v_m. In the high temperature approximation, for which $\bar{E}_\varphi = KT$, Chipman & Paskin (1959a) have considered the averaging of the wave velocities, reaching the conclusions that Θ_D is usually adequate (Chipman & Paskin, 1959b). At intermediate temperatures the calculation becomes very involved. For very low temperatures it is seen from Fig. 1 that, except for very narrow peaks, the zero point energy terms dominate the correction factor σ, e.g. for $Y > 0.03$ the difference between Z for $\Theta/T = 1000$ and Z for $\Theta/T = 100$ becomes small. Therefore, in order to obtain a low temperature estimate for v_m, the TDS at 0°K was calculated for the general case that $v_l = p v_t$. The mean velocities which would give the same TDS, are as follows, (1) in the immediate vicinity of the centre of the Brillouin zone the mean velocity is given by $v_m^{-1} \simeq p v_t^{-1}$, (2) a quarter of the way towards the zone boundary $v_m^{-1} \simeq [1 + 0.838(p-1)]v_t^{-1}$, (3) half way towards the zone boundary $v_m^{-1} \simeq [1 + 0.666(p-1)]v_t^{-1}$ and (4) near the zone boundary $v_m^{-1} \simeq v_t^{-1}$. Because measurements of the integrated intensities are usually confined to the vicinity of the peak, Θ_D which for $p = 2$ is equivalent to $v_m^{-1} = 1.78 v_t^{-1}$, or Θ_M which for $p = 2$ is equivalent to $v_m^{-1} = 1.67 v_e^{-1}$ could both be approximately applicable.

A more important aspect of selecting a Θ value is the inapplicability of the Debye frequency distribution which has been assumed throughout. A real frequency distribution can only give equivalent Θ_M's and Θ_D's which can differ considerably at low temperatures, Θ_M, in general, varying less with temperature than Θ_D. It can be expected that Θ_M is the better estimate to be used in equation (3) because the averaging over the Brillouin zone for TDS is more like that used for the Debye–Waller factor than that for the specific heat. Therefore, Θ_M should be preferred when both Θ_M and Θ_D are known.

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Bond Type in the Dioxides of Titanium, Germanium and Tin

BY M. F. C. LADD

Department of Chemical Physics, University of Surrey, Guildford, Surrey, England

The crystal energies of TiO_2, GeO_2 and SnO_2 have been calculated by both the Born–Haber cycle and Born–Mayer equations. The agreement between the results suggests strongly ionic character in the M–O bonds.

Calculations by Baur (1961) and by Kingsbury (1968) have led to the suggestion of appreciable covalent character of the M–O bond in the dioxides of Ti, Ge and Sn, because the calculated crystal energies have been found to be about 25% larger (more positive) than the corresponding Born–Haber (thermodynamic) values. The following calculations, however, based upon the Born–Mayer electrostatic model, lead to results in good agreement with the thermodynamic values.

For present purposes, the Born–Haber cycle may be cast into the equation:

$$\Delta U = \Delta H_f(MO_2, \text{cryst})$$
$$- I_M - S_M - D(O_2) - 2E(O^{2-}) + 3RT. \quad (1)$$

The enthalpies of formation and of sublimation have been taken from Kubaschewski, Evans & Alcock (1967), the ionization potentials from Moore (1949, 1952, 1958), the dissociation energy from Rossini, Wagman, Evans, Levine & Jaffe (1952) and the electron affinity from Ladd & Lee (1960). The results are listed in Table 1.

The simple Born–Mayer ionic model leads to the equation

$$U(r) = \frac{-NAe^2}{10^3 Jr}(1 - \varrho/r) \text{ kcal.mole}^{-1}, \quad (2)$$

where ϱ/r is given by

$$\varrho/r = \frac{Ae^2/r}{9V/\beta + 2Ae^2/r}. \quad (3)$$

Table 1. *Crystal energy calculations*

	$-\Delta U$ (kcal.mole^{-1})	$-U(r)_1$ (kcal.mole^{-1})	ϱ/r	$-U(r)_2$ (kcal mole^{-1})
TiO$_2$	2930 ± 20 ·	2931	0·095	2949 ± 150
GeO$_2$	3090 ± 20	3054	0·093	3080 ± 150
SnO$_2$	2834 ± 20	2800	0·084	2850 ± 150

The Madelung constant, A, has been evaluated by the single series method of Bertaut (1952), as extended by Templeton (1955) and by Jones & Templeton (1956). A linear charge distribution has been assumed and adequate convergence was ensured. Crystal data were taken from Wyckoff (1963). The results for A/r are compared with previous data below:

	Bollnow (1920)	Templeton & Johnson (1961)	Baur (1961)	Kingsbury (1968)	This work
TiO$_2$	9·824	9·764	9·811	9·805	9·808
GeO$_2$					10·22
SnO$_2$					9·369

In the case of rutile, the variation of A/r with ionic charge was studied; it is nearly linear and follows equation (4) with a precision of $\pm 0.5\%$ over the range $z(\text{Ti}) = 4$ to $z(\text{Ti}) = 3$.

$$A/r(\text{rutile}) = 4.291z(\text{Ti}) - 7.454 . \quad (4)$$

In many studies of crystal energies (Waddington, 1959; Ladd & Lee, 1960; Tosi, 1964), it is general experience that ϱ/r is approximately 0·1. The crystal energies have been evaluated firstly on this basis, $U(r)_1$ in Table 1.

An attempt has been made to calculate ϱ/r using equation (3). Compressibility data are available for TiO$_2$ (Gmelin, 1951), and for SnO$_2$ (Madelung & Fuchs, 1921); the corresponding coefficient, β, has been estimated for GeO$_2$ from molar volume proportionalities (Partington, 1952), with TiO$_2$ and SnO$_2$. It may be noted that an error of $\pm 10\%$ in β produces a concomitant error of $\pm 1\%$ in a crystal energy of 3000 kcal.mole^{-1}. The term ϱ/r and the second estimate, $U(r)_2$, are listed also in Table 1.

The Born–Mayer calculation usually evaluates the energies of ionic crystals to within 5% of the thermodynamic values, Waddington (1959), Ladd & Lee (1964). Furthermore, the thermodynamic values must represent, within their limits of error, the lowest energy data. There seems to be evidence of notable ionic character in these dioxides.

The above analysis is based upon the rutile structure model, with ions of the type M^{4+}, O^{2-}. If the ionic charges were less than this, then, from equation (4), the crystal energy would be more positive. To maintain parity with the thermodynamic value, corrections for covalent character would then need to be introduced.

There is no evidence that this should be the case, and this feature cannot be deduced from this type of model-dependent energy study. However, in other examples of predominantly ionic crystals, such as the alkali metal halides and the alkaline earth metal chalcogenides, good agreement is usually obtained between the calculated [equation (2)] and the Born–Haber crystal energies. As far as is known, there are no experimental electron distribution data available of sufficient accuracy for reliable electron counts to be made for these dioxides.

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