

ON THE USE OF THE MOLLWO-IVEY RELATIONSHIP

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Departures from the Mollwo-Ivey relationship are expected to be pronounced in crystals containing large cations.

The F and M centre transition energies in alkali halides are given to a first approximation by

$$E = \alpha a^{-n} \quad (1)$$

where a is the lattice spacing and α and n are constants which depend on the type of colour centre. This (Mollwo-Ivey) relationship [1] is an empirical rule which is often useful for interpolation. It is not a general rule and does not describe, for example, F centre emission in alkali halides [2]. It is not a reliable substitute for experimental and theoretical investigation and recently it has been used in a way which is not valid [3]. We wish to stress the limits within which (1) may be used and to show that its misuse led to an incorrect assignment of the F band in BaF_2 .

The F band peak in BaF_2 has recently been experimentally located at 611 nm [4]. The sequence of investigations which led to this identification was as follows:

1) The $2S$ ground state of the F centre in additively coloured CaF_2 , SrF_2 and BaF_2 was thoroughly explored by e.p.r. and ENDOR methods [5].

2) The ENDOR parameters were calculated [5] using point ion wavefunctions [6] and compared with experiment [5].

3) The F band peaks were identified and the spin-orbit coupling constant in the $2P$ state of the F centre was measured in additively coloured CaF_2 , SrF_2 and BaF_2 using the large temperature dependent magneto-optical effect characteristic of F centres. The crystals were first

checked for F centre content by e.p.r. methods.

4) The spin-orbit coupling constant in the excited $2P$ state of the F centres was calculated [4] using point ion wave functions [6] and compared with experiment [4].

Using (1) and the F band peak positions in CaF_2 and SrF_2 it was estimated [4] that the F band peak would occur at 513 nm in BaF_2 ; this value may be compared with the calculated point ion value of 475 nm [6]. However, careful investigation showed that no absorption band peak occurs in the region of 500 nm in additively coloured BaF_2 crystals known from e.p.r. measurements to contain $\sim 10^{18}$ F centres/cm³ and it was pointed out [4] that, on the basis of experiment, the Mollwo-Ivey relation does not apply to BaF_2 .

Theoretically, the transition energy will depend on the lattice parameter alone only if the potential in which the colour centre electrons move scales with the lattice parameter, i.e. $V = V(r/a)$. The only simple potential of this sort is the point ion potential [7]. If, in addition, the electronic wave-function scales with the lattice parameter, $\psi = \psi(r/a)$, it may then be readily shown [8] that the coefficient in (1) lies in the range $1 \leq n \leq 2$. The applicability of (1) is in doubt when n is much greater than 2.

Detailed quantitative estimates of corrections to the point ion model have been made recently for F centres in alkali halides and alkaline earth fluorides [9]. This work showed that deviations from (1) occurred because the detailed electronic structure of the ions cannot be ignored. These "ion-size" effects are particularly striking when the nearest neighbour cations are large, as in

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CsF and BaF₂. In such cases the potential is not a function just of lattice parameter and the Mollwo-Ivey rule does not apply [9]. The importance of ion size effects should show up in deviations from predictions of the point ion model, increasing along the sequence CaF₂, SrF₂, BaF₂. Precisely this trend is shown by the transition energy [4], the h.f.s. constants in the ²S ground state [5] and the spin-orbit coupling constant in the ²P excited state of the F centre [4].

The F band peak in BaO has been found experimentally [10] to be at 620 nm. This assignment has also been questioned [3] on the basis of (1). However, the objections that apply to the use of (1) in BaF₂ are expected to apply also in BaO.

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DEUTERON SPIN-LATTICE RELAXATION AND PHASE TRANSITIONS IN GeD₄

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Deuteron spin-lattice relaxation time (T_1) measurements in polycrystalline GeD₄ show discontinuities at the first-order phase transition points at 75.5 and 77.8°K, and a change in the temperature dependence of T_1 at the λ -point at 67.7°K. A deuteron quadrupole coupling constant of 82 kHz was obtained.

The spin-lattice relaxation time T_1 of deuterons in solid GeD₄ was measured in the temperature range 40 to 110°K at 6 MHz, using NMR pulse methods [1]. The results are shown in fig. 1. The sample was prepared by reduction of GeCl₄ by LiAlD₄ in ethereal solution [2], and it was purified of oxygen impurities by the mischmetal getter technique [3].

The principal relaxing mechanism for deuterium is the electric quadrupole interaction with the molecular field gradient. The temperature dependence of T_1 suggests that this relaxation takes place through the reorientational motion of the molecules. Thus the conventional formula [4]

$$\frac{1}{T_1} = C \left[\frac{\tau_c}{1 + (\omega_0 \tau_c)^2} + \frac{4\tau_c}{1 + (2\omega_0 \tau_c)^2} \right]$$

was used to interpret the results. Here $C = \frac{3}{10} \pi^2 (1 + \frac{1}{3} \eta^2) (e^2 q Q / \hbar)^2$, and τ_c is the correlation time for the reorientation of the field gra-

dient. Assuming that C does not change appreciably in the temperature range of interest, and assuming a thermally activated Arrhenius process for the random molecular reorientations, $\tau_c = \tau_0 \exp(E_a/kT)$, where E_a is the apparent activation energy for the molecular motion, the temperature dependence of τ_c was deduced from the experimental data, and is shown in fig. 1.

Calorimetric investigations indicate that GeH₄ has four solid state phases in the temperature range from about 12°K to the melting point [5]. The heat capacity curve is discontinuous at 73.2 and 76.6°K, indicating first-order phase transitions. The low temperature transition at 62.9°K occurs over a range of a few degrees and shows a λ -anomaly suggesting a higher-order transition. No structural investigation has been found for either GeH₄ or GeD₄ in the available literature.

In the present data, discontinuities in T_1 versus T occur at temperatures 77.8 and 75.5°K, and a pronounced change in the temperature de-