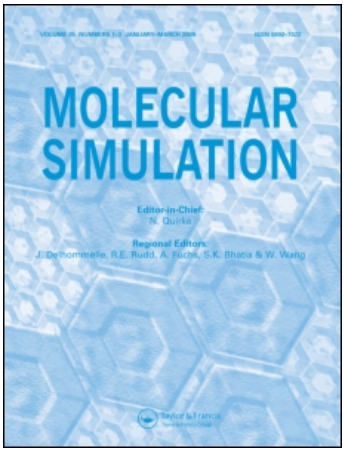

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Is Beryllium Carbide Ionic?

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Preliminary Communication

IS BERYLLIUM CARBIDE IONIC?

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Ab initio cluster calculations show that solid Be_2C is ionic and contains carbide ions with a charge close to the nominal -4 and a polarisability of $\sim 20a_0^3$ (~ 2.9 Å^3).

KEY WORDS: Beryllium carbide, ionic solid, cluster calculation

Anions carrying multiple charges are unstable in the gas phase but can exist in crystals where they may be stabilised by long-range electrostatic interactions and short-range overlap forces. Beryllium carbide is a transparent (colourless when pure) crystalline solid with the antifluorite structure, stable in dry air to > 2200°C, is an electrical insulator and yields methane on hydrolysis [1, 2]. Does it contain discrete C^{4-} ions? Our *ab initio* calculations of optical and dielectric properties suggest that it does, in agreement with earlier semi empirical density functional calculations [3] which assigned a near nominal charge to the carbide ion in Be_2C.

Although experimental data on beryllium carbide are limited, and likely to remain so in view of the extreme toxicity of beryllium compounds, there is a measurement of the refractive index of the crystal [4]: $n = 2.635(10)$ at a wavelength of $\lambda = 6640$ Å. Using the Clausius–Mossotti formula

$$\frac{n-1}{n+2} = \frac{4\pi}{3}\frac{\alpha_m}{V_m}$$

and noting that the lattice parameter is 4.432 Å, the polarisability per formula unit is found to be $\alpha_m = 21.9 \pm 0.1a_0^3$ ($1a_0^3 \equiv 0.14819$ Å$^3 \equiv 1.6488 \times 10^{-41}$ C^2 J^{-1} m^2). On the ionic hypopthesis, α_m is a sum of anion and cation contributions $\alpha_m = \alpha(C^{4-}) + 2\alpha(Be^{2+})$ and as the beryllium cation is almost unpolarisable ($\alpha(Be^{2+}) \simeq 0.052a_0^3$) this value implies that carbide ions, if present in Be_2C, have the large polarisability of $21.8 \pm 0.1a_0^3$. (*cf.* α(Ne) $= 2.68a_0^3$, $\alpha(F^-$ in LiF$) = 5.98a_0^3$. $\alpha(O^{2-}$ in MgO$) = 11.35a_0^3$, see for example reference 5).

A series of theoretical investigations of ionic solids [6–9] has established that accurate anionic polarisabilities may be obtained by simulating the local environment of the ion in an all-electron calculation on a cluster consisting of the anion and its first shell of cationic neighbours embedded in a lattice of point charges. The success of the approach is well documented for alkali halides and alkaline earth chalcogenides. It depends on the fact that the anion wavefunction in a cubic site is compressed, both by the spherical average of the Madelung potential i.e. the long-range electrostatic

Table 1 *Ab initio* calculations of the carbide polarisability (in a.u.)

Basis	C^{4-} α	*Effects included*
[17s12p6d]	26.95	Madelung potential
[17s12p6d/1s]	19.42	Beryllium cores
[17s12p6d/2s1p]	19.54	Beryllium α + charge-transfer

interaction with the infinite lattice of charges, and by overlap interactions i.e. Pauli repulsion from the nearest cationic neighbours.

In the calculations described here we follow the method established for simple ionic solids [6–9] and build up a simulated crystalline environment step by step. The anion is represented by a large, flexible basis of Guassian functions (17s12p6d); the neighbouring cations are treated first as point charges then as fully polarisable electron clouds (in a 2s1p basis) and a sufficient number of shells of more distant neighbours are included as point charges. At each stage the energy, electron distribution and response to a uniform electric field are calculated at the self-consistent field/coupled Hartree–Fock level using a version of the SYSMO program [10]. A summary of the main results is given in Table 1 and full details of the full calculations may be found in [11].

The main physical factors are:

(1) Madelung potential: Although the isolated carbide anion would have an effectively infinite polarisability, the Madelung potential of point-charge neighbours reduces this to only $\sim 27a_0^3$.

(2) Overlap effects: First-shell overlap and electrostatic forces compress the C^{4-} density so that it is smaller and less polarisable than the ion in a purely electrostatic environment. As shells of point-charge neighbours are added the polarisability increases at first, but stabilises to the infinite-lattice limiting value of $\sim 19.5a_0^3$. Thus the net effect of the short-range forces simulated by introducing "real" beryllium ion cores is a reduction of the carbide polarisability by a factor of $\sim\frac{2}{3}$.

(3) Charge transfer/Covalency: Finally, the beryllium *s* functions were split to allow for the possibility of charge transfer from the anion to the empty 2s orbitals. The cluster polarisability remained stable. Thus even when the ionic hypothesis implicit in the use of a minimal Be basis is relaxed, very little charge transfer is observed and we can conclude that the electronic structure of Be_2C is dominated by ionic contributions.

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