A study of erbium, thulium and other rare earth ethyl sulphates

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Abstract. The available sets of crystal field parameters for erbium and thulium ethyl sulphates are used to calculate the Stark levels, g-values, Schottky specific heat, magnetic anisotropy, hyperfine interaction parameters and low temperature specific heat of these compounds. A comparison of these calculations with experimental data shows that one of these sets can be taken to be optimum within the accuracy of various measurements. These parameters along with the already optimised ones for other ethyl sulphates are discussed in the frameworks of electrostatic, angular overlap and superposition models for the crystalline fields. The antibonding energy parameter and ionicity are found to be different for light and heavy compounds and almost constant in either half of the series.

Keywords. Rare earth ethyl sulphates; erbium ethyl sulphate; thulium ethyl sulphate; angular overlap model; lanthanide ethyl sulphates.

1. Introduction

The series of hydrated rare earth ethyl sulphates [R $(9H_2O)$ $(C_2H_5SO_4)_3$] has been of considerable interest since last four decades and constitutes the most intensely investigated class of lanthanide compounds. The optical and electron paramagnetic resonance (EPR) spectra, and magnetic susceptibility (χ) of almost all the ethyl sulphates have been studied either alone or diluted with isostructural LaES or YES. In addition, data are also available for Schottky specific heat (C_s), quadrupole splitting ($\langle \triangle E_Q \rangle_T$), spin-lattice relaxation, and low temperature specific heat ($C_\perp$) for most of the compounds. Based on the microwave spectral data of Bleaney and co-workers, Stevens and others developed a phenomenological theory for the then available susceptibility data (*see* Low 1960). However, since EPR experiments refer only to the lowest Stark level and susceptibility is an average of the magnetic moments of various levels, these do not portray the entire picture. Furthermore, the results of these investigations failed to account for the observed optical spectra. Consequently, new schemes of parametrization were proposed to explain the absorption, fluorescence and infra-red spectra. But in some cases, even these were found to be inadequate to account for the temperature dependence of magnetic anisotropy and quadrupole splitting. As a result, different sets of crystal field (CF) parameters were put forward for the same compound, with the consequence that though these systems have been studied extensively, their theoretical interpretation is quite confusing. Recently an attempt has been made to reconcile a major part of experimental data on various ethyl sulphates and to define single sets of CF parameters (Vishwamittar 1973). In the case of PrES, NdES and DyES new schemes of parametrization have been proposed such that these explain various physical properties

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within the accuracy of their measurements (Vishwamittar and Puri 1974 *b*, 1975). However, one of the old sets of CF parameters is found to be optimum for ErES and TmES; the details of which constitute the contents of section 3 of this paper. However, an identical attempt for YbES does not yield encouraging results. Because of limited measurements on TbES, an effort of this kind was not considered advisable, and the calculations for HoES have not been carried out as the results for this are already explained without any contradiction (Cooke *et al* 1965). After defining only a single set of CF parameters for each compound it becomes more meaningful to correlate these with the theoretical models and the results of such studies are included in section 4. Furthermore, understanding of the static crystalline fields will be helpful in analysing the dynamic component and hence the relaxation processes, etc. in the ethyl sulphates.

2. Theory

The crystal structures of some of the ethyl sulphates were determined by Ketelaar (1937), and refined by Fitzwater and Rundle (1959) in the case of PrES, ErES, and YES. The nearest neighbours of the metal ion are nine oxygens belonging to H_2O molecules so that their site symmetry is C_{3h}. If the slight distortion (giving $\phi \sim 4 - 6°$) of mirror-plane oxygens (1–3) is ignored, the symmetry about the metal ion is almost D_{3h} (figure 1 and table 1). The crystal field hamiltonian $\hat{H}_{CF}$
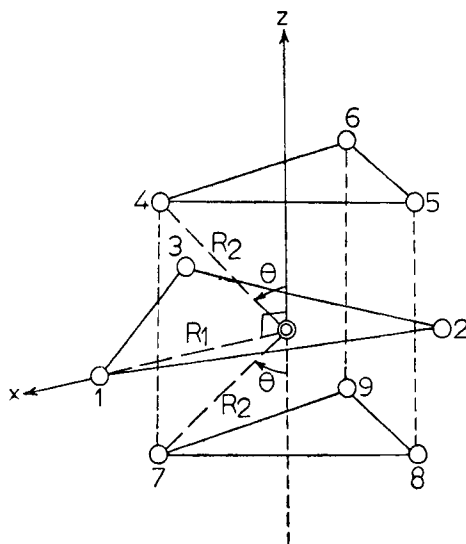

Figure 1. Arrangement of water oxygens around the metal ion in ethyl sulphates. Oxygens 1–3 are at R_1 and coplanar with the central ion ($\theta = 90°$); 4–6 at R_2 and make an angle θ with z-axis; whereas 7–9 at R_2 form an angle $180° - \theta$.

Table 1. Oxygen distances and polar angles for various rare earth ethyl sulphates (Fitzwater and Rundle 1959).

Compound	R_1 (Å)	R_2 (Å)	θ
PrES	2·65	2·47	47·6°
ErES	2·52	2·37	45·2°
YES	2·55	2·37	45·5°

for the latter differs from that for the former only by the term $\gamma_J A_6^{6'} \langle r^6 \rangle \hat{O}_6^{-6}$, which can be rendered zero by a suitable choice of coordinates. Consequently, it is customary to regard the CF as having D_{3h} pseudo-symmetry, and in usual notation (Low 1960):

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

Once the CF parameters $A_n^m \langle r^n \rangle$ are known from some studies, these can be checked by comparing the measurements on other physical quantities with the calculations through these parameters as summarised in earlier communications (Vishwamittar and Puri 1974 a, and Vishwamittar et al 1972). In addition to the interactions discussed therein, in the case of concentrated compounds at very low temperatures ($\lesssim 2K$), there usually exist dipole-dipole, quadrupole-quadrupole, and exchange interactions between neighbouring ions in the crystals. However, the contribution of the last two interactions to specific heat and magnetic susceptibility is known to be very small in the ethyl sulphates (Cooke et al 1957, Baker 1971), whereas that of the dipole-dipole interactions to specific heat is given by (Daniels 1953, Wong et al 1969)

$$C_{dd} = (R\mu_B^4)/32 \, k^2 \, T^2) \, [(g_\parallel^4 + 5g_\perp^4) \, \Sigma \, (1/r_{ij}^6) - 6 \, (g_\parallel^2 - g_\perp^2) \, (g_\parallel^2 - 2g_\perp^2)$$

$$\Sigma \, (z_{ij}^2/r_{ij}^8) + 9 \, (g_\parallel^2 - g_\perp^2)^2 \, \Sigma \, (z_{ij}^4/r_{ij}^{10})] \quad (2)$$

and to susceptibility by (Daniels 1953).

$$(\chi_{dd})_j = (\triangle_j/T) \, \chi_j \quad (3\,a)$$

where χ_j is principal paramagnetic susceptibility;

$$\triangle_\parallel = (g_\parallel^2 \, \mu_B^2/4k) \, \Sigma \, (3z_{ij}^2 - r_{ij}^2) r_{ij}^{-5} \quad (3\,b)$$

and

$$\triangle_\perp = - (g_\perp^2 \, \mu_B^2/8k) \, \Sigma \, (3z_{ij}^2 - r_{ij}^2) \, r_{ij}^{-5}. \quad (3\,c)$$

The effect of hyperfine interactions on susceptibility is negligible even at very low temperatures (Cooke et al 1957).

3. Optimum CF parameters for ErES and TmES

3.1. *ErEs*

The CF analysis of ErES was carried out by Erath (1961, 1963) on the basis of best fit for 46 Stark levels belonging to 10 *J*-manifolds and Gerstein et al (1962 b) showed that the calculations through these parameters were in good agreement with their measurements on Schottky specific heat. This work was followed by the measurements on magnetic anisotropy by Mookherji (1964) who observed a change in the direction of the principal magnetic axes with variation in temperature from 300 K to 80 K and attributed it to a change in the symmetry of the crystal from hexagonal to either monoclinic or triclinic at lower temperatures. However, the details of this work were not published and we have ignored this observation in view of the works reported later on (Cooke et al 1965, Hill and Wheeler 1966,

Larson and Jeffries 1966, Syme *et al* 1968, etc.) and the fact that such an effect was not observed by others (A. H. Cooke and F. H. Spedding, private communications). Cooke *et al* (1965) carried out measurements pertaining to magnetic susceptibility down to very low temperatures ($\simeq 1 \cdot 5$ K) and concluded that not only the CF parameters of Erath were adequate but also the effects of thermal expansion over this temperature range were very small. Later on, Hill and Wheeler (1966) modified Erath's CF parameters to get a better accord for the Stark structure of $^4I_{15/2}$ observed in the far infra-red spectra. Dieke (1968) has, however, catalogued the positions of 52 energy levels deriving from 11 J-states and their comparison with the calculations through the parameters of Erath and Hill and Wheeler gives root mean square deviations (σ) $4 \cdot 8$ and $4 \cdot 9$ cm^{-1}, respectively. As is common in the erbium systems, the deviations between the measured and calculated Stark energies are large for $^4I_{11/2}$, $^2H_{11/2}$, and $^2H_{9/2}$ states and must be due to the approximations involved in the free-ion hamiltonian. Both the sets of CF parameters are given in table 2. C_s derived with the eigenvalues obtained through the two schemes of parametrization is shown in figure 2, along with the experimental data of Gerstein *et al* (1962 *b*). Evidently, the curve estimated through the Hill and Wheeler scheme is in relatively closer accord with the data, though the two plots are not much separated. A smooth curve through the experimental points gives a peak of $8 \cdot 14$ J/(mole deg) at 48 K, which is nearly 10 per cent higher than the calculated magnitudes.

Table 2. Crystal field parameters $A_n^m \langle r^n \rangle$ and rms deviation σ (in cm^{-1}) for various rare earth ethyl sulphates.

Compound	$A_2^0 \langle r^2 \rangle$	$A_4^0 \langle r^4 \rangle$	$A_6^0 \langle r^6 \rangle$	$A_6^6 \langle r^6 \rangle$	ρ_6^{60}	Ref.
PrES	25·	−78·	−45·	700·	−15·6	Vishwamittar and Puri (1975)
NdES	58·4	−68·2	−40·	615·	−15·4	Vishwamittar and Puri (1975)
TbES	110·	−74·8	−34·	465·	−13·7	Hüfner (1962)
DyES	120·	−79·	−30·	500·	−16·7	Vishwamittar and Puri (1974 *b*)
HoES	125·	−79·	−30·	391·	−13·0	Hüfner (1962)
ErES	125·8	−81·19	−31·06	387·19	−12·5	Erath (1961, 1963)·
*	118·8	−73·9	−30·4	375·9	−12·4	Hill and Wheeler (1966)
TmES	129·8	−71 0	−28·6	432·8	−15·1	Wong and Richman (1961)
*	135·3	−71·35	−28·8	428·1	−14·9	Krupke and Gruber (1965)
	130·5	−65·9	−28·6	427·3	−14·9	Barnes *et al* (1964)
YbES	155·4	−57·7	−25·6	472·9	−18·5	Wheeler *et al* (1968)

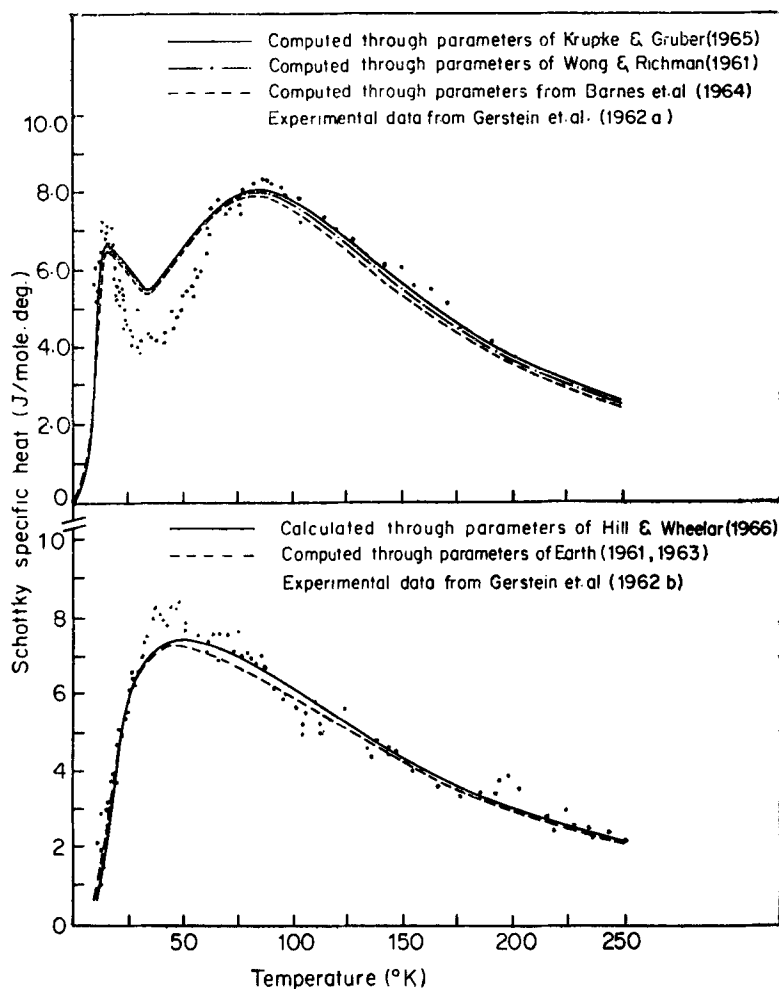* The sets shown to be optimum in this paper.

Figure 2. Estimated and experimental temperature variation of Schottky specific heat of ErES and TmES; the lower curve refers to the former and the top curve to the latter.

The principal components of g-tensor as extracted through the wavefunctions obtained from the CF parameters of Erath, and Hill and Wheeler are $g_{\parallel} = 1\cdot31$, $|g_{\perp}| = 8\cdot86$, and $g_{\parallel} = 1\cdot47$, $|g_{\perp}| = 8\cdot86$, respectively. The corresponding values obtained from the EPR experiments on Er^{3+}: LaES are $|g_{\parallel}| = 1\cdot47 \pm 0\cdot03$, $|g_{\perp}| = 8\cdot85 \pm 0\cdot02$ (Bleaney and Scovil 1951) and for YES diluent are $|g_{\parallel}| = 1\cdot50 \pm 0\cdot05$, $|g_{\perp}| = 8\cdot77 \pm 0\cdot03$ (Larson and Jeffries 1966). Obviously, the Hill and Wheeler scheme produces a better agreement. Next, the two sets are used to generate the temperature dependence of $K_{\parallel}$, $K_{\perp}$ and $\triangle K$. To highlight the small difference in the values, these are compared with the results of Cooke *et al* (1965) in table 3. Mookherji's data has been ignored in view of its dubious nature. It is found that the calculations through the Hill and Wheeler scheme give a better overall agreement in this case also. An attempt to derive a set of CF parameters which could provide better accord for $\triangle K$ at low T, does not yield encouraging results.

Table 3. Measured and calculated susceptibility parameters for ErES.

T (°K)	$K_\parallel T$ (emu °K/mole) (1)	(2)	(3)	$K_\perp T$ (emu °K/mole) (1)	(2)	(3)	$\triangle K$ (memu/mole) (1)	(2)	(3)
300	10·60	10·47	10·54	11·58	11·66	11·63	−3·3	−3·97	−3·63
250	10·31	10·28	10·35	11·60	11·68	11·64	−5·2	−5·59	−5·15
200	10·0	10·00	10·07	11·60	11·70	11·65	−8·0	−8·51	−7·93
150	9·39	9·49	9·56	11·62	11·70	11·66	−14·9	−14·73	−14·01
100	8·0	8·41	8·43	11·65	11·70	11·66	−36·5	−32·87	−32·28
80	7·23	7·57	7·56	11·58	11·70	11·68	−54·4	−51·71	−51·57
50	5·0	5·24	5·15	11·45	11·74	11·73	−129·0	−129·9	−131·6
30	2·0	2·63	2·54	11·0	11·51	11·49	−300	−296·0	−298·2
20·4	1·05	1·36	1·34	10·61	10·91	10·86	−500	−468	−466
5	0·428	0·354	0·395	7·839	8·326	8·290	−1482	−1608	−1592
4	0·389	0·315	0·357	7·631	8·106	8·076	−1810	−1968	−1950
3	0·350	0·276	0·319	7·423	7·870	7·846	−2360	−2569	−2546

(1) Experimental data of Cooke *et al* (1965).
(2) and (3), respectively, are calculations through the CF parameters of Erath (1961, 1963) and Hill and Wheeler (1966).

Table 4. Calculated and measured *hfs* parameters (in 10^{-4} cm^{-1}) and nuclear specific heat (in 10^5 erg K/mole) for ^{167}ErES.

	Calculations through the parameters of Erath (1961, 1963)	Hill and Wheeler (1966)	Experimental data* of Bogle *et al* (1952)
$A_\parallel$	−46·5	−52·4	52±1
$\lvert A_\perp \rvert$	315·0	314·8	314±1
P	− 2·7	− 2·5	30±3
$C_N T^2$	4·5	4·5	..

* The EPR experiments do not give the sign of *hf* interaction parameters.

The *hfs* parameters computed with the constants listed by Vishwamittar and Puri (1974 *a*) are compared with the experimental data of Bogle *et al* (1952) in table 4. Once again, $A_\parallel$ and $A_\perp$ are better reproduced by the CF parameters of Hill and Wheeler. The values of P are equally diverse in both the cases, and C_N, having same magnitude for both the sets, cannot be checked for want of such measurements. Furthermore, $C_{dd} T^2 = 5·6 \times 10^5$ erg K/mole and $C_L T^2 = 6·6 \times 10^5$ erg K/mole. The parameters for the effect of dipole-dipole interaction on principal susceptibilities turn out to be $\triangle_\parallel = 2·3 \times 10^{-3}$ K and $\triangle_\perp = - 4·2 \times 10^{-2}$ K. The calculated susceptibilities, after including this effect, are compared with the data of Cooke *et al* (1965) in table 3 and the results obtained through the Hill and Wheeler parameters are found to be in better agreement with the experiments.

3.2 *TmES*

After preliminary work by a number of groups, the CF parameters of *TmES*

diluted with *LaES* were derived by Gruber and Conway (1960), and Wong nad Richman (WR) (1961). Gerstein *et al* (1962 *a*) used these parameters to correlate the calculations with their measurements on specific heat and susceptibility from 4 to 200 K and concluded that the WR parameters give a better agreement. Later on, Krupke and Gruber (KG) (1965) reported a set of parameters which explained the ground state splitting more accurately. Barnes *et al* (B) (1964) studied the temperature dependence of the quadrupole splitting of $^{169}TmES$ by Mössbauer technique and propounded still another set of parameters to explain the results. Recently, Chachra *et al* (1974) measured the principal magnetic susceptibilities over the temperature range 100–300 K and compared these with the calculations through WR and B sets. They did not use the KG parameters for computations and concluded that B set gives an excellent agreement. In the present work, the WR, KG, and B sets are employed to deduce various properties with a view to choose the optimum set. It is found that though the B set reproduces the energy levels of $^3H_6$ state most faithfully, the rms deviation for the complete energy spectrum is minimum (8·9 cm^{-1}) in the case of WR parameters; σ comes out to be 11·0 and 11·3 cm^{-1} for the KG and B sets, respectively. Of course, the situation may change if all the energy levels are observed, as the present incomplete data are adjusted to give best fit with the WR set. It may be pointed out that $^1G_4$ and $^3F_4$ states are mainly responsible for the large deviations. The α_J, β_J, and γ_J for these states in the intermediate coupling scheme are also appreciably different from their values in the LS coupling scheme.

The temperature dependence of C_s as obtained through the three schemes of parametrization is compared with the experimental data of Gerstein *et al* (1962 *a*) in figure 2. A smooth curve through the experimental points gives two peaks of 7·1 and 8·3 J/(mole deg) at 16 and 85 K, respectively. The three calculations yield nearly same values for the positions (18 and 83 K) and magnitudes [6·4 and 8·0 J/(mole deg)] of two Schottky peaks and as such cannot serve as a basis to decide the suitability of the CF parameters. However, the overall agreement of the results through the KG set is little better.

Johnsen (1958) investigated the Zeeman spectra of a number of Stark levels pertaining to various *J*-states of TmES. The three sets of CF parameters are used to compute the values of $g_{\parallel}$ for these levels and the results are compared with the corresponding experimental magnitudes in table 5. It turns out that the calculations through the KG set are in best correspondence with the measurements. The large difference of $g_{\parallel}$ for $\mu = \pm 2$ of $^3F_3$ state from the corresponding experimental value must be due to the effect of crystal field *J*-mixing on this state.

Since anisotropy is more sensitive to the crystal field, the $\triangle K$ values have been obtained from the data of Gerstein *et al* and Chachra *et al*, and in order to bring out the difference clearly, are compared with the calculations in table 6. Evidently, the KG calculations produce best agreement for this parameter also. Of course, at higher temperatures the calculations through this set exhibit more deviation; efforts to define a set of parameters which could give overall good agreement did not prove fruitful.

It may be pointed out that Chachra *et al* have used the perturbation theory for nondegenerate systems to find the first and second-order coefficients for accidentally degenerate CF levels, which is conceptually wrong (Vishwamittar and Puri 1974 *b*).

Table 5. Experimental (Johnsen 1968) and calculated $g_{\parallel}$-values for various CF levels originating from different J-states of TmES

State	CF level (μ)	$\mid g_{\parallel} \mid$ (exp.)	$g_{\parallel}$ (WR)	$g_{\parallel}$ (KG)	$g_{\parallel}$ (B)
$^3H_6$	±1	1·14	1·09	1·16	1·03
$^3F_4$	±2	3·14	3·71	3·85	3·77
	$\pm2'$	0·00	0·12	0·01	0·07
$^3F_3$	±2	3·78	−4·33	−4·33	−4·33
$^3F_2$	±2	3·08	−3·02	−3·02	−3·02
$^1G_4$	±2	3·6	3·02	3·16	2·84
	$\pm2'$	0·00	0·79	0·65	0·99
rms deviation for 7 values (σ_g):			0·48	0·45	0·58

Table 6. Temperature dependence of magnetic anisotropy (in emu/mole) of TmES.

T (°K)	Expt.†	Calculated		
		WR	KG	B
4	−416·5	−419·8	−412·5	−436·4
6	−414·6	−419·3	−412·1	−435·8
8	−410·4	−416·5	−409·7	−423·2
10	−401·3	−409·4	−403·4	−423·6
20	−317·5	−328·5	−326·5	−333·8
30	−244·5	−251·5	−251·5	−253·4
40	−198·3	−199·0	−199·5	−199·6
50	−163·0	−162·0	−162·8	−162·0
100	− 72·5	−68·6	− 69·9	− 68·1
160	− 28·0	− 30·5	− 31·3	− 30·2
200	− 13·9 (− 13·3)*	− 19·8	− 20·4	− 19·6
250	− 9·2*	− 12·6	− 13·0	− 12·5
300	−7·0*	− 8·7	− 9·0	− 8·6

† Results of Chachra *et al* (1974) are marked by asterisks, while the remaining data are from Gerstein *et al* (1962 a).

Their calculations give an impression that all the doublets remain degenerate even after the effect of second-order perpendicular perturbation due to magnetic inter-action is included, whereas, in fact, their degeneracy is lifted by this perturbation. Furthermore, the calculations through KG set explain the data for $\chi_{\perp}$ as nicely as is done by the results of B set, while the deviations of $\chi_{\parallel}$ at low temperatures are equally significant for both the cases.

To check the schemes of parametrization with respect to temperature dependence of the quadrupole splitting, following values of various constants have been used: $Q = 1\cdot3\,b, (1 - R)\,Q = 1\cdot08 \pm 0\cdot08$ (Cohen 1964); $\langle r^{-3}\rangle_{4f} = 12\cdot96\,a_0^{-3}$, $\langle r^2\rangle_{4f} = 0\cdot62\,a_0^2$ (K. M. S. Saxena, private communcation); $\gamma_\infty = -72\cdot86$, $\sigma_2 = 0\cdot601$

(Gupta *et al* 1971). The three calculations are found to differ from each other by at most 4 per cent which is within the experimental accuracy. However, in a literal sense the experimental magnitudes are close to the calculations through the KG parameters below about 90 K whereas for higher temperatures the agreement is better with the B set (figure 3). The results of calculations through the WR set lie in between those through the KG and B sets and hence are not depicted here. It may be pointed out that the present calculations at high temperatures differ appreciably from those of Barnes *et al* due to difference of input data. Since the lattice contribution ($0 \cdot 46$ or $0 \cdot 45 \mu$ eV) becomes reasonably important at high temperatures (the 4 f-electron part at 300 K is about $- 0 \cdot 73$ or $- 0 \cdot 70 \mu$eV as compared to $- 2 \cdot 70$ or $- 2 \cdot 69 \mu$eV at 4 K, for the KG and B sets, respectively), this discrepancy indicates that there is some error in the estimation of this part. Also the enhanced lattice contribution to the quadrupole splitting will not change the agreement at low temperatures much, whereas the situation will improve at
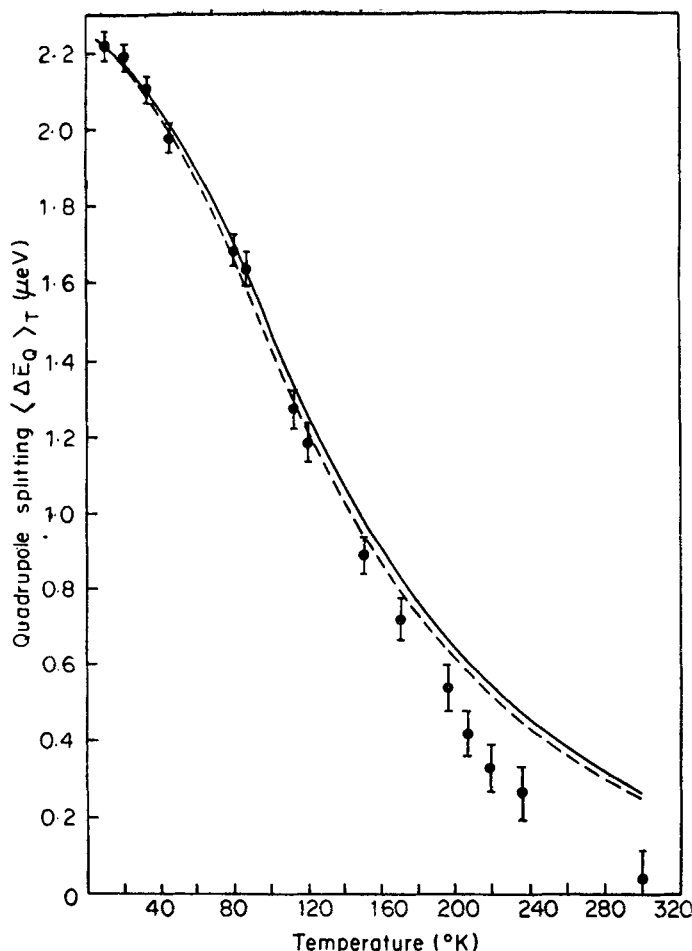

Figure 3. Temperature dependence of the quadrupole splitting of ^{169}TmES. The full curve is obtained from the calculations through the KG set and the broken curve through the parameters of Barnes *et al*. The experimental data (⧙) are from Barnes *et al* (1964).

higher temperatures. This, in turn, can be rendered better by using different values of σ_2, which has been shown to be a lattice dependent parameter. Furthermore, the present calculations are based on the assumption that the CF parameters (and hence the characteristics of the Stark levels) and the lattice part of the quadrupole splitting do not depend on temperature, though Edmonds and Lindop (1966) have reported temperature dependence of $A_2^0 \langle r^2 \rangle$ in LaES and LuES.

4. Analysis of the phenomenological CF parameters

With a view to having a better understanding of the nature of the crystalline field in rare earth ethyl sulphates, the CF parameters shown to be most suitable in recent work and listed in table 2 are discussed in this section. A perusal of table 2 shows that the ratio $\rho_6^{60} = A_6^6 \langle r^6 \rangle / A_6^0 \langle r^6 \rangle$ may be taken as $-14 \cdot 6 \pm 1 \cdot 5$ if the results for TbES and YbES, which have not been optimised, are excluded. Now, in the electrostatic CF model with various parameters as depicted in figure 1:

$$\rho_6^{60} = 115 \cdot 5 \frac{(\cos 6\phi / R_1^7) + (2 \sin^6 \theta / R_2^7)}{[(-5/R_1^7) + \{231 \cos^6 \theta - 315 \cos^4 \theta + 105 \cos^2 \theta - 5\} (2/R_2^7)]} \tag{4}$$

Since this ratio neither involves the lattice sum nor the CF shielding parameters σ_n, it is electrostatic in nature only so far as power law is involved. Taking ErES as a typical representative (with $\phi = 4° 23'$ and the other data from table 1), it is found that $\rho_6^{60} = -12 \cdot 5$; for $\phi = 0$, which makes symmetry exactly D_{3h}, this ratio becomes $-13 \cdot 5$. However, if instead of considering point charges at O^{2-} sites, extended charge distribution is taken for the H_2O ligands (Burns 1965), this ratio becomes $-12 \cdot 4$; and for $\phi = 0$, it is $-13 \cdot 4$.

In view of the difficulties involved in understanding the origin of crystalline field in the framework of electrostatic model, Jørgensen *et al* (1963) suggested that the CF splittings be considered as a σ — antibonding effect and developed the so called angular overlap model to understand the behaviour of the CF parameters. Though this has been extended to include the effect of ligand p_π orbitals (Schäffer and Jørgensen 1965, Jørgensen 1971), it is not easy to be used for the rare-earth ion systems. Nonetheless, it has been shown that the basic assertion of this model is correct (Ellis and Newman 1969). In this model, the angular part E^2 of the antibonding energy is calculated from the crystallographic data and the radial part σ^* is determined by correlating the theoretical values of orbital energies with those obtained from the symmetry appropriate one electron CF hamiltonian using the (optimum) CF parameters (Jørgensen 1971, Jørgensen *et al* 1963). The one electron energies derived through the CF parameters listed in table 2 and in the notation used by Jørgensen *et al*, are catalogued in table 7. The relative order of the one-electron energy levels in the first half of the rare earth series is

$$\phi_1 < \sigma < \delta < \pi < \phi_2, \tag{5}$$

which is different from that in the second half

$$\phi_1 < \sigma < \phi_2 < \delta < \pi. \tag{6}$$

The difference in the values of energies from one ion to the other is a result of interactions involving two or more electrons. The variation of these energies is almost

Table 7. One-electron orbital energies (in cm^{-1}) for various rare earth ethyl sulphates derived through the optimum CF parameters

Compound	$\phi_1(a_2')$	$\sigma(a_2')$	$\phi_2(a_1')$	$\delta(e'')$	$\pi(e')$
PrES	−326	−268	196	82	117
NdES	−310	−217	148	71	119
TbES	−295	−177	52	89	121
DyES	−318	−163	55	100	113
HoES	−281	−160	11	100	115
ErES	−267	−158	13	91	115
TmES	−296	−139	23	89	117
YbES	−317	− 96	36	69	120

smooth throughout the series and the abrupt increase in the energy of σ-orbital in TmES pointed out by Jørgensen *et al* is a result of mistake in their calculations; this energy is $-141\ cm^{-1}$ rather than $-76\ cm^{-1}$ (for WR set) as given by these authors. It may be remarked that if Gruber's set based on spectroscopic data alone is used to compute the orbital energies for PrES, nonbonding ϕ_1 comes out to be higher than antibonding σ- orbital, which is not an acceptable hypothesis. Jørgensen *et al* have given the relationships for determining $\varXi^2$ from x-ray data; these involve $\xi_s = (R_2/R_1)\ \sin\theta$ and $\xi_c = (R_2/R_1)\ \cos\theta$. In view of the strain experiments on cubic systems (Axe and Burns 1966) the effect of the ligands at R_2 is weighted by $(R_1/R_2)^7$ so that the estimated σ^* corresponds to R_1 as the reference value. Thus, in the present work, the parameters ξ_s and ξ_c are treated semi-empirically, while Jørgensen *et al* took $\xi_s = \xi_c = 1/\sqrt{2}$ or $(0 \cdot 2)^{1/6}$. The coordinates compiled in table 1 are employed to estimate the theoretical one-electron orbital energies for PrES, ErES, and the rare earth ion in YES. It turns out that the relative orders of these levels are quite different from those derived through the optimised CF parameters. However, the situation improves if θ is taken to be smaller than the crystallographic value; it seems justified as the ligands are H_2O and not O^{2-}. For example, in the case of PrES, $\theta = 47 \cdot 6°$ gives

$$\phi_1 < \sigma < \pi < \delta < \phi_2; \tag{7}$$

whereas $\theta = 45 \cdot 5°$ yields

$$\phi_1 < \sigma < \delta < \pi < \phi_2. \tag{8}$$

Evidently, the latter is in complete harmony with the order given in (5) for the light rare earth ethyl sulphates. In the case of ErES, as a representative of the heavy compounds, $\theta = 45 \cdot 2°$ gives the order quite different from that obtained experimentally; $\theta \lesssim 44°$ provides a better correspondence. This, thus, implies that the rare earth ions in ethyl sulphates see a field corresponding to polar angles smaller than those obtained through the x-ray work. It may be remarked that in the case of rare earth hydroxides also the agreement between theoretical and experimental one-electron energy levels is improved if θ is taken to be smaller than that obtained from x-ray data (Vishwamittar and Puri 1973). The energy levels corresponding to the crystallographic as well as smaller angles are listed in table 8. Kuse and Jørgensen (1967) have already commented on the degree of confidence in the order of one-electron orbital energies obtained with this model.

Table 8. Theoretical one-electron orbital energies for five *f*-levels (in units of corresponding σ^* for PrES, ErES and YES host lattices.

	PrES		ErES		YES	
	$\theta=47\cdot6°$	$\theta=45\cdot5°$	$\theta=45\cdot2°$	$\theta=44°$	$\theta=45\cdot5°$	$\theta=44°$
$\phi_1 (a_2')$	$-12\cdot8$	$-12\cdot8$	$-12\cdot2$	$-12\cdot2$	$-13\cdot0$	$-13\cdot0$
$\sigma (a_2'')$	$-8\cdot7$	$-10\cdot3$	$-10\cdot1$	$-10\cdot8$	$-10\cdot5$	$-11\cdot5$
$\phi_2 (a_1')$	$7\cdot3$	$6\cdot0$	$6\cdot1$	$5\cdot4$	$5\cdot9$	$5\cdot0$
$\delta (e'')$	$4\cdot6$	$3\cdot6$	$3\cdot0$	$2\cdot4$	$3\cdot7$	$2\cdot8$
$\pi (e')$	$2\cdot5$	$5\cdot0$	$5\cdot1$	$6\cdot4$	$5\cdot1$	$6\cdot9$

Table 9. Estimated values of antibonding energy parameters σ^* (in cm^{-1})† and ionicity for various rare earth ethyl sulphates.

	PrES	NdES	TbES	DyES	HoES	ErES	TmES	YbES
σ^*	25·8	23·0	20·0	20·2	18·4	17·8	18·4	16·9
Ionicity	0·52	0·51	0·49	0·49	0·49	0·49	0·48	0·48

†σ^* refers to $R_1 = 2\cdot65$ Å for the first half of the rare earth series and to $R_1 = 2\cdot52$ Å for the second half.

The experimental one-electron orbital energies are used to parametrize σ^* with the theoretical values for θ less than the crystallographic angle. The calculations for PrES and ErES are taken as representative of the two halves of the series, and the estimated σ^* are tabulated in table 9. The σ^* in the light ethyl sulphates ($\simeq 24$ cm^{-1}) is larger than that for the heavy compounds ($\simeq 18$ cm^{-1}) and it is in accordance with the fact that the overlap integrals for the former are larger than those for the latter (Burns and Axe 1967). Decrease in the value of σ^* along the series may be a result of the interelectron coulomb interactions. The present magnitudes of σ^* differ from those of Jørgensen *et al* because of different method adopted for taking care of $R_2 \neq R_1$. The situation about the evaluation of σ^* from first principles is not changed much even if better estimates of the overlap integrals are used and hybridisation of O in H_2O ligands is considered rather than simple O^{2-} ligands for the evaluation of non-diagonal elements. However, σ^* for the light rare earth ethyl sulphates ($\simeq 290$ cm^{-1}) is found to be more than that for the heavy compounds ($\simeq 150$ cm^{-1}) in conformity with the experimental findings. This difference of the calculations from experiments is not surprising in view of large π-bonding effects in these compounds (Borchi *et al* 1969) and other approximations involved.

Sanderson (1967) has shown that dependable comparison of ionicity in different compounds can be sought through the calculations employing compactness scale of electronegativity and the principle of its equalisation. The results of such calculations for various rare earth ethyl sulphates are catalogued in table 9. Evidently, these magnitudes for the light ethyl sulphates differ from those for the heavy ones and are almost constant for a group. The ionicities of LaES and YES are 0·52 and 0·46 respectively, so that the bond polarities corresponding to these two diluents are different, which is supported by the difference in the *g*-values of an ion in these host lattices.

Recently, Newman and co-workers (see Newman 1971) have shown that the superposition model, based on the validity of local field and superposition approximations, provides a good intermediary between the experimental data and *ab initio* calculations, as it does not assume the dominance of σ- bonding and deals directly with the CF parameters. In this model, the CF parameters for D_{3h} systems are connected with the positive intrinsic parameters $\bar{A}_n(R_1)$ through the relation:

$$A_n^m \langle r^n \rangle = [K_n^m + K_n'^m (R_1/R_2)^{t_n}] \, \bar{A}_n (R_1)$$

$$= k_n^m \bar{A}_n (R_1). \tag{9}$$

Here K_n^m and $K_n'^m$ are coordination factors for the in-plane and prismatic oxygens respectively, k_n^m being effective coordination factors and t_n the power law coefficients. Generally, for oxygen ligands $t_2 \simeq 7$, $t_4 \simeq t_6 \simeq 10$ (Newman 1971); of course, the ligands are practically H_2O rather than O^{2-}. Using these values in conjunction with the data of table 1 for ErES, as a typical example, one gets

$$k_2^0 = 0\cdot 76, \quad k_4^0 = -3\cdot 40, \quad k_6^0 = -2\cdot 49, \quad \text{and} \quad k_6^6 = 31\cdot 87 \tag{10}$$

Evidently, the signs of CF parameters are correctly reproduced. Also these give $\rho_6^{60} = k_6^6/k_6^0 = -12\cdot 8$; ρ_6^{60} is expected to be identical for all the models as it is basically a function of coordination angles (Bradbury and Newman 1967) if R_2 is not much different from R_1. Since the bonding angles (and the ligand distances) change from one ethyl sulphate to another, the variation in the semi-empirical values of ρ_6^{60} is justified. However, in view of uncertainty in the validity of local field approximation for these compounds, further discussion may not be of much significance.

5. Concluding remarks

The available CF parameters for ErES and TmES are used to calculate various physical quantities, which are, in turn, compared with the corresponding measurements and it is shown that one of these sets can safely be taken as optimal. These phenomenological parameters along with the ones for other ethyl sulphates are discussed in the light of electrostatic, angular overlap and superposition models. The one-electron antibonding parameter σ^* and ionicity turn out to be different for light and heavy compounds and almost same in either half of the series.

References

Axe J D and Burns G 1966 *Phys. Rev.* **152** 331
Baker J M 1971 *J. Phys. C* **4** 1631
Barnes R G, Mössbauer R L, Kankeleit E and Poindexter J M 1964 *Phys. Rev.* **136** A175
Bleaney B and Scovil H E D 1951 *Proc. Phys. Soc.* A **64** 204
Bogle G S, Duffus H J and Scovil H E D 1952 *Proc. Phys. Soc.* A **65** 760
Borchi E, Gennaro S D and Mancini M 1969 *Lett. Nuovo Cimento* **1** 92

Bradbury M I and Newman D J 1967 *Chem. Phys. Lett.* **1** 44
Burns G 1965 *J. Chem. Phys.* **42** 377
Burns G and Axe J D 1967 *Optical properties of ions in crystals*, eds H M Crosswhite and) H W Moos (New York: Interscience) 53
Chachra S P, Neogy D and Neogy A 1974 *Physica* **71** 630
Cohen R L 1964 *Phys. Rev.* **134** A 94
Cooke A H, Lazenby R and Leask M J M 1965 *Proc. Phys. Soc.* **85** 767
Cooke A H, McKim F R, Meyer H and Wolf W P 1957 *Phil. Mag.* **2** 928
Daniels J M 1953 *Proc. Phys. Soc.* A **64** 673
Dieke G H 1968 *Spectra and energy levels of rare earth ions in crystals* (New York: Interscience)
Edmonds D T and Lindop A J 1966 *Proc. Phys. Soc.* **87** 721
Ellis M M and Newman D J 1969 *J. Chem. Phys.* **49** 4037
Erath E H 1961 *J. Chem. Phys.* **34** 1985
Erath E H 1963 *J. Chem. Phys.* **38** 1787
Fitzwater D R and Rundle R E 1959 *Z. Kristallogr.* **112** 362
Gerstein B C, Jennings L D and Spedding F H 1962 *a J. Chem. Phys.* **37** 1496
Gerstein B C, Penney C J and Spedding F H 1962 *b J. Chem. Phys.* **37** 2610
Gruber J B and Conway J G 1960 *J. Chem. Phys.* **32** 1531
Gupta R P, Rao B K and Sen S K 1971 *Phys. Rev.* A3 545
Hill J C and Wheeler R G 1966 *Phys. Rev.* **152** 482
Hüfner S 1962 *Z. Phys.* **169** 417
Johnsen U 1958 *Z. Phys.* **152** 454
Jørgensen C K 1971 *Modern aspects of ligand field theory* (Amsterdam: North Holland)
Jørgensen C K, Pappalardo R and Smidtke H-H 1963 *J. Chem. Phys.* **39** 1422
Ketelaar J A A 1937 *Physica* **4** 619
Krupke W F and Gruber J B 1965 *Phys. Rev.* **139** A2008
Kuse D and Jørgensen C K 1967 *Chem. Phys. Lett.* **1** 314
Larson G H and Jeffries C D 1966 *Phys. Rev.* **141** 461
Low W 1960 *Paramagnetic resonance in solids* (New York: Academic Press)
Mookherji T 1964 *Indian J. Phys.* **38** 587
Newman D J 1971 *Adv. Phys.* **20** 197
Sanderson R T 1967 *Inorganic chemistry* (New York: Van Nostrand-Reinhold Co.)
Schäffer C E and Jørgensen C K 1965 *Mol. Phys.* **9** 401
Syme R W G, Haas W J and Spedding F H 1968 *Chem. Phys. Lett.* **2** 132
Vishwamittar 1973 *Ph.D. Thesis* (Roorkee: University of Roorkee)
Vishwamittar and Puri S P 1973 *Chem. Phys. Lett.* **23** 510
Vishwamittar and Puri S P 1974 *a Phys. Rev.* B 9 4673
Vishwamittar and Puri S P 1974 *b Chem. Phys. Lett.* **28** 582
Vishwamittar and Puri S P 1975 *Indian J. Pure Appl. Phys.* (to appear)
Vishwamittar, Taneja S P and Puri S P 1972 *J. Phys. Chem. Solids* **33** 813
Wheeler R G, Reames F M and Wachtel E J 1968 *J. Appl. Phys.* **39** 915
Wong E Y and Richman I 1961 *J. Chem. Phys.* **34** 1182
Wong S, Dembinski S T and Opechowski W 1969 *Physica* **42** 565