

## VARIABLE ANION POLARISABILITY IN IONIC CRYSTALS

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THE concept of individual polarisabilities of ions has been found to be very useful in the description of many solid state properties. Apart from its widespread use in systematising optical data, it is also used in the study of interionic potentials in crystals where the van der Waals' interaction is usually written in terms of the polarisabilities of the interacting ions. Although the concept of individual ionic polarisability has come under question in recent times<sup>1</sup>, it is still freely used in semi-empirical theories of crystal physics and chemistry.

Tessman *et al.*<sup>2</sup> tabulated individual polarisabilities for many ions. Their values, which have been extensively used by later workers, were obtained under the assumptions that the polarisability of an ion is independent of crystal structure, temperature, pressure, etc. and that the individual ionic polarisabilities in a crystal are simply additive. Calculations along similar lines have been made by others<sup>3-5</sup> on various families of crystals. However, Tessman *et al.*<sup>2</sup> (hereafter referred to as TKS) noted that their best fit alkali and halogen ion polarisabilities did not reproduce the experimental polarisabilities very well when carried over to other crystals (table 2). Ruffa<sup>6</sup> suggested on theoretical grounds that both cation and anion polarisabilities should depend on the crystal environment. An interaction law<sup>3</sup>, and a  $r_{\pm}^3$  relation<sup>7</sup> (where  $r_{\pm}$  are the radii of the cation and anion) were some of the schemes proposed by later workers. Recently, Mahan<sup>8</sup> reported an *a priori* calculation of the polarisabilities of many ions in simple crystals by taking the crystalline environment about an ion as a spherically-averaged sum of pseudopotentials. He found that the anion polarisability is rather strongly dependent on the interionic distance whereas the cation polarisability was essentially constant. His result is understandable in terms of the compressible ion theory of Narayan and Ramaseshan<sup>9</sup> where the anions are much more compressible than the cations and thus should have a more strongly variable polarisability. Mahan<sup>8</sup> argues that the variable cation polarisability obtained by Ruffa<sup>6</sup> arises because Ruffa's theory is valid only when the interionic distance  $r \rightarrow \infty$ .

In the following discussion we use an empirical relation to re-estimate the polarisabilities of ions in the alkali halide and alkaline earth chalcogenide crystals. We assume a constant polarisability for cations, in line with the results of Mahan<sup>8</sup>, while for the anions

we propose a specific dependence on the interionic distance. We fit only two extra parameters (one for the halogen ions and one for the chalcogen ions) over and above the TKS formulation, but obtain significantly better agreement with the experimental data. Our modification would therefore appear to be well motivated.

The electronic polarisability per molecule  $\alpha_m$  is related to the high frequency dielectric constant  $\epsilon$  through the Clausius-Mossotti relation<sup>10</sup>

$$\frac{\epsilon - 1}{\epsilon + 2} \frac{3 V_m}{4 \pi} = \alpha_m \quad (1)$$

where  $V_m$  is the volume per molecule. We propose that  $\alpha_m$  can be written in terms of the polarisabilities of the constituent ions through the relation

$$\alpha_m = \alpha_{cat} + \alpha_{an} (r/3)^n \quad (2)$$

where  $r$  (in Å) is the interionic distance in the crystal and  $\alpha_{cat}$  and  $\alpha_{an}$  are constant polarisabilities associated with the two ions in the crystal. The new feature in our relation is the parameter  $n$  which is taken to be constant for a set of anions; the case  $n=0$  corresponds to the simple additive law of TKS. The normalisation of  $r$  by (the arbitrarily chosen value of)  $3 \text{ Å}$  is clearly not an extra parameter since it can always be absorbed into the definition of  $\alpha_{an}$ . We note that the relation (2) may be expected to be valid only over the experimentally observed range of lattice constants. It would be unrealistic to extrapolate it to free ions or to a highly compressed crystal.

The various parameters in a given family of crystals ( $\alpha_{cat}$ 's,  $\alpha_{an}$ 's and  $n$ ) were optimised by minimising

$$S = 100 \sqrt{\frac{1}{N} \sum_m \left( \frac{\alpha_m - \alpha_{m \text{ expi}}}{\alpha_{m \text{ expi}}} \right)^2} \quad (3)$$

where  $\alpha_{m \text{ expi}}$  is derived from the measured room temperature  $\epsilon$  through relation (1) and  $\alpha_m$  is obtained

TABLE 1

Estimated ionic polarisabilities corresponding to the TKS<sup>2</sup> approach ( $n=0$ ) and our approach (optimised  $n$ )

| Ion             | Polarisability (in Å <sup>3</sup> ) |          | Ion              | Polarisability (in Å <sup>3</sup> ) |         |
|-----------------|-------------------------------------|----------|------------------|-------------------------------------|---------|
|                 | $n=0$                               | $n=0.26$ |                  | $n=0$                               | $n=0.9$ |
| Li <sup>+</sup> | 0.029                               | 0.029    | Be <sup>2+</sup> | 0.0                                 | 0.0     |
| Na <sup>+</sup> | 0.281                               | 0.242    | Mg <sup>2+</sup> | 0.063                               | 0.063   |
| K <sup>+</sup>  | 1.147                               | 1.053    | Ca <sup>2+</sup> | 1.140                               | 0.889   |
| Rb <sup>+</sup> | 1.714                               | 1.593    | Sr <sup>2+</sup> | 1.795                               | 1.369   |
| Cs <sup>+</sup> | 2.793                               | 2.617    | Ba <sup>2+</sup> | 3.497                               | 2.826   |
| F <sup>-</sup>  | 0.877                               | 0.984    | O <sup>2-</sup>  | 1.695                               | 2.377   |
| Cl <sup>-</sup> | 3.013                               | 3.097    | S <sup>2-</sup>  | 4.761                               | 5.267   |
| Br <sup>-</sup> | 4.189                               | 4.215    | Se <sup>2-</sup> | 6.149                               | 6.504   |
| I <sup>-</sup>  | 6.288                               | 6.163    | Te <sup>2-</sup> | 8.570                               | 8.317   |
| $S_{\min}$      | 1.27%                               | 0.58%    |                  | 2.63%                               | 1.84%   |

from (2). The summation is over the  $N$  crystals in a given family. For each value of  $n$  we optimised the various values of  $\alpha_{\text{cat}}$  and  $\alpha_{\text{an}}$  and computed  $S_{\min}(n)$ . By varying  $n$  we could then find its best value. For well known reasons<sup>2,4</sup>, it was necessary to fix the  $\alpha$  of one of the ions in each family of crystals; we took the polarisabilities of Li<sup>+</sup> and Mg<sup>2+</sup> to be 0.029 Å<sup>3</sup> and 0.063 Å<sup>3</sup> respectively<sup>2,3</sup>. Since these are very small quantities, any fractional errors are likely to be unimportant.

The dielectric constants of the alkali halides were taken from Lowndes and Martin<sup>11</sup> and the lattice

constants from Wyckoff<sup>12</sup>. The results are given in table 1. The value of  $S_{\min}(n)$  decreased from about 1.3% at  $n=0$  to 0.58% at  $n=0.26$ . This large reduction for the addition of a single parameter  $n$  clearly shows that the effect we are trying to model through equation (2) really does exist. Table 1 also gives the results on the alkaline earth chalcogenides. The molecular polarisabilities were taken from Van Vechten<sup>13</sup> except for the barium chalcogenides for which data from TKS were used. In this case  $S_{\min}(n)$  decreased from 2.6% at  $n=0$  to 1.8% at  $n=0.9$ , again confirming the dependence of anion polarisability on

TABLE 2

Calculated molecular polarisabilities for a few crystals using the parameters of table 1

| Crystal           | Inter-ionic distance<br>$r$ (Å) | $\alpha_{m,\text{exp}}$ (Å <sup>3</sup> ) | $\alpha_{m,\text{calc}}$ (Å <sup>3</sup> ) |            |          |         |
|-------------------|---------------------------------|---|--|------------|----------|---------|
|                   |                                 |   | $n=0$                                      | error %    | Best $n$ | error % |
| MgF <sub>2</sub>  | 2.000                           | 1.800                                     | 1.817                                      | 0.94       | 1.834    | 1.89    |
| MgCl <sub>2</sub> | 2.540                           | 6.040                                     | 6.089                                      | 0.81       | 5.995    | -0.75   |
| CaF <sub>2</sub>  | 2.366                           | 2.534                                     | 2.894                                      | 14.2       | 2.738    | 8.05    |
| SrF <sub>2</sub>  | 2.511                           | 3.066                                     | 3.549                                      | 15.7       | 3.248    | 5.94    |
| SrCl <sub>2</sub> | 3.021                           | 7.222                                     | 7.821                                      | 8.29       | 7.574    | 4.88    |
| BaF <sub>2</sub>  | 2.685                           | 4.002                                     | 5.251                                      | 31.2       | 4.738    | 18.4    |
| BaCl <sub>2</sub> | 3.180                           | 8.930                                     | 9.523                                      | 6.64       | 9.115    | 2.07    |
| KMgF <sub>3</sub> | 2.420                           | 3.933                                     | 3.841                                      | -2.34      | 3.908    | -0.65   |
| (at 300K)         | (average)                       |   |  |            |          |         |
| Li <sub>2</sub> O | 2.000                           | 2.150                                     | 1.753                                      | -18.5      | 1.679    | -21.9   |
| BeO               | 1.660                           | 1.320                                     | 1.695                                      | 28.4       | 1.395    | 5.72    |
| BeSe              | 2.230                           | 5.520                                     | 6.149                                      | 11.4       | 4.980    | -9.78   |
|                   |                                 |   |  | rms error  | 16.0%    | 9.9%    |
|                   |                                 |   |  | mean error | 8.8%     | 1.3%    |

interionic distance. The higher value of  $n$  shows that the effect is stronger in the more compressible chalcogen ions compared to the halogens.

In order to make an independent test of our approach, we have calculated the molecular polarisabilities of a few crystals whose data were not used in our parameter fitting. The results are given in table 2. The present approach is clearly an improvement over that of TKS ( $n=0$ ). Apart from the reduced overall rms error, we notice that in 9 out of 11 cases our predicted values are better than the  $n=0$  values.

Narayan<sup>14</sup> has shown that van der Waals forces play an important role in determining the crystal structure of ionic crystals. Since an important input in such calculations is the ionic polarisability, the present results could be important. For example, in  $\text{Rb}_2\text{O}$  ( $r=2.92 \text{ \AA}$ ), the simple TKS ( $n=0$ ) approach gives a dipole-dipole interaction coefficient between anions ( $\text{C}_{--}$ ) of  $55 \times 10^{-60} \text{ ergs cm}^6$  while our results ( $n=0.9$ ) imply  $\text{C}_{--} = 88 \times 10^{-60} \text{ ergs cm}^6$  which is 60% larger. Also, current indications<sup>15</sup> are that the van der Waals interaction is progressively quenched at shorter interionic distances. The present approach could be a good model for this effect.

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## ANNOUNCEMENT

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