PHYSICAL REVIEW B VOLUME 9, NUMBER 11 1 JUNE 1974

Analysis of the behavior of Er^{3+} in zircon-structure systems*

Vishwamittar and S. P. Puri
Department of Physics, Punjab Agricultural University, Ludhiana-141004, India

(Received 30 May 1973)

New sets of crystal-field parameters have been derived for Er^{3+} in $YAsO_4$, YPO_4, YVO_4, and $ScVO_4$ crystals, which give a simultaneous good account for the ground-level g values, the hyperfine interaction constants, and susceptibility in addition to the observed Stark levels. Moreover, calculations of the anisotropy and quadrupole splitting for these systems are included. The old as well as new sets of crystal-field parameters are discussed in the framework of electrostatic crystal field, angular overlap, and superposition models. The ionic bonding is found to decrease in the order ($YAsO_4$, YPO_4), YVO_4, $ScVO_4$. An attempt has also been made to estimate the spin-lattice relaxation time. Furthermore, based on the analysis of the observed spectroscopic splitting factors and hyperfine interaction constants, crystal-field parameters are reported for Er^{3+} in $ZrSiO_4$, $HfSiO_4$, and $ThSiO_4$.

I. INTRODUCTION

The cathodoluminescent behavior of Eu^{3+}-doped YVO_4 and its subsequent use as a color-television phosphor[1] has aroused considerable interest in the study of rare-earth compounds with zircon-structure (i.e., $ZrSiO_4$ type) and the rare-earth ions doped in isostructural host lattices. The investigation of such systems has been further stimulated by their structural similarity to commonly used laser host materials, the scheelites (with $CaWO_4$ as representative), and by the fact that the concentrated compounds seem to constitute ideal cases for studying Ising- as well as Heisenberg-type three-dimensional magnetic systems. It is found that $DyASO_4$, $DyPO_4$, $DyVO_4$, etc., despite their chemical and crystallographic similarities, exhibit distinct differences in their physical properties like magnetic susceptibility, specific heat, etc., at low temperatures.[2-7] Consequently, it is interesting to investigate the detailed behavior of such host lattices and, for this purpose, the study of dilute systems is more convenient, since their theoretical analysis is comparatively straightforward. In the wake of Dieke's[8] comment that the Er^{3+} ion serves as a useful probe for a crystal field, quite a large effort has been directed towards the study of the Er^{3+}-doped zircon-structure systems.

When a rare-earth ion is embedded in a crystal, it experiences static as well as dynamic interactions due to a crystalline field having the same symmetry as that of the lattice site. The former splits each J state into a number of Stark levels and can be represented adequately by the crystal-field (CF) parameters obtained through the interpretation of spectroscopic or magnetic data.[9] The latter, on the other hand, manifests itself in spin-lattice relaxation and linewidths in optical spectra, and by treating it as a fluctuation in the static part, the parameters required to describe it have also been expressed in terms of the static CF parameters.[10,11] Consequently, the CF parameters should serve as a good gauge of the effect of surroundings on a rare-earth ion and for these to be physically significant, maximum body of experimental findings must be faithfully derivable through the same set. However, in the case of Er^{3+}-doped $YAsO_4$, YPO_4, YVO_4, and $ScVO_4$, it has been found[12] that the spectroscopic CF parameters[13-15] fail to explain the electron-paramagnetic-resonance results[16-18] and this, in turn, restrains confidence in the parameters. Therefore, it is imperative to obtain the CF parameters which reconcile various measurements; this paper is the outcome of such an effort. It turns out that the agreement for various micro- as well as macro-characteristics is improved with the new sets of CF parameters, though the root-mean-square (rms) deviation for the energy-level fit is increased. The static crystalline field in these systems is discussed in light of various theoretical models and also included are the comments on the dynamic component of the crystal field.

In view of the similarity of structure and expected potential use of the silicates as solid-state laser materials, the CF parameters have also been obtained for $ZrSiO_4$, $HfSiO_4$, and $ThSiO_4$ host lattices doped with Er^{3+}, such that these account for the observed g values. However, for want of other particularly spectroscopic data (for which these results will provide a useful starting point), these parameters need be given only limited importance.

II. CRYSTAL STRUCTURE

The crystals $YAsO_4$, YPO_4, YVO_4, $ScVO_4$, $ZrSiO_4$, $HfSiO_4$, and $ThSiO_4$ (RXO_4) have tetragonal structure[19] with zircon ($ZrSiO_4$) as a typical representative. The trivalent rare-earth impurities substitute for Y^{3+} or Zr^{4+} ion and thus occupy magnetically equivalent sites having noncentrosymmetric D_{2d} point symmetry whose z axis coincides

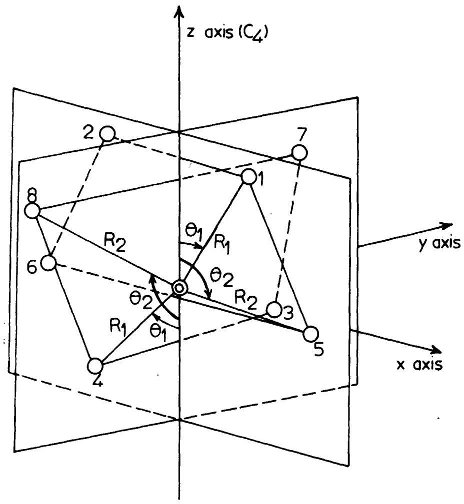

FIG. 1. The dodecahedral arrangement of O^{2-} ions around the central Y^{3+} or Zr^{4+} ion (◎) in the zircon-structure systems. The coordinate system is so chosen that ϕ_i are multiples of $\frac{1}{2}\pi$. The circles 1–4 represent the four oxygens at R_1 and making an angle θ_1 with the fourfold axis, whereas the circles 5–8, the oxygens at R_2 and subtending an angle θ_2.

with the crystalline fourfold axis. This is so even though charge compensation is necessary in the case of silicates.[20] Consequently, the central ion is surrounded by a dodecahedral array of eight neighboring oxygens—four of these are at one distance R_1 and the other four at a slightly different distance R_2 (see Fig. 1). Recently, Lohmüller *et al.*[21] refined the crystal structures of YVO_4, $LuPO_4$, and $LuAsO_4$, and Newman and Urban[22] extrapolated the data to find the position coordinates of oxygens in $YAsO_4$, YPO_4, and $ScVO_4$. These values, with reference to the present symbols, are given in Table I. The crystal structure of $ZrSiO_4$ has been refined by Robinson *et al.*,[23] and the corresponding parameters are also included in Table I. However, in the case of $HfSiO_4$ and $ThSiO_4$ these quantities are not known so accurately and the values used (Table I) have been derived from the data tabulated by Reynolds *et al.*[24] The entries of Table I show a fairly close correlation between θ_1 or θ_2 and the relative distance of the oxygens subtending these angles. $R_1 - R_2$ and θ_1 are minimum for YPO_4, whereas θ_2 is maximum; $ScVO_4$ and $ThSiO_4$ show slight deviations from the linear dependence of θ_1 and θ_2 on $R_1 - R_2$ for these compounds. It is found that $\theta_1 = 28.5°$ and $\theta_2 = 104.8°$ correspond to equal bond length for all the eight ligands.

When a host ion is replaced by Er^{3+}, some distortion will be produced in the dodecahedron because of difference in the ionic radii (see Table I).[25] It is expected that the deformation will be minimum in the compounds YXO_4, and maximum in the case of $ScVO_4$ and $ThSiO_4$ host lattices. Since the mechanisms controlling the atomic rearrangements are not established, the deformations are ignored in the model-dependent calculations. Nevertheless, in order to have an idea of indeterminacy introduced by this distortion, the calculations for $ErPO_4$ and $ErVO_4$ have been carried out and the relevant parameters for these two lattices[26] are also projected in Table I. Evidently, the parameters for $ErVO_4$ differ much from those for $ScVO_4$, but are reasonably close to those for YVO_4.

III. THEORY

In the D_{2d} site the Hamiltonian, because of symmetry, parity considerations, and the nature of $4f$ electrons, takes the form

$$\hat{H} = \hat{H}_0 + (\alpha_J A_2^0 \langle r^2 \rangle \hat{O}_2^0 + \beta_J A_4^0 \langle r^4 \rangle \hat{O}_4^0 + \gamma_J A_6^0 \langle r^6 \rangle \hat{O}_6^0$$
$$+ \beta_J A_4^4 \langle r^4 \rangle \hat{O}_4^4 + \gamma_J A_6^4 \langle r^6 \rangle \hat{O}_6^4) . \qquad (1)$$

Here $\hat{H}_0$ is the free-ion Hamiltonian; the expression in parentheses represents the static crystal-field interaction $\hat{H}_{CF}$ with the usual meaning for various symbols,[9] and includes the single-particle effects of overlap, covalency, and configuration interaction, in addition to the electrostatic contribution.[27]

When such a system is subjected to a magnetic field $\vec{H}$, the Zeeman interaction, under the valid assumption of J being a good quantum number, is given by

$$\hat{H}_Z = g_J \mu_B \vec{H} \cdot \hat{\vec{J}} . \qquad (2)$$

The Zeeman splittings and hence the spectroscopic splitting factors $g_\parallel$ and $g_\perp$ are derived by treating $\hat{H}_Z$ as a perturbation on the Stark levels:

$$g_\parallel = 2 g_J \langle \alpha | \hat{J}_z | \alpha \rangle ,$$
$$g_\perp = g_J \langle \alpha | \hat{J}_+ | \beta \rangle . \qquad (3)$$

TABLE I. Host central-ion radii and the oxygen-ion coordinates (R_i, θ_i) for various zircon-structure crystals.

Compound	Ion radius[a] (Å)	R_1 (Å)	θ_1	R_2 (Å)	θ_2
$YAsO_4$ [b]	0.893	2.412	31° 53′	2.300	102° 12′
YPO_4 [b]	0.893	2.374	30° 13′	2.313	103° 40′
YVO_4 [b]	0.893	2.433	32° 50′	2.291	101° 54′
$ScVO_4$ [b]	0.732	2.369	33° 50′	2.116	101° 50′
$ZrSiO_4$ [c]	0.79	2.268	32° 26′	2.131	101° 20′
$HfSiO_4$ [d]	0.78	2.26	32° 20′	2.12	101° 22′
$ThSiO_4$ [d]	1.02	2.50	28° 36′	2.46	104° 29′
$ErPO_4$ [e]	0.881	2.364	30° 31′	2.294	103° 29′
$ErVO_4$ [e]	0.881	2.435	33° 04′	2.272	101° 58′

[a] From Ref. 25.
[b] From Ref. 22.
[c] Obtained from the x-ray data of Ref. 23.
[d] Obtained through the values tabulated in Ref. 24.
[e] Based on parameters given in Refs. 19 and 26.

Following Rubins,[28] the eigenfunctions $|\alpha\rangle$ and $|\beta\rangle$ of a Kramers doublet are so assigned that $\langle\alpha|\hat{J}_-|\beta\rangle = 0$, and this, in turn, defines the sign of $g_\parallel$ explicitly, which is consistent with the Karayianis's convention.[29] The first- and second-order Zeeman perturbation coefficients derived from above are used to extract the temperature dependence of the principal gram-atomic magnetic susceptibilities $\chi_\parallel$ and $\chi_\perp$ through the Van Vleck[30] formula, and are, in turn, employed to define anisotropy $\Delta\chi = \chi_\parallel - \chi_\perp$, mean susceptibility $\bar{\chi} = \frac{1}{3}(\chi_\parallel + 2\chi_\perp)$, and mean effective magnetic moment $\bar{\mu}_{\text{eff}} = (3kT\bar{\chi}/N)^{1/2}$.

In addition to the crystal field and Zeeman perturbations, hyperfine (hf) interactions of internal magnetic field and electric field gradient (EFG) with the nuclear magnetic dipole moment and electric quadrupole moment, respectively, are also present in such systems. For dilute systems, such as those under investigation, the magnetic hf interaction arises mainly from the field produced by the $4f$ electrons, and for D_{2d} symmetry may be written[31,32]

$$\hat{H}_m = A_\parallel \hat{S}_z \hat{I}_z + \tfrac{1}{2} A_\perp (\hat{S}_+ \hat{I}_- + \hat{S}_- \hat{I}_+) . \tag{4}$$

Here

$$A_\parallel = 4 g_N \mu_N \mu_B N_J \langle r^{-3} \rangle_{\text{eff}} \langle \alpha | \hat{J}_z | \alpha \rangle$$

and

$$A_\perp = 2 g_N \mu_N \mu_B N_J \langle r^{-3} \rangle_{\text{eff}} \langle \alpha | \hat{J}_+ | \beta \rangle , \tag{5}$$

the sign of $A_\parallel$ being different from that of $g_\parallel$ if g_N is negative. The Hamiltonian for quadrupole interaction, in usual notation, is given by[32]

$$\hat{H}_q = P(\hat{I}_z^2 - \tfrac{1}{3}\hat{I}^2) , \tag{6}$$

where

$$P = \left(\frac{9e^2Q}{4I(2I-1)}\right)\left((1-R)\langle r^{-3}\rangle_{4f}\alpha_J\langle J_z^2 - \tfrac{1}{3}J(J+1)\rangle_T + \frac{4(1-\gamma_\infty)A_2^0\langle r^2\rangle}{3e^2\langle r^2\rangle_{4f}(1-\sigma_2)}\right); \tag{7}$$

the temperature dependence of the lattice contribution of EFG is assumed to be negligible. The parameters $A_\parallel$, $A_\perp$, and P are obtained through EPR or Mössbauer-effect studies; the sign of $A_\parallel$ being significant only for the latter. In the case of Mössbauer experiments, one gets the temperature dependence of the quadrupole splitting, which for ^{166}Er is given by

$$\langle \Delta E_Q \rangle_T = \tfrac{1}{8} e^2 Q \left((1-R)\langle r^{-3}\rangle_{4f}\alpha_J\langle 3J_z^2 - J(J+1)\rangle_T + \frac{4(1-\gamma_\infty)A_2^0\langle r^2\rangle}{e^2\langle r^2\rangle_{4f}(1-\sigma_2)}\right). \tag{8}$$

At very low temperatures, the effect of hf structure also shows up in the specific heat and its contribution can be estimated from the formula[33]

$$C_{\text{hf}} = (R/k^2T^2)\left[\tfrac{1}{9}(A_\parallel^2 + 2A_\perp^2)S(S+1)I(I+1) + \tfrac{1}{45}P^2 I(I+1)(2I-1)(2I+3)\right] , \tag{9}$$

where P refers to the effect of the lowest Stark level only.

IV. CALCULATIONS AND RESULTS

In this section, various physical quantities derived through the already available CF parameters are compared with the corresponding measurements and it is shown that these sets do not produce good agreement for the g values, hf-structure parameters, etc. Therefore, new schemes of parametrization are proposed such that more measurements can be explained simultaneously.

TABLE II. CF parameters and rms deviation (in cm^{-1}) for Er^{3+} spectra in various zircon-structure systems (D_{2d} site symmetry). The data for which references are not given in the last column are the result of the present work.

Host lattice	$A_2^0\langle r^2\rangle$	$A_4^0\langle r^4\rangle$	$A_6^0\langle r^6\rangle$	$A_4^4\langle r^4\rangle$	$A_6^4\langle r^6\rangle$	σ	σ'	Reference
$YAsO_4$	−30.6	11.7	−36.9	±866.4	±69.9	8.9	9.2	13
	−4	12	−37	±875	±70	9.1	9.8	
YPO_4	141.4	18.1	−40.4	±837.2	±88.5	9.1	10.1	14
	185	18	−40.4	±800	±88	10.4	12.1	
YVO_4	−102.8	45.5	−43.0	±968.2	±22.1	9.7	9.2	14
	−65	48	−39	±982	±20	10.4	11.1	
	−65	47.5	−43	+976	−18	10.5	10.8	a
$ScVO_4$	−238.6	52.9	−58.9	±1049.2	±19.9	14.6	14.2	15
	−150	53	−59	±925	±19	18.6	17.4	
$ZrSiO_4$	−65	48.8	−39.7	±962	±20.4	b	b	
$HfSiO_4$	−65	45.5	−43	±982	±21	b	b	
$ThSiO_4$	−79	42.1	−43.9	±943	±20.4	b	b	

[a] The third set of CF parameters in the case of YVO_4 lattice is derived by assigning theoretically determined signs to $A_4^4\langle r^4\rangle$ and $A_6^4\langle r^6\rangle$. Such efforts were not made for other systems due to paucity of funds.

[b] Spectroscopic data are not available for these systems.

TABLE III. Calculated and experimental g values for the ground level $(\bar{\mu}=\pm\frac{3}{2},\ {}^2\Gamma_6)$ of Er^{3+} ion in zircon-type crystals.

Crystal		$g_\parallel$	$\lvert g_\perp\rvert$	$\lvert\bar{g}\rvert$	σ_g
$YAsO_4$	a	−7.291	4.968	5.742	0.075
	b	6.639 ± 0.002	5.177 ± 0.004	5.664	⋯
	c	−6.738	5.276	5.763	0.017
YPO_4	a	−6.47	5.10	5.56	0.086
	b	6.42 ± 0.02	4.81 ± 0.02	5.35	⋯
	c	6.55	4.91	5.46	0.020
YVO_4	a	−4.608	6.634	5.959	0.217
	b	3.544 ± 0.005	7.085 ± 0.005	5.905	⋯
	c	−3.585	7.171	5.976	0.012
	d	−3.592	7.158	5.969	0.012
	e	3.85 ± 0.3	8.5 ± 0.5	6.95	⋯
$ScVO_4$	a	−7.67	4.88	5.81	0.157
	b	6.35 ± 0.5	4.53 ± 0.02	5.14	⋯
	c	−6.78	5.09	5.65	0.099
$ZrSiO_4$	b	3.718 ± 0.002	6.997 ± 0.006	5.904	⋯
	f	3.703 ± 0.001	6.971 ± 0.002	5.882	⋯
	c	−3.765	7.080	5.975	0.012[b] 0.016[f]
$HfSiO_4$	b	4.316 ± 0.005	6.682 ± 0.006	5.893	⋯
	c	−4.348	6.760	5.956	0.010
$ThSiO_4$	b	4.802 ± 0.003	6.309 ± 0.008	5.807	⋯
	c	−4.891	6.443	5.926	0.020

[a] Calculated with the CF parameters of Kahle and Klein (Ref. 13) ($YAsO_4$), Kuse (Ref. 14) (YPO_4, YVO_4), and Hintzmann (Ref. 15) ($ScVO_4$).

[b] Experimental data of Plamper (Ref. 16) ($YAsO_4$), Dzionara *et al.* (Ref. 17) (YPO_4), Ranon (Ref. 18) (YVO_4), Hintzmann (Ref. 15) ($ScVO_4$), and Reynolds *et al.* (Ref. 24) ($ZrSiO_4$, $HfSiO_4$, $ThSiO_4$).

[c] Result of calculations through modified CF parameters (with arbitrary but same signs for $A_4^4\langle r^4\rangle$ and $A_6^4\langle r^6\rangle$)—present work.

[d] Calculated through new set of CF parameters with the signs prescribed by theoretical models.

[e] Spectroscopically derived values for $ErVO_4$ quoted by Metcalfe and Rosenberg (Ref. 37).

[f] EPR data of Ball (Ref. 48) on Er^{3+} in natural single crystal of zircon.

The absorption spectra of $YAsO_4$, YPO_4, YVO_4, and $ScVO_4$ single crystals containing 1–10 at.% of Er^{3+} have been investigated by Kahle and Klein,[13] Kuse,[14] and Hintzmann[15]; and the CF parameters so obtained, after transformation[14,34] to the present notation, are listed in Table II. The spectroscopic data can only define the relative signs of $A_4^4\langle r^4\rangle$ and $A_6^4\langle r^6\rangle$, so that both the signs are used with these parameters. During parametrization they excluded the ${}^4I_{15/2}$ ground state, as all the eight Stark levels are not determined, and employed the operator equivalent parameters α_J, β_J, and γ_J derived from the intermediate coupling free-Er^{3+}-ion wave functions.[35] These parameters have been employed to obtain the positions and wave functions for Stark levels of various J manifolds[36] and the values of rms deviation (σ), as defined by these authors, are included in Table II. Their difference from the values reported in original papers should not be attached any meaning, as it is introduced by the change in computational precision. The eigenfunctions of the lowest Stark level are used to compute the principal components of g tensor and $\bar{g}=(\lvert g_\parallel\rvert+\frac{2}{3}\lvert g_\perp\rvert)$, and are compared with the experimental data[15–18] (see Table III). In order to give equal consideration to the parallel as well as perpendicular components, the rms deviation for the spectroscopic splitting factors is defined as

$$\sigma_g=\left[\frac{1}{2}\left\{\left(\frac{g_\parallel^c-g_\parallel^e}{g_\parallel^e}\right)^2+\left(\frac{g_\perp^c-g_\perp^e}{g_\perp^e}\right)^2\right\}\right]^{1/2};\qquad(10)$$

and included in Table III. Evidently, the derived g values differ significantly from the experimental data. For the $YAsO_4$ host lattice, the deviations of $g_\parallel$ and $g_\perp$ are 9.8% and 4.0%, respectively; in YVO_4 and $ScVO_4$ crystals $g_\parallel$ differs by 30.0% and 20.8%, whereas the difference of $g_\perp$ is 6.4% and 7.7%, respectively. In the case of YPO_4 the situation is comparatively better. It means that though the CF parameters are determined by best fit to the absorption spectra, the eigenfunctions for the Stark levels of the ground J manifold are not correct as the g values, which are extremely susceptible to these, are not reproduced faithfully. This may be due to the fact that Stark levels of the ground state are not considered during parametrization. But, if these are included to calculate the rms deviation (σ'), the latter is affected little (see Table II); indicating that the ground-state components are also generated by the CF parameters almost as reliably as those of the excited states. With the limitation of an incomplete set of ground-state Stark levels, it is advisable to seek a parametrization which expounds the maximum body of physical properties without spoiling much the over-all agreement of the positions of Stark levels for ground as well as excited states. The new CF parameters resulting from such an effort are catalogued in Table II along with the corresponding σ values. Also included is the set of CF parameters with theoretically predicted unambiguous signs of $A_4^4\langle r^4\rangle$ and $A_6^4\langle r^6\rangle$ for $YVO_4:Er^{3+}$. To distinguish this set from the one with ambiguous signs, it is called new theoretical set, while the latter is termed as new empirical set. Since the free-ion parameters are taken to be the same for all the host lattices in spite of the difference in positions of baricenters of various J states, and small changes in the CF parameters do not affect the agreement much, extra accuracy is not warranted in the determination of $A_n^m\langle r^n\rangle$. The g values derived from these parameters are also projected in Table III, wherefrom it is clear that the agreement for both the components is equally good (within 2%) for $YAsO_4$, YPO_4, and YVO_4 crystals and it is much improved for $ScVO_4$ where the deviations of $g_\parallel$ and $g_\perp$ are 6.8% and 12.4%, respectively.

In view of the large separation of the first excited state (${}^4I_{13/2}$) from the ground ${}^4I_{15/2}$ state, the physi-

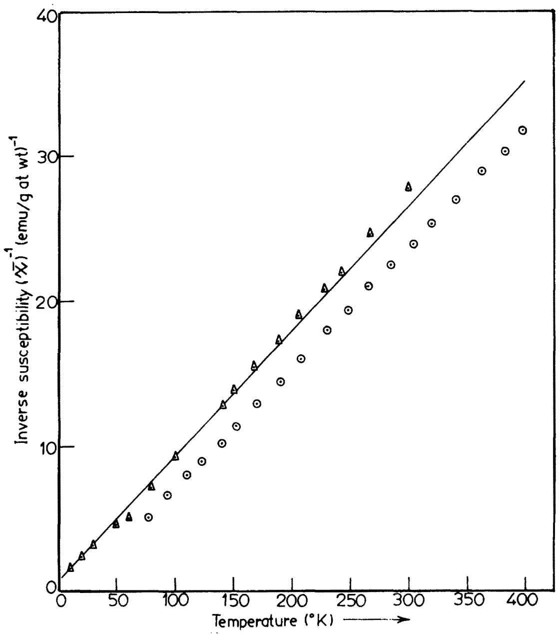

FIG. 2. Comparison of inverse susceptibility for $YPO_4:Er^{3+}$ (solid line) calculated with the new empirical set of CF parameters, with the experimental data on $ErPO_4$ (△ from Ref. 38 and ⊙ from Ref. 39).

cal properties at room temperature or lower will be determined by the ground manifold and as such calculations are performed within that state. Both the old as well as new sets of CF parameters are employed to calculate the temperature dependence of paramagnetic susceptibility over the range 10–400 °K (see Table IV and Figs. 2 and 3). The $\bar{\chi}$ values generated by the old as well as new sets of CF parameters are extremely close to each other for $YAsO_4$ and YPO_4 host lattices, and for YVO_4 and $ScVO_4$ crystals their difference is less than 1% above 50 °K and is about 4.5% at low temperatures. In the case of YVO_4, the calculations through the new empirical and theoretical schemes of parametrization differ by less than 1.6%. On the other hand, the anisotropies show marked departures; therefore, the latter have been catalogued in Table IV, and the comparison of available experimental data[38,39] on $\bar{\chi}$ is given only with the results derived from the present schemes of parametrization (see Figs. 2 and 3).

The constants required for the calculations of hfs parameters are $g_N^e(^{166}Er) = +0.312$[40,41]; $g_N^g(^{167}Er) = -0.161$[42]; $N_{15/2} = 0.782$[31]; $\langle r^{-3}\rangle_{eff} = 10.6 a_0^{-3}$[40]; $R = 0.13$[43]; $(1-R)Q^e(^{166}Er) = -1.60$ b[44]; $Q^g(^{167}Er) = +2.827$ b[42]; $\langle r^{-3}\rangle_{4f} = 12.08 a_0^{-3}$[45]; $\gamma_\infty = -74.0$, obtained by linear interpolation from the theoretical values of $\gamma_\infty(Pr^{3+}) = -84.78$ and $\gamma_\infty(Tm^{3+}) = -72.86$ reported by Gupta *et al.*[46]; $\sigma_2 = 0.604$, obtained by assuming the variation to be similar to that found by Blok and Shirley,[47] and taking $\sigma_2(Pr^{3+}) = 0.745$ and $\sigma_2(Tm^{3+}) = 0.601$ as derived by Gupta *et al.*[46] by including the contributions of all the inner shells; and $\langle r^2\rangle_{4f} = 0.65 a_0^2$.[45] These values are employed to compute $A_\parallel$, $A_\perp$, P, and C_{hf} through the old as well as the new sets of CF parameters and compared with the available experimental data in Table V. The calculations for $\langle \Delta E_Q\rangle_T$ exhibit a marked difference for the old and new schemes of parametrization for all the host lattices and the results for $YPO_4:Er^{3+}$ and $YVO_4:Er^{3+}$ are shown in Fig. 4 as typical examples.

Recently, Ball[48] studied the EPR of Er^{3+} in natural zircon crystals and found that various parameters occurring in the spin Hamiltonian have nearly the same values as in the case of the YVO_4 host lattice. These observations were substantially corroborated by the investigations on $ZrSiO_4:Er^{3+}$ carried out by Reynolds *et al.*,[24] who also reported the EPR parameters for isostructural host lattices $HfSiO_4$ and $ThSiO_4$. Since the results for these three compounds are reasonably close to those for

TABLE IV. Calculated temperature variation of magnetic anisotropy (ΔK in 10^{-3} emu/g at. wt.) for Er^{3+} ion in the zircon-structure systems.

	$YAsO_4$		YPO_4		YVO_4			$ScVO_4$	
T(°K)	a	b	a	b	a	b	c	a	b
10	92.0	−22.8	−124.7	−119.8	−270.6	−430.0	−450.2	317.4	97.4
20	−30.9	−93.6	−172.5	−180.6	−156.0	−241.6	−261.4	151.1	44.0
30	−45.9	−87.2	−152.6	−161.1	−105.2	−163.9	−179.6	103.2	32.7
50	−27.9	−50.1	−100.9	−108.6	−48.6	−83.1	−91.9	64.3	18.0
100	−4.8	−12.4	−39.1	−44.5	−7.1	−19.7	−23.4	29.8	11.4
150	−0.6	−4.3	−19.3	−22.8	0.3	−5.8	−7.9	17.7	8.8
200	0.3	−1.8	−11.3	−13.6	1.7	−1.8	−3.1	11.8	6.6
300	0.5	−0.5	−5.1	−6.4	1.6	0.1	−0.6	6.2	3.7
400	0.4	−0.2	−2.9	−3.7	1.2	0.3	0.0	3.8	2.4

[a] For CF parameters of Kahle and Klein, of Kuse, and of Hintzmann.
[b] For the new empirical schemes of parametrization.
[c] For the new theoretical set of CF parameters.

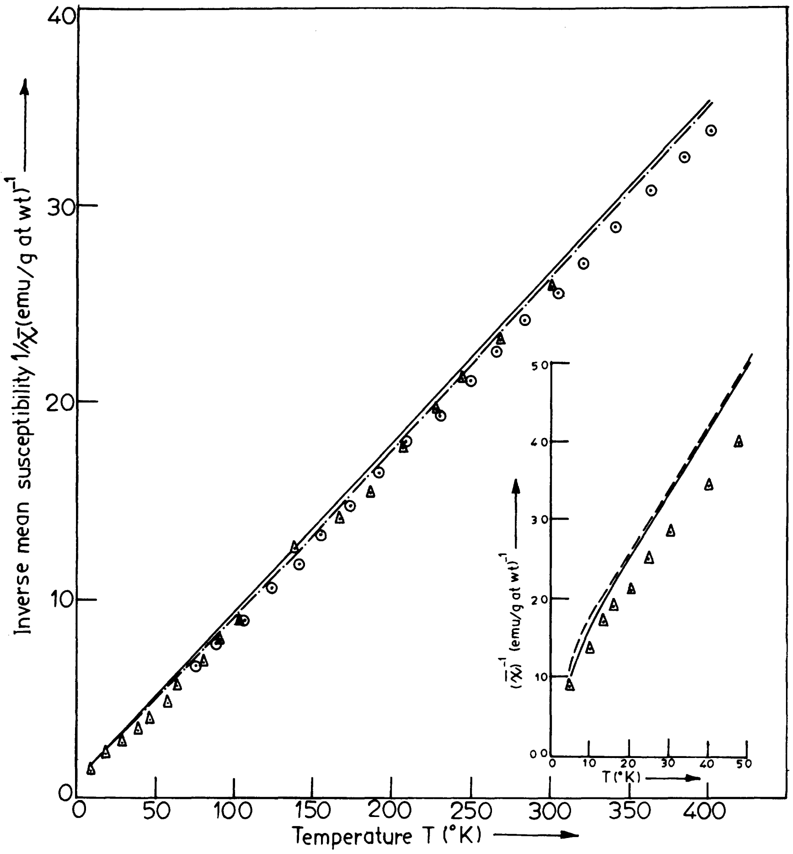

FIG. 3. Inverse mean gram atomic susceptibility as a function of temperature for YVO$_4$: Er^{3+} (solid line) calculated with new empirical scheme of parametrization and (dot-dash line) with the new theoretical scheme) and ErVO$_4$ (△ represent the experimental data from Ref. 38 and ⊙ from Ref. 39). The insert compares the plot for $1/\bar{\chi}$ calculated through the empirical CF parameters given in this paper (solid line) and those of Kuse (dashed line) with the measurements of Will *et al.* (Ref. 38). The calculations through new theoretical and empirical sets do not differ much at low temperatures.

YVO$_4$: Er^{3+} and the bonding parameters of these lattices are not much different, CF parameters giving best fit for the g values have been obtained for these three systems as well (see Table II). The results of calculations for the components of g and A tensors are presented in Tables III and V, respectively. For want of spectroscopic check on the CF parameters, other properties have not been derived.

V. DISCUSSION OF RESULTS

A. CF parameters and g tensor

The rms deviation of the Stark levels is susceptible to changes in all the CF parameters, though the effect of variations in $A_2^0\langle r^2\rangle$ and $A_4^4\langle r^4\rangle$ is comparatively less. The components of the g tensor are found to be most sensitive to changes in $A_2^0\langle r^2\rangle$ and $A_6^0\langle r^6\rangle$. Furthermore, the shift produced in $g_{\parallel}$ by an arbitrary alteration in an $A_n^m\langle r^n\rangle$ value is more than that in $g_{\perp}$. However, when both of these are used in the fitting process by considering their fractional difference from the experimental value, as has been done in the present work, the agreement is improved. In the light of above observations, the parametrization has been done by varying $A_2^0\langle r^2\rangle$ and $A_4^4\langle r^4\rangle$ mainly and minor adjustments achieved by changes in other CF parameters.

Though $A_2^0\langle r^2\rangle$ is not very important in determining the energy levels of the states with high J values,[49] it is the only factor accounting for the splitting of $^4S_{3/2}$ and $^4F_{3/2}$ states. Any variation in this parameter produces diverse effects on the agreement of the positions of Stark levels of these two states. The changes which ameliorate the concord of g values also give better accord for the $^4S_{3/2}$ state; but during parametrization, the agreement of the Stark levels of $^4F_{3/2}$ is also kept in view. It may be pointed out that the CF parameters are not only sensitive to the changes in the free-ion parameters, but also differ from one J state to another. Furthermore, as the experimental g values for higher Stark levels are not available, accuracy of $A_n^m\langle r^n\rangle$ has not been made an issue; the effort has been to narrow the range of the parameters such that these are compatible with the available experiments. A perusal of Tables II and III reveals that the increase in σ for the new sets is tolerable in the case of YAsO$_4$, YPO$_4$, and YVO$_4$ host lattices, when the accompanying decrease in the σ_g values is also considered. The agreement obtained through the new theoretical set of CF parameters for YVO$_4$: Er^{3+} is equally gratifying. However, the agreement of g values for ScVO$_4$ could not be improved much

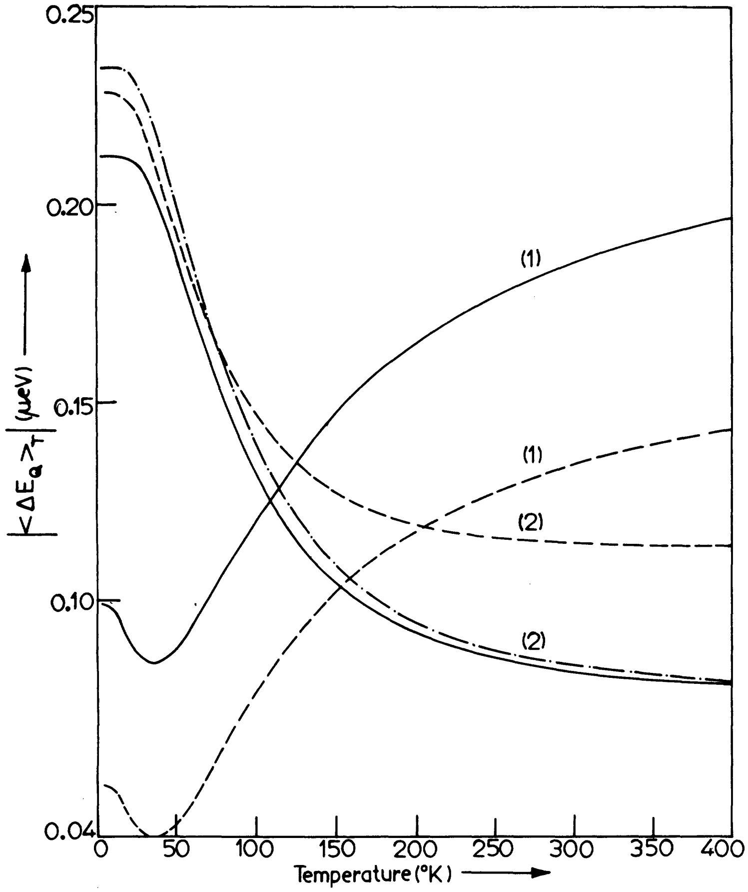

FIG. 4. Temperature dependence of the quadrupole splitting $|\langle \Delta E_Q \rangle_T|$ of (1) $YPO_4:Er^{3+}$ and (2) $YVO_4:Er^{3+}$ calculated through the CF parameters reported in this paper (solid line) and those of Ref. 14 (dashed line). The magnitudes derived through new theoretical scheme of parametrization for $YVO_4:Er^{3+}$ are also depicted (dot-dash line).

even though the increase in σ is maximum.

The relative positions of the Stark levels obtained through the old as well as new CF parameters differ from the experimentally observed positions in one or two cases, for all the host lattices; Hintzmann[15] has not pointed out such a difference in the third and fourth levels of $^4I_{15/2}$ state for $ScVO_4$, though it occurs there also. The deviations between the measured and calculated Stark energies are large for $^4I_{15/2}$, $^2H_{11/2}$, and $^2H_{9/2}$, and in the case of $ScVO_4$ crystal, it is appreciable for $^4G_{11/2}$ also. The deviation for new sets gets enhanced mainly because of these states. The deviation for $^4I_{15/2}$ may be due to the fact that out of eight levels only five or six are known. The occurrence of large errors for $^2H_{11/2}$, $^2H_{9/2}$, and $^4G_{11/2}$ states is quite common in the Er^{3+} systems and should, therefore, be due to the properties of the ion or to approximations made in the free-ion Hamiltonian, rather than to a particular host lattice. It is worth noting that α_J, β_J, and γ_J for these states in the intermediate coupling scheme differ appreciably from those for *LS* coupling scheme. The above mentioned deviations may be due to the fact that the effects of nonlinear shielding of $4f$ electrons as well as the covalency and overlap are considered insofar as these enter into the CF parameters as a whole. Also the correlation crystal-field effects, which give rise to term-dependent deviations of the conventional one-particle crystal field, are neglected. Furthermore, the splitting in the state $^4I_{13/2}$, which (being a relatively pure ^4I term) is expected to be least affected by the correlation crystal field, has not been studied in these systems.

In all the seven systems studied, $\bar{\mu} = \pm\frac{3}{2}(^2\Gamma_6)$ is the lowest Stark level and the g tensor is negative (EPR experiments do not usually determine the signs of $g_\parallel$), implying its correspondence to the extremum $|\bar{g}| = \frac{2}{3} g_J J$,[28] which is the g value for the $^2\Gamma_6$ level in a cubic field. The departure of $\bar{g}_{exp}$ values from the theoretical value 5.976 may be taken as a measure of the extent of distortion superimposed on the cubic field. Table III shows that such a deviation is maximum for the $ScVO_4$ host lattice and minimum for YVO_4 and $ZrSiO_4$. Also the g values for concentrated $ErVO_4$ are closer to those for $YVO_4:Er^{3+}$ rather than for $ScVO_4:Er^{3+}$, which is anticipated as the ionic radius of Er^{3+} is not much different from that for Y^{3+}.

In these calculations the J–J mixing due to crystal field has been ignored and only the static crystal field is used to obtain the g factors, whereas Inoue[50] has shown that the dynamic part of the crystalline field also contributes to the g values.

B. Magnetic susceptibility

Susceptibility measurements on $ErAsO_4$, $ErPO_4$, and $ErVO_4$ show that these remain paramagnetic[51,52] down to 0.5 or 0.6 °K. Consequently, it can safely be assumed that ion-ion interactions will be absent in the dilute systems down to about 5 or 10 °K. It is noted that the temperature dependence of $\overline{\chi}$ and hence $\overline{\mu}_{\text{eff}}$ is not very sensitive to the crystalline environments nor to the scheme of parametrization and thus cannot be employed to test the parameters. However, these do show a difference at low temperatures where only the lower levels are contributing. From Fig. 3 it is seen that low-temperature data for $ErVO_4$ are better explained with the present empirical as well as theoretical schemes of parametrization; at high temperatures the calculations through the theoretical set are slightly closer to experiments than those through the empirical set. The agreement for high temperatures is good for YPO_4 with the new set (Fig. 2). The room-temperature magnitudes of $\overline{\mu}_{\text{eff}}$ ($9.50\mu_B$ for YXO_4 hosts and $9.46\mu_B$ for $ScVO_4$) are also in nice correspondence with the experimental values $9.80\mu_B$,[4] $9.5\mu_B$[38] for $ErPO_4$ and $9.76\mu_B$,[4] $9.5\mu_B$[38] for $ErVO_4$, and the free-ion value $9.55\mu_B$; the new theoretical set for $YVO_4:Er^{3+}$ gives $\overline{\mu}_{\text{eff}}(300\,°\text{K})$ as $9.54\mu_B$. As pointed out in Sec. IV, the magnetic anisotropies not only differ from one crystal lattice to the other, but are also governed by the CF parameters. Consequently, measurements on $\Delta\chi$ can provide a good check on various schemes of parametrization and efforts in this direction are recommended. The low-temperature limit of $\overline{\mu}_{\text{eff}}$ gives a measure of the magnetic moment of the lowest Stark level and, hence, is determined by the nature of the host lattice as well as the set of CF parameters used. For example, the extrapolation of $\overline{\mu}_{\text{eff}}$-vs-$T$ plots for YPO_4 and YVO_4 gives $\overline{\mu}_{\text{eff}}(0\,°\text{K})$ as $4.65\mu_B$ and $5.10\mu_B$, respectively, with Kuse's scheme of parametrization, whereas the present empirical sets of CF parameters yield the values $4.72\mu_B$ and $5.35\mu_B$; in the case of the theoretical set for YVO_4, this magnitude comes out to be $5.28\mu_B$. A comparison of these with $5.0\mu_B$ and $5.3\mu_B$ for $ErPO_4$ and $ErVO_4$[38] reveals that the agreement is better with the new schemes of parametrization.

C. Hyperfine interactions

A comparison of the calculated $A_\parallel$ and $A_\perp$ with the corresponding experimental data (Table V)

TABLE V. Hyperfine structure parameters (in 10^{-4} cm^{-1}) of the ground Stark doublet for $^{166}Er^{3+}$ and $^{167}Er^{3+}$, and nuclear specific heat due to $^{167}Er^{3+}$ in various zircon-structure compounds.

		$^{166}Er^{3+}$		$^{167}Er^{3+}$			
Host Compound		$A_\parallel$	$\lvert A_\perp \rvert$	$A_\parallel$	$\lvert A_\perp \rvert$	P	$C_N T^2$ (J °K/g at. wt.)
$YAsO_4$	a	−464	363	239	187	−2.4	0.029
	b	···	···	223 ± 1	182 ± 1	···	···
	c	−502	342	259	177	−2.6	0.029
YPO_4	a	−451	338	233	174	3.1	0.026
	b	···	···	214 ± 4	163 ± 4	···	···
	c	−446	351	230	181	1.6	0.027
YVO_4	a	−247.0	494.0	127.4	254.9	−7.4	0.033
	b	···	···	122.6 ± 0.4	249.1 ± 0.8	13.9 ± 0.8	···
	c	−317.0	457.0	163.8	235.8	−8.2	0.031
	d	−247.5	493.1	127.7	254.5	−8.2	0.033
$ScVO_4$	a	−467	351	241	181	−9.5	0.028
	c	−528	336	273	173	−10.1	0.031
$ZrSiO_4$	a	−259.4	487.7	133.8	251.7	−7.3	0.033
	b	···	···	130.4 ± 0.6	243.8 ± 1.1	15.7 ± 1.2	···
	e	···	···	130.0 ± 0.5	246.7 ± 1.0	14 ± 1	···
$HfSiO_4$	a	−299.5	465.7	154.6	240.3	−7.2	0.032
	b	···	···	151.3 ± 0.9	232.6 ± 1.3	15.8 ± 1.3	···
$ThSiO_4$	a	−336.9	443.9	173.9	229.0	−7.5	0.030
	b	···	···	167.0 ± 0.6	219.4 ± 2.6	4.9 ± 10	···

[a] Calculations with the new empirical CF parameters.

[b] Experimental data of Plamper (Ref. 16) ($YAsO_4$), Dzionara *et al.* (Ref. 17) (YPO_4), Ranon (Ref. 18) (YVO_4) and Reynolds *et al.* (Ref. 24) ($ZrSiO_4$, $HfSiO_4$, and $ThSiO_4$).

[c] Obtained from the spectroscopic CF parameters.

[d] Calculated through the new theoretical scheme of parametrization.

[e] EPR data of Ball (Ref. 48) on Er^{3+}-doped natural single crystal of zircon.

shows that the new CF parameters produce a far better accord than the old sets. The correspondence in the case of three silicates is also gratifying. The small magnitude of P in $YAsO_4$ and YPO_4 lattices explains their not having been determined in the EPR experiments. Allowing for 22.9% abundance of ^{167}Er, the contribution of hfs to specific heat is estimated to be $(6-8)\times10^{-3}$ J/g at. wt. deg at 1 °K. Furthermore, the calculations for $\langle\Delta E_Q\rangle_T$ depict an explicit effect of the scheme of parametrization (Fig. 4). In the case of $YAsO_4$ crystal, the magnitude of $\langle\Delta E_Q\rangle_T$ is found to be small as the lattice contribution, though having the same sign as that of the $4f$-valence part, is not large. For YVO_4 and $ScVO_4$ crystals the electronic contribution is enhanced by the lattice part and hence the magnitude is quite large at low temperatures. However, since YPO_4 has reasonably large $A_2^0\langle r^2\rangle$ two components differ in sign with the consequence that the magnitude of $\langle\Delta E_Q\rangle_T$ shows an increase with temperature. Mössbauer experiments pertaining to electrostatic and magnetic hyperfine studies on ^{166}Er will offer a confirmatory check on the schemes of parametrization.

VI. APPRAISAL OF THE CRYSTAL-FIELD PARAMETERS

It has been noted in Sec. V that various experimental results are explained to a far better extent by the revised empirical sets of CF parameters though the agreement for the positions of Stark levels is rendered slightly poorer. The success of the present effort in expounding the hfs parameters also gives an indirect confidence in the magnitudes of various quantities used. In order to have a better insight into the nature of the crystal field, the CF parameters are discussed in the framework of prevalent models.

From Table II, it is observed that $A_2^0\langle r^2\rangle$ is negative for all the host lattices except YPO_4. For a $YAsO_4$ crystal, $A_2^0\langle r^2\rangle$ is quite close to zero. In fact, if it is taken to be zero the $g_\parallel$ and $g_\perp$ are generated to within 0.66% and 2.43%, respectively, yielding $\sigma_g = 0.018$ and the deviation of Stark levels is increased slightly. However, positive values of $A_2^0\langle r^2\rangle$, even as small as 5 cm^{-1}, give large errors in $g_\perp$, with the same or somewhat different values of other parameters. The magnitude of this parameter is nearly the same for YVO_4 and the three silicates, and quite large in the case of $ScVO_4$. The reason for the latter may lie in the fact that Sc^{3+} ion is much smaller than Er^{3+} and as such the distortion produced will be large. It should be noted that $A_2^0\langle r^2\rangle$ is most directly related to the twofold symmetry axis perpendicular to the fourfold axis and hence gives a measure of the tetragonal distortion from the cubic coordination. The bonding angles show that the dodecahedron is most oblate in the case of YPO_4 and that there is maximum elongation in $ScVO_4$ ($ThSiO_4$ being an exception), which, respectively, have maximum and minimum $A_2^0\langle r^2\rangle$. Of course, the difference in ionic radii also affects the arrangements. The CF parameters, other than $A_2^0\langle r^2\rangle$, are close for $YAsO_4$ and YPO_4 on the one hand, YVO_4, $ZrSiO_4$, and $HfSiO_4$ on the other, with $ThSiO_4$ in between; $A_4^0\langle r^4\rangle$ and $A_6^0\langle r^6\rangle$ for $ScVO_4$ have larger magnitudes than in the other crystals. The proximity of the values of $A_4^0\langle r^4\rangle$ and $A_6^0\langle r^6\rangle$ in various lattices, perhaps, reflects the similarity of the arrangement of oxygens around the fourfold axis. Thus, the crystal fields of $YAsO_4$ and YPO_4; YVO_4 and the silicates are closer in properties and different from those in $ScVO_4$. It may be pointed out that the crystallographic bonding angles for $YAsO_4$, YPO_4, and $ErPO_4$ are closer to each other and so are those in the case of YVO_4, $ZrSiO_4$, $HfSiO_4$, and $ErVO_4$; $ScVO_4$ has a larger θ_1, while $ThSiO_4$ a smaller value. Furthermore, though the bond lengths in $YAsO_4$ and YVO_4 are not much different, the CF in the former is relatively closer to that in YPO_4, and diverse from that of the YVO_4 lattice. Consequently, it appears that the bonding angles and chemical bonding character of the XO_4^{2-} tetrahedra are more deterministic of the crystal field than mere bond lengths or lattice parameters. This observation is further supported by the fact that even though the same ion Y^{3+} is being replaced by Er^{3+} in $YAsO_4$, YPO_4, and YVO_4 host lattices, the CF parameters are appreciably different.

A. Electrostatic crystal-field model

Following Lempicki *et al.*[53] and assuming that only the nearest-neighbor oxygens [at a common distance $R_0 = \frac{1}{2}(R_1 + R_2)$] contribute to the lattice sums for the CF parameters, one gets

$$\frac{A_4^0\langle r^4\rangle + A_4^4\langle r^4\rangle}{A_2^0\langle r^2\rangle} = \frac{(1-\sigma_4)\langle r^4\rangle_{4f}}{(1-\sigma_2)\langle r^2\rangle_{4f}}\frac{1}{R_0^2} \times \frac{5(\cos^2\theta_1 + \cos^2\theta_2) - 8}{6(\cos^2\theta_1 + \cos^2\theta_2) - 4} \tag{11}$$

and

$$\frac{3A_6^0\langle r^6\rangle + A_6^4\langle r^6\rangle}{A_2^0\langle r^2\rangle} = \frac{(1-\sigma_6)\langle r^6\rangle_{4f}}{(1-\sigma_2)\langle r^2\rangle_{4f}}\frac{1}{R_0^4}\, \frac{63(\cos^4\theta_1 + \cos^4\theta_2) - 63(\cos^2\theta_1 + \cos^2\theta_2) + 12}{24(\cos^2\theta_1 + \cos^2\theta_2) - 16}\,. \tag{12}$$

TABLE VI. One-electron orbital energies for the five levels of f orbitals [in units of σ^* ($R_0 = 2.343$ Å)] computed from the angular overlap model.

	$YAsO_4$	YPO_4	$ErPO_4$	YVO_4	$ErVO_4$	$ScVO_4$	$ZrSiO_4$	$HfSiO_4$	$ThSiO_4$
$f\delta s$	−7.8	−8.0	−8.4	−7.8	−8.0	−11.8	−12.8	−12.7	−5.4
$f(\pi,\phi)_1$	−4.3	−4.1	−4.4	−4.5	−4.7	−7.7	−7.4	−7.2	−2.6
$f\sigma$	−3.6	−2.3	−2.6	−4.0	−4.1	−6.3	−6.7	−6.3	−0.6
$f\delta c$	1.9	2.3	2.4	2.0	2.1	2.9	2.3	−0.7	1.4
$f(\pi,\phi)_2$	9.1	8.1	8.7	9.4	9.8	15.3	16.1	17.1	5.0

To take into account the shielding of the electrostatic crystal field, the CF shielding factors σ_n have been included in these expressions and that constitutes the difference from the relationships given by Brecher *et al.*[54] For Er^{3+}: $\sigma_4 = 0.09$, $\sigma_6 = -0.04$,[55] $\langle r^4\rangle = 1.02a_0^4$, and $\langle r^6\rangle = 3.31a_0^6$.[45] Using these values, it is found that θ_1 and θ_2 cannot be obtained simultaneously if $A_4^4\langle r^4\rangle$ is taken to be positive; as pointed out earlier, the optical fitting does not give definite signs for $A_4^4\langle r^4\rangle$ and $A_6^4\langle r^6\rangle$. This is true whether the old scheme of parametrization is employed in the calculations or the present one. Taking $A_4^4\langle r^4\rangle$ negative and $A_6^4\langle r^6\rangle$ generally positive defines both the angles for all the systems under investigation. The values of θ_1 are found to range from about 35° in YPO_4 to 48° in $ThSiO_4$ and θ_2 from 99° to 117°, respectively. These values are, in general, larger than the corresponding crystallographic magnitudes. The situation about the values of angles is not changed appreciably by using the bond lengths for $ErPO_4$ and $ErVO_4$ rather than YPO_4 and YVO_4. Following Burns,[56] if the effect of induced point dipoles of polarizability α_D at the ligand sites is also included by taking $\alpha_D = 2$ Å^3 for O^{2-} ion,[57] the angles obtained with negative $A_4^4\langle r^4\rangle$ still do not satisfy Eqs. (11) and (12) simultaneously. Furthermore, to give due consideration to radial expansion of $4f$ wave functions in the crystals, the calculations have also been performed with $\langle r^2\rangle = 0.82a_0^2$, $\langle r^4\rangle = 2.36a_0^4$, and $\langle r^6\rangle = 12.7a_0^6$; obtained from the values of $\langle r^n\rangle$ for Tb^{3+} and Tm^{3+} required to explicate the data on neutron diffraction[58] and assuming their variation in accordance with the trend of calculations of Mann.[45] Once again, positive $A_4^4\langle r^4\rangle$ fail to define the θ's while Eqs. (11) and (12) are satisfied together if $A_6^4\langle r^6\rangle$ is taken negative in addition to its general positive-sign condition obtained earlier. These calculations yield θ's which are about 3–6% less than those obtained with theoretical values of $\langle r^n\rangle$. Consequently, the bond angles obtained by considering the effect of induced point dipoles and the radial expansion in solids are in reasonably good agreement with the x-ray data. These calculations, at the risk of extra emphasis (as clear from the following discussion), indicate that $A_4^4\langle r^4\rangle$ is negative, whereas the sign of $A_6^4\langle r^6\rangle$ is yet uncertain.

B. Angular overlap model

In view of the difficulties in understanding the origin of CF parameters from electrostatic considerations, Jørgensen *et al.*[59] developed a phenomenological model in which CF splittings are taken as a weak σ-antibonding effect. No doubt, this is an oversimplification, as the contributions of p_π bonds to the crystalline field have been shown to be large,[60,61] but it is found that the basic assumption of this so called angular overlap model (AOM) is essentially correct.[61] Kuse and Jørgensen[62] used this model to analyze the CF data[14] for Er^{3+} in YPO_4 and YVO_4, and their results were quite consistent.

In this model, the radial part σ^* of the antibonding energy effect is treated as a parameter and the angular part Ξ^2 is calculated from the crystallographic data.[63,64] With a view to see the effect of the nature of XO_4^{2-} tetrahedra on σ^*, the latter is evaluated corresponding to the same distance in all the host lattices and $R_0 = 2.343$ Å, the mean bond length for YPO_4 has been chosen for this purpose. In view of the results of strain experiments on cubic compounds[65] that the orbital splitting varies as R^{-7}, the contribution of a ligand at R is weighted by $(R_0/R)^7$. The theoretical one-electron orbital energies are calculated through the data compiled in Table I, and the results in usual notation[62] are catalogued in Table VI. The $f\delta s$ orbital is not σ antibonding and lies lowest in all the cases, and the predicted order of orbital energies is

$$f\delta s < f(\pi,\phi)_1 < f\sigma < f\delta c < f(\pi,\phi)_2 \qquad (13)$$

for all the host lattices. The present values for $ErPO_4$ and $ErVO_4$ differ from those of Kuse and Jørgensen,[62] first because the scaling factor σ^* refers to $R_0 = 2.343$ Å rather than 2.294 Å used by them, and second because they assumed the radial dependence of orbital splitting to follow a purely covalent R^{-8} law for cubic-field splitting.

Once again, since the signs of $A_4^4\langle r^4\rangle$ and $A_6^4\langle r^6\rangle$ are unknown, the experimental one-electron energies have been obtained[36] by taking these positive as well as negative in both the old and new schemes of parametrization. When $A_4^4\langle r^4\rangle$ is taken to be negative, the semiempirical calculations yield $f\delta c$

TABLE VII. Estimated values of antibonding energy parameter σ^* ($R_0 = 2.343$ Å) in cm^{-1} for various host lattices with zircon-structure.[a]

	$YAsO_4$	YPO_4	$ErPO_4$	YVO_4	$ErVO_4$	$ScVO_4$	$ZrSiO_4$	$HfSiO_4$	$ThSiO_4$
(1a)	27.6	32.7	30.7	32.3	31.0	23.9			
(2a)	29.0	33.2	31.3	32.7	31.4	24.1			
(1b)	27.9	32.3	31.1	31.8	30.5	20.8	18.5	18.1	55.4
(2b)	29.2	33.3	31.4	31.5 (32.5)[b]	30.9	21.0	18.8	18.4	55.9

[a] The experimental data correspond to positive $A_4^4\langle r^4\rangle$ and (1) positive or (2) negative $A_6^4\langle r^6\rangle$; and (a) old or (b) new schemes of parametrization.

[b] This value pertains to the new theoretical set of CF parameters.

as the lowest orbital, which is not at all an acceptable proposition. Thus $A_4^4\langle r^4\rangle$ should be positive and this result of AOM is contrary to the conclusion drawn in Sec. VI A. The relative orders of the experimentally derived orbital energies, in general, turn out to be

$$f\delta s < f\sigma < f(\pi, \phi)_1 < f\delta c < f(\pi, \phi)_2 . \tag{14}$$

However, the results of the revised set of parameters with $A_4^4\langle r^4\rangle$ positive and $A_6^4\langle r^6\rangle$ negative in the case of $YAsO_4$ crystal, and for YPO_4 with either sign of $A_6^4\langle r^6\rangle$ and both the schemes of parametrization, are exceptions as these yield $f(\pi, \phi)_1 < f\sigma$, in accord with the theoretical findings. The relative trends of variations in the positions of various orbital levels as derived experimentally from one host to the other are generally in accord with those for theoretical predictions.

By correlating theoretical values of orbital energies (Table VI) with those derived through the CF parameters, $\sigma^*(R_0 = 2.343$ Å) has been estimated for different host lattices and the values corresponding to positive $A_4^4\langle r^4\rangle$, positive as well as negative $A_6^4\langle r^6\rangle$ for both sets of parameters are given in Table VII. The total splitting (Σ) obtained by considering the same signs of the parameters for both schemes differ by only about 4 cm^{-1}, except in $ScVO_4$ where the difference is about 70 cm^{-1}. The difference in signs of $A_6^4\langle r^6\rangle$ for a particular scheme results in a total splitting differing at most by 35 cm^{-1} in YPO_4. In all the cases, the correspondence between theoretical and experimental positions is far better when $A_6^4\langle r^6\rangle$ is taken negative. Furthermore, the deviation is less for the results of the new schemes of parametrization than for the old ones, except in the case of YPO_4 (and $ErPO_4$) where the CF parameters of Kuse produce better correspondence between theory and experiment than the present parameters do. Comparatively large deviations are obtained for $ScVO_4$ and silicate lattices, perhaps because R_1 and R_2 for these differ appreciably from R_0. Also the values of σ^* are quite close for $YAsO_4$, YPO_4, YVO_4, and the concentrated compounds, whereas these differ from those for $ScVO_4$ and the silicate host lattices. The variations in σ^* could be due to difference in covalency, overlap, and the effect of chemical bonding in the XO_4^{2-} tetrahedra. Since the x-ray data for $HfSiO_4$ and $ThSiO_4$ are approximate, it is possible that the situation is changed when a more accurate structure analysis is available. However, it appears credible to conclude that AOM favors positive $A_4^4\langle r^4\rangle$ and negative $A_6^4\langle r^6\rangle$ and that the CF parameters obtained in the present work are in better harmony with the model than the old schemes. Consequently, Σ obtained only through these parameters are listed in Table VIII. Furthermore, nearly the same values of σ^* ($\simeq 30$ cm^{-1}) may be taken as supporting the validity of the AOM on one hand, and indicating the consistency of the CF parameters on the other. The σ^* as estimated from first principles comes out to be 450 cm^{-1} and such an order of magnitude difference has already been discussed by Jørgensen *et al.*[59]

C. Nephelauxetic effect and ionicity

The experimental baricenters[8,13-15] of various J states of Er^{3+} in different host lattices are projected in Fig. 5, which shows a shift to the red (the nephelauxetic effect) in the order LaF_3, ($YAsO_4$, YPO_4), YVO_4, $ScVO_4$, and Y_2O_3. Accordingly, the Slater parameters for Er^{3+} in these host lattices should decrease in this order and it should be taken care of in more accurate analysis of the spectra. In view of the same immediate neighbors in all the lattices except LaF_3, the difference in the red shift must be due to dependence of overlap on the radial separations, angular dispositions, and also due to different bondings in the XO_4^{2-} tetrahedra.

Sanderson[66] has shown that the ionicities of polyatomic systems can be compared reliably through the calculations based on equalization of electronegativity defined in terms of electron density. The results of such calculations for the systems under investigation are included in Table VIII. Evidently, the substitution of Er^{3+} in place of Y^{3+} does not lead to much change in the bond polarities and hence bonding; while the effect is more pronounced in the case of $ScVO_4$, whose ionicity is appreciably different from that of $ErVO_4$. Also the ionicity is maximum for $YAsO_4$ and YPO_4, and least for $ScVO_4$; YVO_4 and the silicates having values between these two extremes. Furthermore, taking $\Sigma/(H_M - H_X)$ as a measure of delocalization,[67] it is noted (Table VIII) that the percent delocalization (Δ) is minimum for $YAsO_4$ and YPO_4, and maximum for $ScVO_4$; while YVO_4 and the silicates have intermediate values. Thus, the spectroscopic data, the principle of equalization of electronegativity, and the AOM calculations, all exhibit a similar trend of variation of red shift, 1 – ionicity, and delocalization. Since it is known that covalent bonding in Y_2O_3 (ionicity = 0.26) is much more than that in LaF_3 (ionicity = 0.46); following Jørgensen,[67] it may be said that the nephelauxetic effect follows the same trend as covalency and in that case, ionicity may be taken as its measure. However, in the spirit of Newman's[68] recent interpretation of the nephelauxetic effect, it is determined by the dielectric constant of the crystal, which itself is a function of bond lengths and bond polarities (ionicity). For want of any sound theoretical model, these qualitative observations seem to be quite encouraging.

D. Superposition model

The superposition model, recently evolved by Newman and co-workers,[69–71] is based on the assumption that the total crystal field can be regarded as a superposition of the fields due to each of the ligating ions and various contributions are taken care of by parametrization. Thus, it provides a generalization of the AOM in which the assumptions based on a particular interaction mechanism have been dropped. The positive parameters so obtained are the effective single ligand parameters $\bar{A}_n(R_0)$, called the intrinsic parameters, and are related to the experimental parameters $A_n^m\langle r^n\rangle$ by

$$A_n^m\langle r^n\rangle = \sum_i K_{ni}^m (R_0/R_i)^{t_n} \bar{A}_n(R_0), \qquad (15)$$

where the coordination factors K_{ni}^m are determined

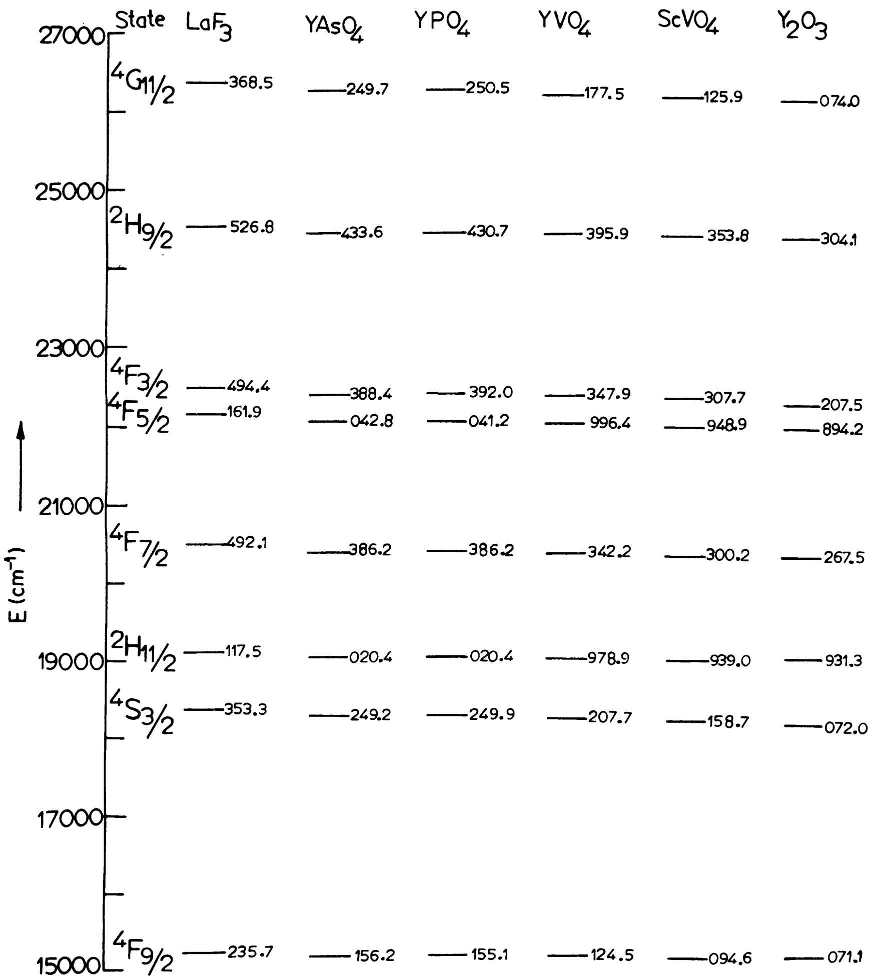

FIG. 5. Positions of the baricenters of various J manifolds (with respect to $^4I_{15/2}$) for Er^{3+} in different host lattices.

TABLE VIII. Calculated total one-electron splitting (Σ), percent delocalization (Δ) corresponding to new schemes of parametrization, and ionicity in various Er^{3+}-doped systems.

	$YAsO_4$	YPO_4	YVO_4	$ScVO_4$	$ZrSiO_4$	$HfSiO_4$	$ThSiO_4$
Σ (cm^{-1})	496	507	635 (642)[a]	686	630	640	621
Δ	0.83	0.84	1.06 (1.07)[a]	1.14	1.05	1.07	1.03
Ionicity	0.43 (0.45)[b]	0.42 (0.44)[b]	0.35 (0.37)[b]	0.30	0.38	0.39	0.39

[a] The values obtained through the new CF parameters, where $A_4^4\langle r^4\rangle$ and $A_6^4\langle r^6\rangle$ have been assigned opposite signs as given by the theoretical models.

[b] Ionicity for concentrated compounds $ErAsO_4$, $ErPO_4$, and $ErVO_4$.

by the angular positions of all the ligands at R_i and the power-law coefficients t_n are so chosen that not only the relative magnitudes and signs of $A_n^m\langle r^n\rangle$ in a given series of host lattices are explained but also the derived $\bar{A}_n(R_0)$ show the least deviation. Since the zircon-structure systems have two groups of four ligands each at different dispositions (Fig. 1), the CF parameters can be written as the sum of the contributions from the sets (1) 1–4 and (2) 5–8 of O^{2-} ligands:

$$A_n^m\langle r^n\rangle = [K_n^m(1)(R_0/R_1)^{t_n} + K_n^m(2)(R_0/R_2)^{t_n}]\bar{A}_n(R_0) = k_n^m\,\bar{A}_n(R_0)\,. \qquad (16)$$

Here k_n^m is the effective coordination factor which includes the effect of the power-law dependence.

The old sets of CF parameters for Er^{3+} in $YAsO_4$, YPO_4, YVO_4, and $ScVO_4$ have been analyzed in terms of intrinsic parameters by Newman and Stedman[72] and by Newman and Urban.[22] The results of Ref. 72 are based on the assumption that the ligands in all the host lattices are at 2.24 Å and also the then-available bond angles were not very accurate. The more recent work[22] presents results for the second-order CF parameters $A_2^0\langle r^2\rangle$ using accurate crystallographic data; but the values refer to radial positions which are different for different host lattices. As pointed out earlier, in this case also, to obtain information about the effect of XO_4^{2-} bonding on intrinsic parameters, the mean distance 2.343 Å is taken as the reference distance. The data compiled in Table I are employed to calculate $K_n^m(1)$ and $K_n^m(2)$ for all the host lattices except $HfSiO_4$ and $ThSiO_4$ as the crystallographic data for these are not so accurate. These are, in turn, used to obtain k_n^m corresponding to various values of t_n for each n. It is found that $t_2 < 6$ fails to predict the correct sign for $A_2^0\langle r^2\rangle$ in $YAsO_4$, whereas higher powers give the sign in identity with the experimental one. The signs of $A_4^0\langle r^4\rangle$ and $A_6^0\langle r^6\rangle$ are reproduced to be the same as those obtained through parametrization. These calculations indicate that $A_4^4\langle r^4\rangle$ should be positive, whereas $A_6^4\langle r^6\rangle$ is negative for all the host lattices except phosphate, for which $A_6^4\langle r^6\rangle$ comes out to be positive. These observations corroborate the conclusions of AOM calculations; YPO_4 being an exception. Thus, the model calculations show that $A_4^4\langle r^4\rangle$ and $A_6^4\langle r^6\rangle$ differ in sign for $YAsO_4$, YVO_4, and $ScVO_4$. In order to verify this conjecture, a new (theoretical) scheme of parametrization with opposite signs for $A_4^4\langle r^4\rangle$ and $A_6^4\langle r^6\rangle$, has been obtained for $YVO_4:Er^{3+}$. From the discussion in the preceding sections, it is clear that this scheme is as reliable as the one (empirical) in which both the parameters are taken to be in phase. In view of the fact that these two parameters are invariably coupled in the matrix elements of $\hat{H}_{CF}$, similar parametrization for the other systems seems tractable. However, such an effort has not been made because of financial handicaps.

It may be pointed out that k_2^0 and k_6^4 are most sensitive to t_n and hence will be most susceptible to the distortions at the Er^{3+} site. Consequently, the information obtained through these is expected to be least reliable. The factor k_6^0 shows minimum variation with the change in the value of t_6 and, hence, the results obtained through these must be most dependable. k_4^0 and k_4^4 are also not very sensitive to the value of t_4.

It is found that $\bar{A}_n(R_0 = 2.343$ Å) derived from $A_n^0\langle r^n\rangle$ for old as well as new schemes of parametrization for $YAsO_4$, YPO_4, YVO_4, and $ScVO_4$ are most consistent for

$$t_2 = 7\,,\quad t_4 = 12\,,\quad t_6 = 11\,. \qquad (17)$$

In the case of $A_4^4\langle r^4\rangle$ and $A_6^4\langle r^6\rangle$ the diversity is less with a power exponent of 5 or smaller. The k_n^m corresponding to these power law coefficients are listed in Table IX. The intrinsic parameters appropriate to the nominal separation 2.343 A of Er^{3+} and O^{2-} in various systems as obtained through these k_n^m form the contents of Table X. As anticipated, the single-ligand CF parameters derived from $A_2^0\langle r^2\rangle$ and $A_6^4\langle r^6\rangle$ show large variations and

TABLE IX. Effective coordination factors k_n^m for O^{2-} ligands in the systems having zircon structure.

	$k_2^0(t_2=7)$	$k_4^0(t_4=12)$	$k_6^0(t_6=11)$	$k_4^4(t_4'=5)$	$k_6^4(t_6'=5)$
$YAsO_4$	−0.073	0.927	−1.456	18.700	−0.674
YPO_4	0.440	0.886	−1.333	17.690	1.045
$ErPO_4$	0.363	0.955	−1.521	18.506	0.880
YVO_4	−0.324	0.937	−1.436	19.201	−0.971
$ErVO_4$	−0.470	1.030	−1.450	19.973	−1.126
$ScVO_4$	−1.586	2.604	−2.332	28.321	−3.489
$ZrSiO_4$	−0.579	2.504	−3.335	27.689	−2.970

are most sensitive to the distortions, which is also supported by the fact that these show noticeable difference when coordination factors for YXO_4 or corresponding $ErXO_4$ are employed. The parameter $\bar{A}_6(R_0)$ can be taken as 27 ± 3 cm^{-1} for all the host lattices where charge compensation is not necessary. Furthermore, since the CF parameters for $ZrSiO_4$ are yet to be confirmed from spectroscopic data, it is omitted from further discussion. The present value of $\bar{A}_6(R_0 = 2.343$ Å) is higher than 21 ± 1 cm^{-1} for the garnets with $R_0 = 2.38$ Å, as expected; this finding is contrary to that of Newman and Stedman[72] based on the calculations with old crystallographic data. The values of $\bar{A}_4(R_0)$ derived from $A_4^0\langle r^4\rangle$ differ appreciably from those obtained from $A_4^4\langle r^4\rangle$ and show remarkable variation from one host to the other. Also the ratio $\bar{A}_4(R_0)/\bar{A}_6(R_0)$ depends on the host lattices in contrast with the observation made by Newman,[71] and is quite different from that for the garnets.[73] The difficulty in the evaluation of $\bar{A}_4(R_0)$ is well known and the reason generally ascribed[72] is that the electrostatic contributions from the next-nearest neighbors are not as small as for $\bar{A}_6(R_0)$, which poses a question about the soundness of local-field approximation in these systems, (particularly, for fourth-order crystal field). This is also supported by large variations in $\bar{A}_2(R_0)$ from one system to another as well as the fact that the experimental ratios $A_4^4\langle r^4\rangle/A_4^0\langle r^4\rangle$ and $A_6^4\langle r^6\rangle/A_6^0\langle r^6\rangle$ are not reproduced by these calculations. Since the power-law exponents are large, the effect of other than ligand ions should be supplemented by the effects of stronger chemical bonding in the XO_4^{2-} tetrahedra than between Er–O. However, for strong bonding in XO_4^{2-} complexes, it is probably not good to assume that the ligands make axially symmetric contributions. But quantitative estimates of such effects are not yet available, though some efforts are in progress.[74] It may be added that the ligand-ligand overlap in these systems is expected to be small.[75]

Although the Y^{3+} ion is replaced by Er^{3+} in three host lattices, the extent of distortions produced appears to be different as indicated by the variation in $\bar{A}_6(R_0)$ values. This is expected because the Er-O bond lengths will tend to adjust to a relatively constant value in all the host lattices, which will lead to different angular distortions. This is also supported by the fact that k_n^m vary more from one system to another (of course, variation is less than that observed by Newman and Stedman[72]) than do the CF parameters, implying that the bonding of Er^{3+} does not change as much as that of Y^{3+}. However, it may be remarked that the variation of $A_n^m\langle r^n\rangle$ (old as well as new schemes) from one crystal to another is, in general, compatible with the results of the superposition model. The parameters obtained by Kuse[14] show that $|A_6^0\langle r^6\rangle(\mathrm{YPO_4})| < |A_6^0\langle r^6\rangle(\mathrm{YVO_4})|$, which is opposite to the result of the present empirical schemes of parametrization. The calculations show that $|k_6^0(\mathrm{YPO_4})| < |k_6^0(\mathrm{YVO_4})|$, whereas $|k_6^0(\mathrm{ErPO_4})| > |k_6^0(\mathrm{ErVO_4})|$, so that the difference is not unexpected.

The large values of the power-law coefficients are compatible with the results for garnets[73] and chlorides,[70] which have been discussed by Curtis and Newman.[76] Of course, $t_4 > t_6$ is a little unusual. Nonetheless, the local-field-superposition approximation seems reliably accurate for the sixth-order parameters.

Recently, Schopper *et al.*[77] measured the temperature dependence of lattice parameters of some compounds with zircon structure and showed that the linear coefficients are most anisotropic in the case of $ScVO_4$. It is found that the decrease in the values of R_1 and R_2, when temperature is lowered from that of x-ray data work to that corresponding to the spectroscopic investigations, is less than 0.3% and the change in angles is also of the same order. The combined effect of all these changes is small for the fourth- and sixth-order components of the crystal field, and are within other uncertain-

TABLE X. Derived intrinsic parameters $\bar{A}_n$(in cm^{-1}) corresponding to $R_0 = 2.343$ Å for various zircon-structure compounds containing Er^{3+} ion.

				$n\ m(t_n)$		
Compound		2 0(7)	4 0(12)	6 0(11)	4 4(5)	6 4(5)
$YAsO_4$	a	417	12.6	25.3	46	104
	b	55	12.9	25.4	47	104
YPO_4	a	321	20.4	30.3	47	85
	b	420	20.3	30.3	45	84
$ErPO_4$	a	390	19.0	26.6	45	101
	b	510	18.9	26.6	43	100
YVO_4	a	317	48.6	29.9	50	23
	b	201	51.2	27.2	51	21
	c	201	50.7	29.9	51	19
$ErVO_4$	a	219	44.2	29.7	48	20
	b	138	46.6	26.9	49	18
	c	138	46.1	29.7	49	16
$ScVO_4$	a	151	20.3	25.3	37	6
	b	95	20.3	25.3	33	5
$ZrSiO_4$	b	112	19.5	11.9	22	7

[a] Pertaining to the old CF parameters.

[b] Derived through the new empirical schemes of parametrization.

[c] Obtained through the new theoretical set of CF parameters.

ties involved. However, the angular and radial distortions in the neighborhood of a substituted site may be different at low temperatures.

VII. DYNAMIC CRYSTAL FIELD

Following Orbach,[10] Scott and Jeffries[11] proposed a scheme for obtaining average dynamic crystal-field parameters $a_n^m\langle r^n\rangle$ from the static ones $A_n^m\langle r^n\rangle$, and Huang[78] pointed out that the dynamic parameters so obtained should be multiplied by the respective electrostatic power-law exponents for static CF parameters. Recently, Newman and coworkers[70,79] showed that when it is necessary to use an extrapolation method, the Huang model with the following modifications is the best rule-of-thumb procedure: (1) power-law exponents derived from experiments or *ab initio* calculations are used, and (2) factor $1/9^{2q}$ ($q=1$ for direct processes and $q=2$ for Raman process) is included.

For Kramers ions, when an external magnetic field is applied parallel to the z axis, the relaxation rate for the direct process is given by[10,11]

$$T_{1d}^{-1}=AH^4T \tag{18}$$

with

$$A=\frac{12g_{\parallel}^2g_J^2\mu_B^4k}{\pi\rho\bar{v}^5\hbar^4}\sum_n\sum_m\left|\sum_q\frac{\langle -p/2|\hat{J}_z|q/2\rangle\langle q/2|\hat{v}_n^m|p/2\rangle}{\Delta_q}+\frac{\langle -p/2|\hat{v}_n^m|q/2\rangle\langle q/2|\hat{J}_z|p/2\rangle}{\Delta_q}\right|^2, \tag{19}$$

where

$$\hat{v}_n^m=a_n^m\langle r^n\rangle\,\theta_n\hat{O}_n^m\,. \tag{20}$$

Here $\bar{v}$, the velocity of sound, is obtained through the averaging process defined by Shiren.[80] The $a_n^m\langle r^n\rangle$ for $YAsO_4:Er^{3+}$ obtained through the Scott-Jeffries-Huang scheme and using the exponent values of superposition model calculations are given in Table XI, both for the old and new CF parameters; only those parameters which are required for calculations of T_{1d}^{-1} are tabulated.

For $YAsO_4$: $\rho=4.84$ g cm^{-3} and $\bar{v}=2.2\times10^5$ cm sec^{-1} (derived from the fact that $C_{66}=1.4\times10^{11}$ dyn cm^{-2} for $DyVO_4$ and $TbVO_4$,[81] which corresponds to $v_{trans}=1.5\times10^5$ cm sec^{-1}, and in scheelites, which are isostructural with zircons $v_{long}=2v_{trans}$[82]). Substituting these values, A comes out to be 11.6 $\times10^{-11}$ sec^{-1} Oe^{-4} °K^{-1} when the old scheme of parametrization is employed and 9.8×10^{-11} sec^{-1} Oe^{-4} °K^{-1} for the new scheme. Schowalter[83] studied the paramagnetic relaxation of $YAsO_4:Er^{3+}$ over the temperature range 1.5–4.2 °K in a magnetic field of 1.03 kOe parallel to the c axis. The expected relaxation time for this field is $T_{1d}=0.0076/T$ sec or $T_{1d}=0.0091/T$ sec, depending on whether the old or new set of static CF parameters is used. However, if the factor of $\frac{1}{9}$, as suggested by Stedman and Newman,[79] is included in Eq. (18) the relaxation times are given by $0.068/T$ sec or $0.082/T$ sec. These values are to be compared with the experimental temperature dependence

$$T_{eff}=(0.0022/T)+(0.001/T^2) \tag{21}$$

obtained by Schowalter.[83] In view of the crudity involved in the determination of $a_n^m\langle r^n\rangle$ and the approximate value of $\bar{v}$, the agreement is not bad, particularly when the factor of $\frac{1}{9}$ is not included. As data on other crystals are not available, such calculations have not been carried out for these.

VIII. CONCLUDING REMARKS

The CF parameters for Er^{3+}-doped $YAsO_4$, YPO_4, YVO_4, and $ScVO_4$ crystals have been modified so that simultaneous nice agreement is obtained for the ground-level g values and the Stark levels of various J states. Such an effort is remarkably successful for the yttrium compounds and appreciably so for $ScVO_4$. The agreement for hyperfine interaction parameters and the magnetic parameters at low temperature is also far better. The experimental data on magnetic anisotropy and on quadrupole splitting shall be welcome to check the parametrization, as these are quite sensitive to the schemes. Furthermore, the g factors for excited levels will also offer a confirmatory test for the proposed parameters. Keeping in view the importance of understanding the nature of zircon-structure silicates, CF parameters have also been obtained for Er^{3+}-doped $ZrSiO_4$, $HfSiO_4$, and $ThSiO_4$ crystals so that the g values are reproduced well. These parameters need confirmation from spectroscopic and other experiments and, in turn, are expected to provide good starting raw data for these studies.

TABLE XI. Dynamic CF parameters (cm^{-1}) for $YAsO_4:Er^{3+}$ estimated through Scott-Jeffries-Huang scheme using power-law exponents from the superposition model calculations.

n	t_n	$\lvert m\rvert$	From old static parameters	From new static parameters
2	7	1	1049	137
4	12	1	1256	1288
		3	3322	3408
6	11	1	5261	5275
		3	8318	8341
		5	21371	21428

The variation of semiempirical CF parameters with host lattices has been discussed and correlated with the crystallographic structure. It is shown that bonding angles and character of XO_4^{2-} tetrahedra play a more important role in the determination of the crystal field than do the ligand distances or lattice parameters. It is shown that Er–O ionic bonding decreases in the order ($YAsO_4$, YPO_4), YVO_4, and $ScVO_4$. Also the silicates are found to be closer to YVO_4 in their behavior. The analysis in the frameworks of angular overlap and superposition models reveals that $A_4^4\langle r^4\rangle$ is positive whereas $A_6^4\langle r^6\rangle$ is negative in $YAsO_4$, YVO_4, and $ScVO_4$. A set of CF parameters having these signs is derived for YVO_4 and found to be as good as an empirical one, in which these parameters have the same, but ambiguous, signs. For a YPO_4 lattice $A_4^4\langle r^4\rangle$ comes out to be positive, but the two models differ in the sign for $A_6^4\langle r^6\rangle$; the superposition model favoring positive $A_6^4\langle r^6\rangle$. These observations are contrary to the conclusions made on the basis of the electrostatic CF model. Because of doubts about the validity of local field approximation in these systems (discussed in Sec. VI D), the use of Eqs. (11) and (12) to find the bonding angles appears to be unjustified. The superposition model calculations show that the intrinsic parameter $\bar{A}_6(R_0)$ is 27 ± 3 cm^{-1} for Er–O bond separation of 2.343 Å and the result is in concord with that for the garnets. The large deviations in the case of $ScVO_4$ are also discussed.

The spin-lattice relaxation rate for $YAsO_4:Er^{3+}$ has been calculated using the Scott-Jeffries-Huang scheme and incorporating the observations made by Newman and co-workers. These too are compared with the experimental data. However, because of the approximations involved, these cannot be used to verify the schemes of parametrization.

To conclude, it can be said that the present sets of CF parameters give a better agreement for the available data, except that rms deviation is slightly increased. These calculations give a useful guide to the nature of crystal fields in zircon-structure systems. However, far more detailed calculations including *J-J* crystal-field coupling and correlation effects, etc., as well as the study of the splitting in $^4I_{13/2}$ state, need to be carried out if the agreement is to be improved further.

ACKNOWLEDGMENTS

The authors record their gratitude to Professor Dr. H. G. Kahle, Universität Karlsruhe, Karlsruhe, for sending the unpublished operator-equivalent coefficients computed by Dr. D. Kuse and for examining the first draft of the paper; to Professor Dr. K. H. Hellwege, Technischen Hochschule, Darmstadt, for comments on crystal quantum numbers; to Dr. H. Saji, Matsushita Research Institute, Tokyo, for the unpublished data on susceptibilities of $ErPO_4$ and $ErVO_4$; and to Dr. D. J. Newman, Queen Mary College, London, for useful comments on the manuscript. One of us (V) is thankful to Professor S. K. Joshi, Head, Dept. of Physics, University of Roorkee, Roorkee, for the hospitality during a summer visit when most of the computation work was done at the Computer Center, Structural Engineering Research Center, Roorkee; and to the Council of Scientific and Industrial Research , New Delhi, for awarding the research fellowship.

---

*Based on a chapter of the Ph. D. thesis submitted by Vishwamittar to the University of Roorkee, Roorkee, India.

[1] A. K. Levine and F. C. Palilla, Appl. Phys. Lett. 6, 118 (1964).

[2] J. H. Colwell, B. W. Mangum, D. D. Thornton, J. C. Wright, and H. W. Moos, Phys. Rev. Lett. 23, 1245 (1969).

[3] J. C. Wright and H. W. Moos, J. Appl. Phys. 41, 1244 (1970).

[4] H. Saji, T. Yamadaya, and M. Asanuma, J. Phys. Soc. Jap. 28, 193 (1970).

[5] A. H. Cooke, C. J. Ellis, K. A. Gehring, M. J. M. Leask, D. M. Martin, B. M. Wanklyn, M. R. Wells, and R. L. White, Solid State Commun. 8, 689 (1970).

[6] R. P. Hudson and B. W. Mangum, Phys. Lett. 36A, 157 (1971).

[7] J. C. Wright, H. W. Moos, J. H. Colwell, B. W. Mangum, and D. D. Thornton, Phys. Rev. B 3, 843 (1971).

[8] G. H. Dieke, *Spectra and Energy Levels of Rare Earth Ions in Crystals* (Interscience, New York, 1968).

[9] M. T. Hutchings, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1964), Vol. 16, p. 227.

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

[11] P. L. Scott and C. D. Jeffries, Phys. Rev. 127, 32 (1962).

[12] See for example, Vishwamittar, S. P. Taneja, and S. P. Puri, J. Phys. Chem. Solids 33, 965 (1972). In the present work the calculations for YPO_4, YVO_4, and $ScVO_4$ with the parameters of Kuse and Hintzmann have been revised, as the operator-equivalent coefficients used in our previous work are different from the ones used by the authors.

[13] H. G. Kahle and L. Klein, Phys. Status Solidi 42, 479 (1970).

[14] D. Kuse, Z. Phys. 203, 49 (1967).

[15] W. Hintzmann, Z. Phys. 230, 213 (1970).

[16] J. Plamper, Phys. Status Solidi B 47, 129 (1971).

[17] M. Dzionara, H. G. Kahle, and F. Schedewie, Phys. Status Solidi B 47, 135 (1971).

[18] U. Ranon, Phys. Lett. 28A, 228 (1968).

[19] R. W. G. Wyckoff, *Crystal Structures* (Interscience, New York, 1965), Vol. 3, pp. 15–18.

[20] M. M. Abraham, G. W. Clark, C. B. Finch, R. W. Reynolds, and H. Zeldes, J. Chem. Phys. 50, 2057 (1969).

[21] G. Lohmüller, G. Schmidt, B. Deppisch, V. Gramlich,

and C. Scheringer, Acta. Cryst. B 29, 141 (1973).

[22] D. J. Newman and W. Urban, J. Phys. C 5, 3101 (1972).

[23] K. Robinson, G. V. Gibbs, and P. H. Ribbe, Am. Mineral. 56, 782 (1971).

[24] R. W. Reynolds, L. A. Boatner, C. B. Finch, A. Chatelain, and M. M. Abraham, J. Chem. Phys. 56, 5607 (1972).

[25] *Handbook of Chemistry and Physics*, 49th ed. (The Chemical Rubber Co., Cleveland, Ohio, 1968) p. F152.

[26] E. Patscheke, H. Fuess, and G. Will, Chem. Phys. Lett. 2, 47 (1968).

[27] S. S. Bishton and D. J. Newman, J. Phys. C 3, 1753 (1970).

[28] R. S. Rubins, Phys. Rev. B 1, 139 (1970).

[29] N. Karayianis, J. Chem. Phys. 55, 3734 (1971).

[30] J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities*, (Oxford U. P., London, 1965), p. 182.

[31] R. J. Elliot and K. W. H. Stevens, Proc. R. Soc. A 218, 553 (1953).

[32] S. Ofer, I. Nowik, and S. G. Cohen, in *Chemical Applications of Mössbauer Spectroscopy*, edited by V. I. Goldanskii and R. H. Herber (Academic, New York, 1968), p. 427.

[33] B. Bleaney, Phys. Rev. 78, 214 (1950).

[34] A. J. Kassman, J. Chem. Phys. 53, 4118 (1970).

[35] D. Kuse (unpublished work) [derived from the wave functions obtained by K. Rajnak, J. Chem. Phys. 43, 847 (1965)].

[36] Vishwamittar, Ph.D. thesis (University of Roorkee, Roorkee, 1973) (unpublished).

[37] M. J. Metcalfe and H. M. Rosenberg, J. Phys. C 5, 474 (1972).

[38] G. Will, W. Lugscheider, W. Zinn, and E. Patscheke, Phys. Status Solidi B 46, 597 (1971).

[39] H. Saji (private communication).

[40] H. Dobler, G. Petrich, S. Hüfner, P. Kienle, W. Wiedemann, and H. Eicher, Phys. Lett. 10, 319 (1964).

[41] L. L. Hirst and E. R. Seidel, J. Phys. Chem. Solids 31, 875 (1970).

[42] K. F. Smith and P. J. Unsworth, Proc. Phys. Soc. Lond. 86, 1249 (1965).

[43] R. M. Sternheimer, Phys. Rev. 146, 140 (1966).

[44] R. L. Cohen and J. H. Wernick, Phys. Rev. 134, B503 (1964).

[45] K. M. S. Saxena and J. B. Mann (private communications).

[46] R. P. Gupta, B. K. Rao, and S. K. Sen, Phys. Rev. A 3, 545 (1971).

[47] J. Blok and D. A. Shirley, Phys. Rev. 143, 278 (1966).

[48] D. Ball, Phys. Status Solidi B 46, 635 (1971).

[49] G. Burns, Phys. Rev. 128, 2121 (1962).

[50] M. Inoue, Phys. Rev. Lett. 11, 196 (1963).

[51] Unpublished work of D. M. Martin and M. R. Wells, quoted in Ref. 37.

[52] W. Becher, H. Kalbfleisch, and G. Muller-Vogt, Phys. Status Solidi B 52, K81 (1972).

[53] A. Lempicki, H. Samelson, and C. Brecher, J. Molec. Spectrosc. 27, 375 (1968).

[54] C. Brecher, H. Samelson, R. Riley, and A. Lempicki, J. Chem. Phys. 49, 3303 (1968).

[55] R. M. Sternheimer, M. Blume, and R. R. Peierls, Phys. Rev. 173, 376 (1968).

[56] G. Burns, J. Chem. Phys. 42, 377 (1965).

[57] J. R. Tessman, A. H. Kahn, and W. Schockley, Phys. Rev. 92, 890 (1953).

[58] T. O. Brun, G. H. Lander, and G. P. Felcher, Bull. Am. Phys. Soc. 16, 325 (1971).

[59] C. K. Jørgensen, R. Pappalardo, and H.-H. Smidtke, J. Chem. Phys. 39, 1422 (1963).

[60] G. Burns and J. D. Axe, in *Optical Properties of Ions in Crystals*, edited by H. M. Crosswhite and H. W. Moos (Interscience, New York, 1967), p. 53.

[61] M. M. Ellis and D. J. Newman, J. Chem. Phys. 49, 4037 (1968).

[62] D. Kuse and C. K. Jørgensen, Chem. Phys. Lett. 1, 314 (1967).

[63] C. E. Schäffer and C. K. Jørgensen, Mol. Phys. 9, 401 (1965).

[64] C. K. Jørgensen, J. Phys. 26, 825 (1965).

[65] J. D. Axe and G. Burns, Phys. Rev. 152, 331 (1966).

[66] R. T. Sanderson, *Inorganic Chemistry* (Van Nostrand Reinhold, New York, 1967).

[67] C. K. Jørgensen, Prog. Inorg. Chem. 4, 73 (1962).

[68] D. J. Newman, J. Phys. Chem. Solids 34, 541 (1973).

[69] M. I. Bradbury and D. J. Newman, Chem. Phys. Lett. 1, 44 (1967).

[70] M. M. Curtis, D. J. Newman, and G. E. Stedman, J. Chem. Phys. 50, 1077 (1969).

[71] D. J. Newman, Adv. Phys. (N. Y.) 20, 197 (1971).

[72] D. J. Newman and G. E. Stedman, J. Phys. Chem. Solids 32, 535 (1971).

[73] D. J. Newman and G. E. Stedman, J. Chem. Phys. 51, 3013 (1969).

[74] D. J. Newman (private communication).

[75] M. M. Curtis and D. J. Newman, J. Chem. Phys. 52, 1340 (1970).

[76] M. M. Curtis and D. J. Newman, Chem. Phys. Letters 9, 606 (1971).

[77] H. C. Schopper, W. Urban, and H. Ebel, Solid State Commun. 11, 955 (1972).

[78] C. Y. Huang, Phys. Rev. 139, A241 (1965).

[79] G. E. Stedman and D. J. Newman, J. Chem. Phys. 55, 152 (1971).

[80] N. S. Shiren, in *Magnetic and Electric Resonance and Relaxation*, edited by J. Smidt (North-Holland, Amsterdam, 1963), p. 415.

[81] J. R. Sandercock, S. B. Palmer, R. J. Elliot, W. Hayes, S. R. P. Smith, and A. P. Young, J. Phys. C 5, 3126 (1972).

[82] B. W. James, Phys. Status Solidi A 13, 89 (1972).

[83] R. Schowalter, Phys. Status Solidi B 48, 743 (1971).