# Nonthermalization and Large Variation in Multiphonon Relaxation Rate among Rare-Earth-Ion Stark Levels*

Edward D. Reed, Jr. and H. Warren Moos†
*Department of Physics, The Johns Hopkins University, Baltimore, Maryland 21218*
(Received 29 January 1973)

In $^5D_1$ of $YVO_4$:$Eu^{3+}$ at 2.0 °K, multiphonon relaxation occurs from the Stark level because it is not in thermal equilibrium with the lower of the two levels in the manifold. The energy levels of $^5D_1$ were simple enough to allow the construction of a detailed mathematical model which provided an excellent fit to the temperature-dependent multiphonon relaxation rate. The two Stark levels of $^5D_1$ also differ in multiphonon relaxation rate by factor of about 15. The Eu $^5D_1$ fluorescence was too weak in $YAsO_4$ and $YPO_4$ for these systems to be investigated for these effects. Similar effects appear also with $Ho^{3+}$ $E(^5S_2, ^5F_4)$ in $YVO_4$ and $YAsO_4$.

## I. INTRODUCTION

In the preceding paper[1] we reported the multiphonon (MP) relaxation of excited states of rare-earth ions in $YVO_4$, $YAsO_4$, and $YPO_4$, It was noted that the phonon energy distributions probably had a strong effect on the MP relaxation rates. The rates studied were also quite fast, ~ $10^5$ $sec^{-1}$. During the course of this study, unusual temperature dependences of excitation spectra and phase-shift measurements were noted in certain manifolds, and it is these which are reported here.[2] As will be shown, the experimental data can be explained by (i) large differences in MP relaxation rates among Stark levels of a manifold, possibly caused by the sharp variations in the phonon energy distribution and (ii) a relaxation rate between Stark levels which is not high enough to permit the thermalization among them, contrary to the usual assumption.

## II. Eu $^5D_1$ IN $YVO_4$

The energy levels of $Eu^{3+}$ in $YVO_4$ have been established by Brecher *et al.*[3] The $^5D_0$ lies at 17183 $cm^{-1}$ and $^5D_1$ is composed of two levels: a nondegenerate one at 18 932 $cm^{-1}$ and a double degenerate one at 18 941 $cm^{-1}$. At 4.2 °K and below, the weak $^5D_1$ fluorescence (radiative quantum efficiency ≈4%) originates principally from the lower of the two levels (no fluorescence from the upper level was seen at any temperature). This was determined from fluorescence spectra using the fluorescence identifications in Ref. 3. At 77 °K the radiative quantum efficiency of $^5D_1$ was $<<1\%$. The data consist of the MP transition rate ($W_{mp}$) temperature dependence plus four excitation spectra of the $^5D_1$ manifold.

### A. Excitation Spectra

Figure 1 shows the four excitation spectra. These were recorded by monitoring the $^5D_1 \rightarrow {}^7F_3$ and $^5D_0 \rightarrow {}^7F_2$ fluorescences at 77 and 2.0 °K, respectively, while the premonochromator was scanned across the two $^5D_1$ levels. At 2.0 °K it is seen that the relative pumping strength of the two $^5D_1$ levels depends on whether the $^5D_0$ ($A/B = 2.10$) or $^5D_1$ ($A/B = 1.05$) fluorescence is monitored. At 77 °K the relative pumping strength is the same no matter which fluorescence is used, and is equal to 2.1. These observations were not dependent on pump-light intensity, They can be explained by the occurrence of MP relaxation at 2.0 °K, from the upper $^5D_1$ level to $^5D_0$, bypassing the $^5D_1$ lower level (at this temperature the upward transition rate

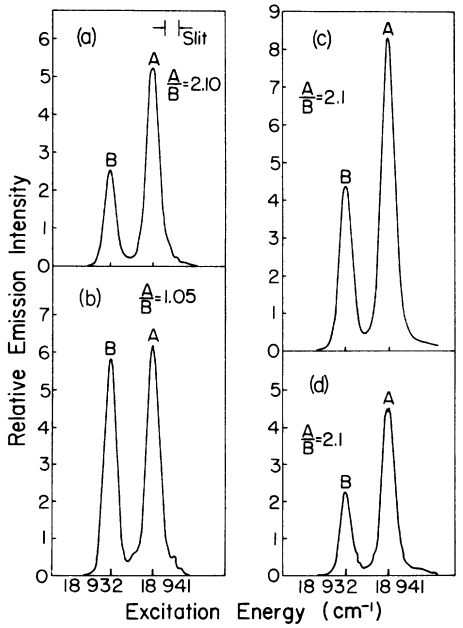


FIG. 1. Excitation spectra of Eu $^5D_1$ in $YVO_4$ monitoring (a) the 2.0 °K $^5D_0 \rightarrow {}^7F_2$ fluorescence, (b) the 2.0 °K $^5D_1 \rightarrow {}^7F_3$ fluorescence, (c) the 77 °K $^5D_0 \rightarrow {}^7F_2$ fluorescence, and (d) the 77 °K $^5D_1 \rightarrow {}^7F_3$ fluorescence.

between the two $^5D_1$ levels, seperated by 9 $cm^{-1}$, is negligable). Roughly half of the ions excited to the upper $^5D_1$ level appear to relax directly to $^5D_0$, which requires that the one-phonon spontaneous relaxation rate between the $^5D_1$ levels be approximately equal to the spontaneous MP relaxation rate of the upper level. At 77 °K the upward and downward transition rates between the $^5D_1$ levels were large, so that the two levels were then strongly coupled and incapable of responding independently to the MP process that depleted the manifold. This picture predicts that the 2.0 °K excitation spectrum using the $^5D_0$ fluorescence (which simply shows the "true" relative pumping strength of the $^5D_1$ levels) should look the same as both 77 °K spectra; this is indeed observed. It should be noted that the small (about 4% at 2.0 °K and $\ll 1\%$ at 77 °K) radiative depopulation of $^5D_1$ (which bypasses $^5D_0$) has been neglected in this discussion.

### B. MP Relaxation Rate

Further evidence of the weak coupling between the $^5D_1$ Stark levels is contained in the $W_{mp}$-versus-temperature data shown in Fig. 2. Each value of $W_{mp}$ was obtained from the reciprocal of the measured fluorescence lifetime after a small correction (negligible at all but very low temperatures, where it was only 4%) for the radiative contribution. Consider first the performance of $W_{mp}$ at low temperatures and neglect the drop in $W_{mp}$ at high temperatures (which will later be shown to be due to thermal population of $^5D_1$ from $^5D_0$). The rapid rise in $W_{mp}$ with increasing temperature at low temperatures indicates that the upper double degenerate level in $^5D_1$ has a much larger MP decay rate than the lower level. The weak coupling between the levels acts as a bottleneck, so that the MP decay rate for the manifold (measured using the fluorescence from the lower level) should not increase as rapidly with temperature as in the tightly coupled case. The level structure is simple enough that this picture can be checked quantitatively. Consider the level scheme in Fig. 3(a). Recall that the fluorescence occurs primarily from the lower level at all temperatures. Remembering that level 2 is doubly degenerate, the following notation is adopted: the $A$'s denote one-phonon transition rates involving the lower and *one* of the upper states; $W_1$ is the spontaneous MP decay rate of level 1 to $^5D_0$; $W_2$ is the spontaneous MP decay rate of *each* of the upper states to $^5D_0$; $g$ is the rate that ions are pumped into level 2 (i.e., the sum of the rates into each state of that level); and $c\,g$ ($c$ is a constant) is the rate ions are pumped into level 1. The weak fluorescence of level 1 will be neglected. It is necessary to consider this situation in which both levels 1 and 2 are pumped, since the lifetime measurements had to be performed with wide premonochromator slits for intensity reasons. If $N_2$ is the number of ions in level 2 (i.e., the sum of the ions in each state) and $N_1$ the number in level 1, the rate equations are

$$\frac{dN_2}{dt} = g + 2A_{12}N_1 - A_{21}N_2 - W_2N_2 ,$$

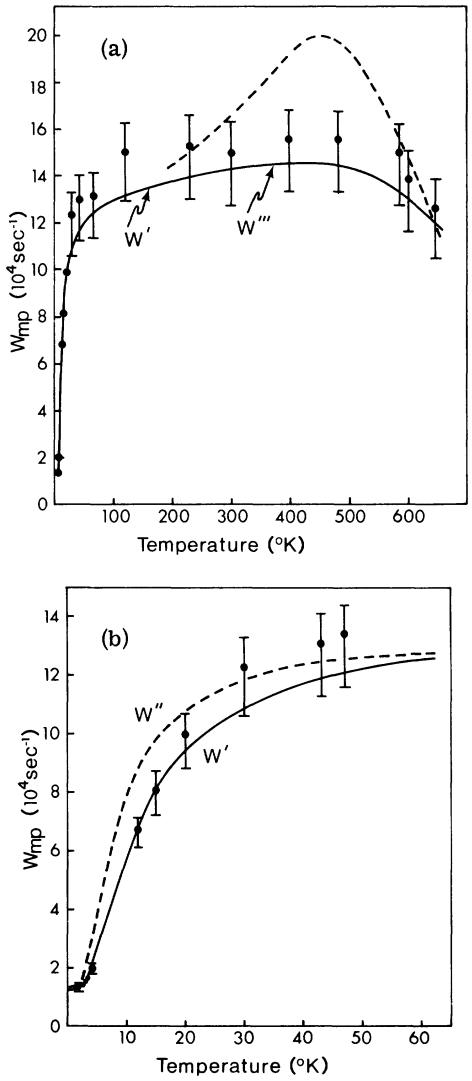


FIG. 2. (a) Temperature dependence of the MP transition rate of Eu $^5D_1$ in $YVO_4$. The relative error between data points is much less than the absolute error indicated by the bars. The solid line is a theoretical fit: $W'$ ($0 \leq T \leq 200$ °K) is the dependence expected from the weakly coupled model [Eq. (2)]; $W'''$ ($T > 200$ °K) is the high-temperature dependence expected when $^5D_1$ and $^5D_0$ are coupled by a two-phonon process [Eq. (7)]. The dashed line is the expected dependence due to a three-phonon process between $^5D_1$ and $^5D_0$. (b) Low-temperature region of (a) expanded. $W'$ is the dependence of the weakly coupled model [Eq. (2)]. $W''$ is the dependence expected from the tightly coupled model [Eq. (4)].

$$\frac{dN_1}{dt} = c\mathcal{I} + A_{21} N_2 - W_1 N_1 - 2 A_{12} N_1. \quad (1)$$

A Fourier series was substituted for the chopped pump $\mathcal{I}$ and the two equations were solved simultaneously for the phase shift of the first Fourier component of $N_1(t)$, since the fluorescence originates from level 1. The result for this model is that the MP relaxation rate $W'$ determined by measuring the phase shift of the fluorescence from the lower $^5D_1$ Stark level is

$$W' = \frac{[A_{21} + c(A_{21} + W_2)][A_{21} W_1 + 2A_{12} W_2 + W_1 W_2] + \omega^2 [c(W_1 + 2A_{12}) - A_{21}]}{A_{21}[W_1 + W_2 + A_{21} + 2A_{12}] + c[2 A_{21} W_2 + A_{21}^2 + 2 A_{21} A_{12} + W_2^2 + \omega^2]} . \quad (2)$$

$\omega$ is the angular chopping frequency. $c$ can be determined from the excitation spectrum of the $^5D_0$ fluorescence [Fig. 1 (a)] and is 1/2.10. A relationship between $W_2$ and the spontaneous part of $A_{21}$ can be found. Let $Q(2)$ be the quantum yield of the $^5D_1$ fluorescence when level 2 is pumped at the rate $\mathcal{I}$ and $Q(1)$ the yield when level 1 is pumped at the rate $c\mathcal{I}$. At 2.0 °K, $A_{12}$ is negligible and

$$\frac{Q(2)}{Q(1)} = \frac{\mathcal{I}}{c\mathcal{I}} \frac{A_{21}}{A_{21} + W_2} \quad (T \leq 2.0\ ^\circ\mathrm{K}).$$

Obtaining the quantum yield ratio from Fig. 1 (b),

$$A_{21}/(A_{21} + W_2) = 1.05/2.10 = 0.50,$$

or $A_{21} = W_2$ ($T \leq 2.0$ °K). The values of $A_{21}$ and $A_{12}$ as functions of temperature are $W_2[n(9) + 1]$ and $W_2 n(9)$, respectively, where $n(9)$ denotes the Bose-Einstein occupation probability[4] at $\hbar\omega = 9$ cm$^{-1}$. Finally, $W_1$ and $W_2$ were determined approximately from the measured values of $W_{mp}$ in the high- and low-temperature limits. They were then varied slightly (± 5%) for a best fit to the data. The resulting fit is the solid line in Fig. 2(b) and the solid line below 200 °K in Fig. 2(a), with the values

$$\begin{aligned} W_1 &= 1.30 \times 10^4\ \mathrm{sec}^{-1}, \\ W_2 &= 2.00 \times 10^5\ \mathrm{sec}^{-1}, \\ c &= 0.476, \\ A_{21} &= 2.00 \times 10^5\,[n(9) + 1]\ \mathrm{sec}^{-1}, \\ A_{12} &= 2.00 \times 10^5\,[n(9)]\ \mathrm{sec}^{-1}. \end{aligned} \quad (3)$$

By contrast, if the spontaneous part of $A_{21}$ were much greater than $W_2$, i.e., the two $^5D_1$ levels were tightly coupled, the MP transition rate of $^5D_1$ would be[5]

$$W'' = \frac{1.30 + 40.0\, e^{-9/kt}}{1 + 2\, e^{-9/kt}} \times 10^4\ \mathrm{sec}^{-1}. \quad (4)$$

This result differs from $W'$ significantly only at low temperatures and is plotted as a dashed line in Fig. 2(b).

Comparing the rates $W'$ and $W''$ in Fig. 2(b), it is clear that $W'$ provides a very good fit to the measured values of $W_{mp}$, while $W''$ does not. There was no way the parameters in the expression for $W''$ could be adjusted to fit the relatively slow rise in the measured $W_{mp}$ with increasing temperature below 15 °K. As shown in Fig. 2(b), when $W''$ is adjusted to pass through the data point at 2.0 °K, it is almost 50% too large at 4.2 °K.

Next consider the high-temperature performance of the measured MP decay rate shown in Fig. 2(a). The drop in $W_{mp}$ at high temperatures is caused by transitions from $^5D_0$ to $^5D_1$ stimulated by thermal phonons. This thermal population is important here because of the relatively narrow energy gap and the small transition rate ($1.74 \times 10^3$ sec$^{-1}$) of $^5D_0$. By fitting a stimulated emission model[1] to the measured $W_{mp}$ values at high temperatures, it will be shown below that $^5D_1$ and $^5D_0$ are coupled by a two-phonon process. Consider the level scheme of Fig. 3(b), in which $^5D_1$ is pumped at rate $\mathcal{I}'$. (For $T \gtrsim 200$ °K the two $^5D_1$ levels are tightly coupled and only the manifold as a whole need be considered in the MP relaxation process.) The fluorescence from $^5D_1$ is negligible. Above 200 °K the three states of $^5D_1$ are approximately equally populated. Using Eq. (3), the $W'$s of Fig. 3(b) are

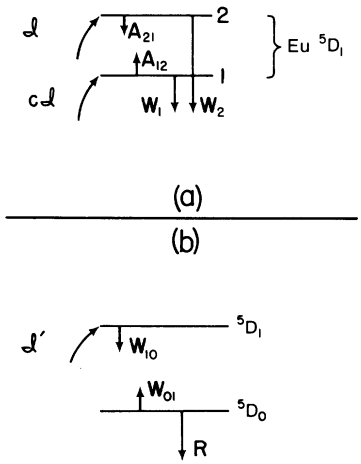


FIG. 3. (a) Energy levels of Eu $^5D_1$ in $YVO_4$. The two are split 9 cm$^{-1}$. The rates are used in Eq. (1). (b) Eu $^5D_1$ and $^5D_0$ manifolds. The energy gaps for the two $^5D_1$ levels are 1749 and 1758 cm$^{-1}$. The rates are used in Eq. (6).

$$W_{10} = 13.8\times10^4\,[n(880)+1]^2\ \text{sec}^{-1},$$
$$W_{01} = 41.3\times10^4\,[n(880)]^2\ \text{sec}^{-1}. \quad (5)$$

A two-phonon model has been assumed. If $N_1$ and $N_0$ are the populations of $^5D_1$ and $^5D_0$, respectively, and $R$ is the transition rate of $^5D_0$, the rate equations are

$$\frac{dN_1}{dt} = g' + W_{01}N_0 - W_{10}N_1\,,$$
$$\frac{dN_0}{dt} = W_{10}N_1 - W_{01}N_0 - R\,N_0\,. \quad (6)$$

Substituting a Fourier series for $g'$ and solving for the phase shift of the fundamental component of $N_1$ $(t)$ results in the following predicted high-temperature MP decay rate of $^5D_1$:

$$W''' = W_{10}\,\frac{R(R+W_{01})+\omega^2}{(W_{01}+R)^2+W_{01}\,W_{10}+\omega^2}\quad (T\geq 200\,^\circ\text{K}). \quad (7)$$

$\omega$ is the angular chopping frequency. Using the measured value $(1.74\times10^3\ \text{sec}^{-1})$ for $R$, and the values of $W_{01}$ and $W_{10}$ from Eq. (5), $W'''$ yielded the solid line above 200 °K in Fig. 2(a). It provides an excellent fit to the data. For comparison, the result predicted by a three-phonon process between $^5D_1$ and $^5D_0$ is shown by a dashed line above 200 °K. There is no question that the high-temperature $^5D_1 \rightarrow {}^5D_0$ decay occurs predominantly via a two-phonon process.

### C. Discussion

The quite different MP decay rates of the two $^5D_1$ levels could be due simply to a difference in their coupling strengths with the lattice; symmetry considerations do not appear to shed any light on this possibility. Another possible explanation can also be given. The gaps (to $^5D_0$) for the levels are 1749 and 1758 $\text{cm}^{-1}$. Considering the $YVO_4$ vibronics,[6] it is seen that transitions from the upper level (which need two 879-$\text{cm}^{-1}$ phonons) can make use of the large, but energetically narrow, density of phonon modes centered at 880 $\text{cm}^{-1}$ (with an error of, at most, 5 $\text{cm}^{-1}$). Transitions from the lower level, however, can only use the less-dense modes removed from the 880-$\text{cm}^{-1}$ peak. Since the density of phonon modes is convoluted with itself in the theoretical expression for the MP transition rate,[7] this could explain the factor of about 15 difference in the two MP decay rates.

The observed one-phonon spontaneous transition rate between the two $^5D_1$ levels was found to be $2.00\times10^5\ \text{sec}^{-1}$. This at first appears to be abnormally small. However, it is possible to estimate the expected rate using an expression due to Orbach[8]:

$$W = (3\delta^3/2\pi\rho v^5\hbar^4)\,|\,\langle {}^5D_1,\ J_z=0\,|\,V_{iv}\,|\,{}^5D_1,\ J_z=\pm1\rangle\,|^2. \quad (8)$$

$V_{iv}$ is the term in the expansion of the ion-lattice interaction which is linear in the normal coordinates.[9] $\delta$ is the energy seperation of the states, $\rho$ is the mass density of the crystal, and $v$ is the speed of sound in the crystal. $v$ was estimated using the Debye temperature for $GdVO_4$[10](which should be close to that of $YVO_4$[11]) to be $3.44\times10^5$ cm/sec. $\rho$ was calculated from the lattice parameters of $YVO_4$[12] to be 4.24 $\text{g/cm}^3$. Following Orbach, an estimate of the matrix element in Eq. (8) can be made using the static crystal-field parameters for $Eu^{3+}$ in $YVO_4$. Using the static crystal-field parameters due to Brecher *et al.*,[3] the tables of Nielson and Koster,[13] the tables of Rotenberg *et al.*,[14] and the $^5D_1$ wave functions of Ofelt[15] (neglecting terms which contributed less than 0.06 to the wave function), the squared matrix element was estimated to have the value 40.5 $\text{cm}^{-2}$. The value of the one-phonon spontaneous decay rate between the Eu $^5D_1$ levels was then calculated to be $1.9\times10^5\ \text{sec}^{-1}$. Thus, the low rate determined experimentally is consistent with that predicted from theory.

Eu $^5D_1$ fluoresced too weakly in $YAsO_4$ and $YPO_4$ for these systems to be investigated for any unusual effects.

## III. Ho $E$ ($^5S_2$, $^5F_4$) IN $YVO_4$

Excitation spectra and lifetime measurements indicated in this case also that MP relaxation at 4.2 °K was occurring from a higher level in $E$ directly to Ho $D$, bypassing the lowest $E$ level. Due to the complexity of the level scheme, however, a detailed mathematical analysis could not be made in this case. Analogous to Fig. 1 for Eu $^5D_1$, four Ho $E$ excitation spectra were recorded (not shown), monitoring $E$ and $D$ fluorescences at 4.2 and 77 °K. As with $^5D_1$, the relative pumping strengths of the $E$ levels (six were seen) differed in the two 4.2 °K spectra, but were the same in the 77 °K spectra (which were complicated by absorption from higher levels in the ground manifold). Phase-shift measurements on the $E$ and $D$ fluorescences when $E$ was pumped at 4.2 °K were even more striking. In such a case the phase shift of a $D$ fluorescence, say $D \rightarrow Z$, should be the sum of the shifts due to $D$ and $E$ separately (obtained by pumping $D$ and measuring $D \rightarrow Y$, and by pumping $E$ and measuring $E \rightarrow Y$). However, this was not observed. When using wide premonochromator slits and pumping $E$, the phase shift of the $D$ fluroescence was about 25% less than that of the fluorescence from $E$. When the premonochromator slits were narrowed to selectively pump one $E$ level at a time, the size of the phase-shift anomaly was found to depend on which $E$ level was pumped. The phase shift discrepancy ranged from none to about 35%. (For example, assume $D$ contributed

a 3° phase shift, and the phase shift of the $E$ fluorescence was 45°. If the $D$ fluorescence when $E$ was pumped had a 35° shift, "the discrepancy," was 48° − 35° = 13°.) Unfortunately, the lowest $E$ level could not be pumped directly at 4.2° K, but it appears from fluorescence spectra that it lies about 8 $cm^{-1}$ below the lowest level seen in the 4.2 °K excitation spectra. The phase-shift discrepancies were consistent with the excitation spectra in the sense that the levels in the 4.2 °K excitation spectrum monitoring the $E$ fluorescence which departed most from their "true" relative pumping strengths (as given in the 4.2 °K excitation spectrum monitoring the $D$ fluorescence) were the ones which showed the largest phase-shift discrepancies. The phase-shift discrepancies disappeared at 77 °K. The temperature dependence of the HO $E$ $W_{mp}$ (not shown) indicates that a level approximately 9 $cm^{-1}$ above the lowest in the manifold has a MP transition rate perhaps ten times that of the lowest.

HO $E$ in $YAsO_4$, also showed phase-shift anomalies, but they were not as large as with $YVO_4$. This system was not investigated in detail because the fluorescences were rather weak.

## IV. CONCLUSION

Measured temperature dependences of MP transition rates ($W_{mp}$) indicate that the $W_{mp}$ of the separate levels in a manifold can differ significantly. Eu $^5D_1$ in $YVO_4$ consists of two levels, separated by 9 $cm^{-1}$, and the upper level has a MP transition rate which is about 15 times that of the lower. The high-temperature $W_{mp}$ data on $^5D_1$ were complicated by effects due to thermally stimulated excitation of $^5D_1$ and $^5D_0$, but it was shown that the MP decay of $^5D_1$ is predominately a two-phonon process. This fact along with the vibronics for $YVO_4$ suggest a reason for the factor of 15 difference in $W_{mp}$ for the two levels: the two phonons for the upper level are in resonance with a spike at about 880 $cm^{-1}$ in the phonon energy distribution. The energy levels of HO $E$ are much more complicated, but it appears from the $W_{mp}$-versus-temperature data at low temperatures that one of the upper levels has a MP relaxation rate perhaps ten times that of the lowest level.

One of the most interesting results of this study was the observation of MP relaxation from manifolds whose Stark levels were not in thermal equilibrium at 4.2 °K. The observation of this phenomenon may have been facilitated by the particular parameters of the levels studied. The ideal conditions for observing the slow thermalization are obtained when the lowest level has a not-too-large MP relaxation rate and an upper level has a large MP relaxation rate. This is precisely the situation with HO $E$ and Eu $^5D_1$ in $YVO_4$. The relatively slow thermalization of a rare-earth manifold in these and other hosts may be an occurrence which is more common than is realized.

---

*Supported by the U.S. Army Research Office, Durham, N. C.

†Visiting Fellow, 1972–1973, Joint Institute for Laboratory Astrophysics—Laboratory for Atmospheric and Space Physics, University of Colorado, Boulder, Colo. 80302

[1]Edward D. Reed, Jr. and H. Warren Moos, preceding paper, Phys. Rev. B 8, 980 (1973).

[2]Based on a Ph.D. dissertation submitted by Edward D. Reed, Jr. to The Johns Hopkins University, 1972 (unpublished). Available from University Microfilms, Ann Arbor, Mich. For further details see the dissertation.

[3]C. Brecher, H. Samelson, A. Lempicki, R. Riley, and T. Peters, Phys. Rev. **155**, 178 (1966).

[4]Equation (3) of Ref. 1.

[5]Using Eq. (5) of Ref. 1.

[6]Figure 3 of Ref. 1.

[7]References 7 and 13 of Ref. 1.

[8]R. Orbach, Proc. R. Soc. A **264**, 458 (1961).

[9]See Eq. (1) of Ref. 1.

[10]J. D. Cashion, A. H. Cooke, L. A. Hoel, D. M. Martin, and M. R. Wells, Colloq. Int. Cent. Natl. Rech. Sci. **2**, 417 (1970).

[11]J. H. Colwell and B. G. Mangum (private communication).

[12]R. W. G. Wyckoff, *Crystal Structures* (Interscience, New York, 1965), Chap. VIII A.

[13]C. W. Nielson and G. F. Koster, *Spectroscopic Coefficients for $p^n$, $d^n$, and $f^n$ Configurations* (M.I.T. Press, Cambridge, Mass., 1964).

[14]M. Rotenberg, R. Bivins, N. Metropolis, and J. K. Wooten, Jr., *The 3-j and 6-j Symbols* (M.I.T. Press, Cambridge, Mass., 1959).

[15]G. S. Ofelt, J. Chem. Phys. **38**, 2171 (1963).