),E2(3),E3(3),P1(3)	2840
	COMMON /M10/ XD(400),YD(400),FFF(400),YC(400),A(18),IND(18),	2850
C	ITB(18),BG,G0,G1,N1,N,NVAR1,NVAR2,FSAVE(3,200)	2860
	DATA MO/0.5,-0.5/,M1/1.5,0.5,-0.5,-1.5/,ME/1.0,0.0,0.6666667,	2870
	1 0.3333333,0.3333333,0.6666667,0.0,1.0/	2880
		2890
C	DO 5 I=1,NVAR	2900
	5 A(ITB(I))=X(I)	2910
	DO 10 I=1,18	2920
10	GRAD(I)=0.0	2930
	DO 12 I=1,N	2940

12	YC(I)=0.0	2950
	VAL=0.0	2960
	DO 13 I1=1,N1	2970
	I2=(I1-1)*6	2980
	P1(I1)=A(I2+1)/2	2990
	C2(I1)=3.*A(I2+3)*A(I2+3)*A(I2+2)*A(I2+2)	3000
	C3(I1)=P1(I1)+2.*A(I2+5)	3010
13	C8(I1)=P1(I1)+A(I2+5)	3020
	IER=0	3030
	IERG=0	3040
C		3050
C	EVALUATE FUNCTION AT EACH DATA POINT FOR N1 SETS OF LINES.	3060
	DO 75 K=1,N	3070
	DO 14 I=1,18	3080
14	G(I)=0.0	3090
	P2=-XD(K)	3100
	DO 68 I1=1,N1	3110
	F(K)=0.0	3120
	I2=6*(I1-1)	3130
	L1=1+I2	3140
	L2=I1*6	3150
C		3160
C	SUM OVER M0 AND M1.	3170
	DO 60 I=1,2	3180
	C0(I1)=G0*M0(I)*A(I2+4)	3190
	DO 60 J=1,4	3200
	IF (ME(I,J) .EQ. 0.) GO TO 60	3210
	IF (M1(J) .GE. 0.) GO TO 15	3220
	C11(I1)=G1*(M1(J)+2.)*A(I2+4)	3230
	GO TO 20	3240
15	C11(I1)=G1*(M1(J)-2.)*A(I2+4)	3250
20	C1(I1)=G1*M1(J)*A(I2+4)	3260
	BETA(I1)=A(I2+3)*(3.*M1(J)*M1(J)-15./4.)	3270
	C4(I1)=P2+BETA(I1)	3280
	C5(I1)=P2-BETA(I1)	3290
	C6(I1)=C1(I1)-C0(I1)	3300
	C7(I1)=C11(I1)-C0(I1)	3310

	A1(I1)=P1(I1)*C3(I1)-C4(I1)*C4(I1)+C6(I1)*C6(I1)	3320
	A2(I1)=2.*C2(I1)*(P1(I1)*C3(I1)-P2*P2+BETA(I1)*BETA(I1)	3330
C	+2.*A(I2+5)*A(I2+5)-C6(I1)*C7(I1)+C2(I1)/2.)	3340
	A3(I1)=2.*C4(I1)*C8(I1)	3350
	A4(I1)=4.*P2*C8(I1)*C2(I1)	3360
	D1(I1)=P1(I1)*C3(I1)-C5(I1)*C5(I1)+C7(I1)*C7(I1)	3370
	D2(I1)=2.*C8(I1)*C5(I1)	3380
	B1(I1)=D1(I1)*C3(I1)-D2(I1)*C4(I1)+C2(I1)*P1(I1)	3390
	B2(I1)=D1(I1)*C4(I1)+D2(I1)*C3(I1)+C2(I1)*C5(I1)	3400
	E1(I1)=D1(I1)*A1(I1)+A2(I1)-D2(I1)*A3(I1)	3410
	E2(I1)=D2(I1)*A1(I1)+A4(I1)+D1(I1)*A3(I1)	3420
	E3(I1)=B1(I1)*E1(I1)+B2(I1)*E2(I1)	3430
	DD(I1)=E1(I1)*E1(I1)+E2(I1)*E2(I1)	3440
	F(K)=F(K)+ME(I,J)*E3(I1)/DD(I1)	3450
C		3460
C	CALCULATE GRADIENTS.	3470
	K1=0	3480
	IF (I1 .EQ. 2) K1=NVAR1	3490
	IF (I1 .EQ. 3) K1=NVAR2	3500
	K1SAVE=K1+1	3510
	K2SAVE=NVAR1	3520
	IF (I1 .EQ. 2) K2SAVE=NVAR2	3530
	IF (I1 .EQ. 3) K2SAVE=NVAR	3540
C		3550
C	CALCULATE PARTIAL DERIVATIVES OF THE LINESHAPE WITH RESPECT	3560
C	TO THE PARAMETERS.	3570
	DO 55 L=L1,L2	3580
	IF (IND(L) .EQ. 0) GO TO 55	3590
	K1=K1+1	3600
	GO TO (25,30,35,40,45,48,25,30,35,40,45,48,25,30,35,40,45,48),L	3610
25	IER=1	3620
	DB1=2.*(C3(I1)*C8(I1)-C5(I1)*C4(I1))+D1(I1)+C2(I1)	3630
	DB2=2.*(C8(I1)*C4(I1)+C5(I1)*C3(I1))+D2(I1)	3640
	DE1=2.*(C8(I1)*(D1(I1)+A1(I1)+2.*C2(I1))-C4(I1)*D2(I1)	3650
C	-C5(I1)*A3(I1))	3660
	DE2=2.*(C8(I1)*(D2(I1)+A3(I1))+C5(I1)*A1(I1)+C4(I1)*D1(I1)+2.*P2	3670
C	*C2(I1))	3680

DA=0.5	3690
GO TO 50	3700
30 IF (A(I2+2) .EQ. 0.) GO TO 32	3710
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)*C2(I1))/A(I2+2)	3740
DE2=2.*A4(I1)/A(I2+2)	3750
DA=1.0	3760
GO TO 50	3770
32 DB1=0.0	3780
DB2=0.0	3790
DE1=0.0	3800
DE2=0.0	3810
GO TO 50	3820
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)	3850
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))	3870
DE2=2.*(-C4(I1)*D2(I1)+C5(I1)*A3(I1)+C8(I1)*(D1(I1)-A1(I1))	3880
C +A4(I1)/BETA(I1))	3890
DA=BETA(I1)/A(I2+3)	3900
GO TO 50	3910
40 DB1=2.*C7(I1)*C7(I1)*C3(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)	3950
DE2=2.*(C6(I1)*C6(I1)*D2(I1)+C7(I1)*C7(I1)*A3(I1))/A(I2+4)	3960
DA=1.0	3970
GO TO 50	3980
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))	4020
DE2=2.*(P1(I1)*(D2(I1)+A3(I1))+C5(I1)*A1(I1)+C4(I1)*D1(I1)	4030
C +2.*P2*C2(I1))	4040
DA=1.0	4050

GO TO 50	4060
48 K3SAVE=K2SAVE	4070
K2SAVE=K2SAVE-1	4080
IERG=1	4090
GO TO 55	4100
50 DE3=DB1*E1(I1)+DE1*B1(I1)+DB2*E2(I1)+DE2*B2(I1)	4110
DDD=2.*(E1(I1)*DE1+E2(I1)*DE2)	4120
G(K1)=G(K1)+ME(I,J)*(DE3-E3(I1)*DDD/DD(I1))/DD(I1)*DA	4130
IF (IER .EQ. 0) GO TO 55	4140
G(K1)=G(K1)-ME(I,J)*E3(I1)/(DD(I1)*A(I2+4))	4150
IER=0	4160
55 CONTINUE	4170
60 CONTINUE	4180
F(K)=F(K)*0.25*A(I2+6)/P1(I1)	4190
DO 65 K2=K1SAVE,K2SAVE	4200
65 G(K2)=G(K2)*0.25*A(I2+6)/P1(I1)	4210
FSAVE(I1,K)=F(K)	4220
YC(K)=YC(K)+F(K)	4230
IF (IERG .EQ. 0) GO TO 68	4240
G(K3SAVE)=F(K)/A(I2+6)	4250
K2SAVE=K2SAVE+1	4260
IERG=0	4270
68 CONTINUE	4280
C	4290
C	4300
CALCULATE FUNCTION VALUE.	4310
FUNC(K)=(YD(K)-YC(K))	4320
FFF(K)=FUNC(K)/((N-NVAR)*(1.-YD(K)))	4330
VAL=VAL+FUNC(K)*FFF(K)	4340
DO 70 K1=1,NVAR	4350
70 GRAD(K1)=GRAD(K1)-2.*G(K1)*FFF(K)	4360
75 CONTINUE	4370
DO 80 I=1,NVAR	4380
80 GRAD(I)=BG*GRAD(I)	4390
VAL=BG*VAL	4400
RETURN	4410
C	4420
END	