

CaF₂ and MgO. In view of the above, the increase in the dispersion of C with increasing temperature in KCl, KBr, KI and NaCl is probably due to large variations in the oscillator strengths and the absorption frequencies of the optical electrons with temperature.

As the slopes of the dispersion curves for potassium halides (Fig. 1) appear to increase with increasing temperature, the λ_{rev} , the wavelengths corresponding to the reversal³⁻⁵ in the sign of C, of these crystals may change with temperature. As the absorption wavelengths λ_a of these crystals on the longer wavelength side, are found² to shift further to longer wavelengths with the increase of temperature, the λ_{rev} also may be expected to shift to longer wavelengths.

Physics Department, K. V. KRISHNA RAO.
Osmania University, V. G. KRISHNA MURTY.
Hyderabad-500007,
December 30, 1972.

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ON THE FORCE FIELD OF PF₅

THE trigonal bipyramidal molecule belongs to D_{3h} symmetry species and has vibrational representation $\Gamma = 2A_1' + 2A_2'' + 3E' + E''$. Consequently, an analysis using general valence force field would involve 13 force constants. As experimental data we have 8 vibrational frequencies¹, 2 coriolis coupling constants¹ and 4 vibrational amplitudes².

The first attempt to work out a force field capable of reproducing these experimental data was made by Levin recently¹. In solving the E' species force field he assumed one of the F_{ij} elements (F₅₅) to be zero. The force field thus obtained by him led to agreement of the frequencies within 2 cm⁻¹ of the experimental values. The ξ values calculated by him were fit within 0.06 and 0.05 for ξ_5 and

ξ_6 respectively. The complete force field led to satisfactory agreement with the vibrational amplitudes.

An entirely different set of force field for the E' species, fitting the coriolis and frequency data, was soon reported by Lockett *et al.*³. He first analysed the possible force fields by setting F₅₇ in the vicinity of zero. He has given two sets of force fields by arbitrarily fixing F₅₇ = -0.18 md. One of the sets resembles that of Levin and the other is drastically different. However, on replacement of Levin's E' force field, with this later set, we note marked deviation from the experimental values in the vibrational amplitudes.

Here we have made a fresh approach to the problem of fixing the E' force field, fitting all the experimental data in a better way and avoiding constraints such as one of the F_{ij} = 0.

The symmetry coordinates and the potential function are the same as those used by Levin¹. The force field obtained by us using the usual FG matrix method⁴ is given in Table I along with the sets reported by Levin¹ and Lockett³. The calculated and experimental values of coriolis coupling constants and vibrational amplitudes are included in Table II. The agreement obtained for our values are excellent, except the slight discrepancy in the value of l (F_{eq}...F_{eq}).

TABLE I
The E' force field of PF₅

F _{ij}	Present set	Set by Levin	Set by Lockett
F ₅₅ md/A	.. 4.838	4.19 ± 0.19	4.5
F ₆₆ md/A	.. 0.299	0.28 ± 0.03	1.7
F ₇₇ md/A	.. 3.443	4.19 ± 0.08	2.47
F ₅₆ md	.. -0.049	0	0.91
F ₅₇ md	.. -0.014	0.18 ± 0.04	-0.18
F ₆₇ md/A	.. -0.380	0.35 ± 0.11	1.64

TABLE II
Coriolis and vibrational amplitude data
experimental and calculated values

	Experimental value	Present set	Set by Levin	Set by Lockett
ξ_5	0.77 ± 0.05	0.77	0.83	..
ξ_6	0.31 ± 0.05	0.31	0.31	..
l(P-F _{eq})	.. 0.041 ± 0.002	0.041	0.042	0.045
l(P-F _{ax})	.. 0.043 ± 0.002	0.043	0.044	0.043
l(F _{ax} ...F _{eq})	0.059 ± 0.003	0.061	0.060	0.088
l(F _{eq} ...F _{eq})	0.081 ± 0.008	0.094	0.094	0.098

The present result is interesting, since the diagonal terms are only a slightly modified form of the diagonal force field reported by Levin¹

($F_{55} = 4.94$ md. A, $F_{66} = 0.22$ md. A, $F_{77} = 3.9$ md. A, $F_{56} = F_{57} = F_{67} = 0$) fitting the frequency data alone. Moreover the interaction force constants $F_{56} = -0.049$ md. and $F_{57} = -0.014$ md. are quite small. The value of $F_{67} = -0.38$ md. A compares well with that of Levin¹. The P-F equatorial stretching force constant $f_e = 5.712$ md/A is in excellent agreement with the value⁵ of $f_e = 5.70$ md/A for the P-F equatorial bond in PF_3Cl_2 . The axial bending force constant $f_r = 4.344$ md. A works out to be 76% less than the equatorial force constant. This is in very good agreement with the general result arrived at by Selig *et al.*⁶ through orbital valence force field studies in penta fluorides that, the axial stretching force constant is approximately 80% less than the equatorial stretching force constant.

Thus one arrives at an interesting situation with two different sets of force fields—the present one and the one suggested by Levin—both capable of reproducing all the experimental data satisfactorily. Though the present set may be preferred at the first sight due to the smallness of the interaction force constants and better reproduction of coriolis coupling constants (which are very sensitive to the variation in force field), one cannot discard completely the set suggested by Levin. The multiplicity of such solutions fitting large number of experimental data has been observed⁷ before in molecules like NF_3 , PF_3 , BF_3 , RuO_4 , etc. The authors⁷ have reported that vibrational amplitudes for bonded interatomic distances serve as criteria to fix one of the sets uniquely in the case of 2×2 degenerate vibrational species. However, in the case of 3×3 degenerate vibrational species this becomes impossible and a unique fixing of the force field demands more additional data than these.

Dept. of Physics, T. R. ANANTHAKRISHNAN,
Univ. of Kerala, G. ARULDHAS,
Kariavattom.
Trivandrum, January 27, 1973.

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X-RAY DETERMINATION OF THE DEBYE TEMPERATURE OF EUROPIUM FLUORIDE

THE purpose of this communication is to report the results of an X-ray determination of the Debye temperature of europium fluoride (EuF_2). The general procedure is the same as described in an earlier communication¹ from this laboratory.

X-ray powder diffractograms were obtained with the help of a Philips PW 1051 diffractometer using filtered copper radiation and an argon-filled G. M. counter. The integrated intensities were corrected for thermal diffuse scattering². Theoretical intensities for a static lattice were calculated from the relation:

$$I_0 = \text{constant (L.P.) } \sum F^2$$

where the various terms have the same significance as discussed earlier¹. Europium fluoride has the fluorite structure. As such, the structure factors have the forms³:

$$\begin{aligned} F &= 4f_{Eu} & \text{for } h+k+l &= 4n \pm 1 \\ F &= 4(f_{Eu} + 2f_F) & \text{for } h+k+l &= 4n \\ F &= 4(f_{Eu} - 2f_F) & \text{for } h+k+l &= 4n + 2. \end{aligned}$$

In the evaluation of the structure factors, Dirac-Slater atomic scattering factors⁴ corrected for anomalous dispersion⁵ were used for Eu^{+2} and F^- . In view of the limited number of reflections available, no attempt was made to obtain the B-factor separately for the three types of reflections. Instead, the mean B-factor was obtained by plotting $\log(I_0/I_c)$ against $(\sin \theta/\lambda)^2$. This plot is shown in Fig. 1. The slope of the linear plot was obtained

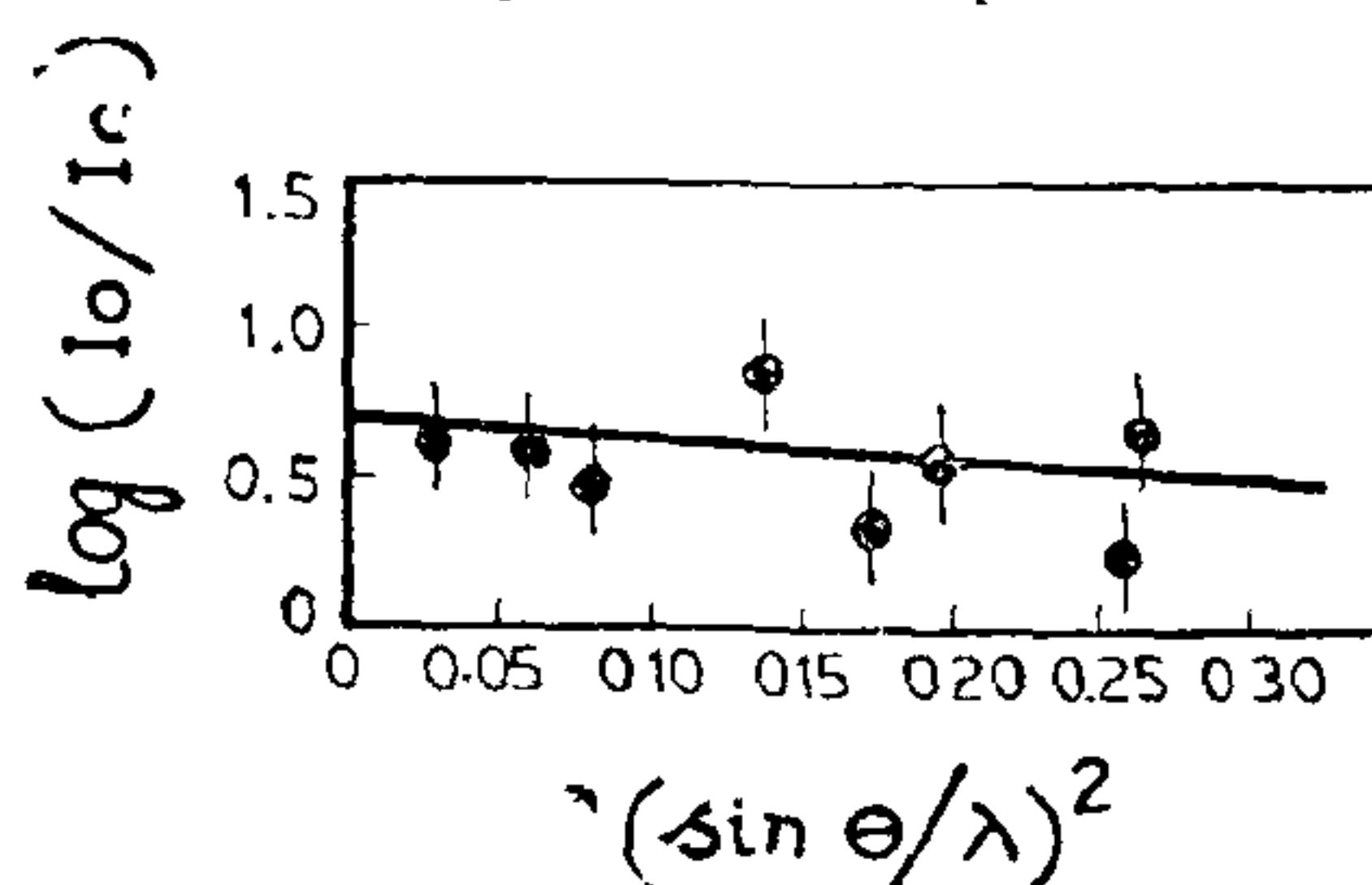


FIG. 1. Plot of $\log(I_0/I_c)$ against $(\sin \theta/\lambda)^2$.

by a least squares procedure. From the value of B, the Debye temperature was calculated with the help of tables compiled by Benson and Gill⁶.

A value of $431 \pm 28^\circ$ K is obtained for the Debye temperature of europium fluoride at room temperature. This value is much higher than the value 329° K obtained by Lauer *et al.*⁷ from elastic constants. It must be noted that exact agreement is not to be expected between Debye tempera-