Theoretical Evidence for the C^{4-} Ion in Beryllium Carbide

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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 $\sim 20\ a_0^3$ (~ 2.9 Å^3).

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. A charge of -2 is relatively common, and many oxides and sulphides show ionic character. Triple negative charges are rare but there is strong evidence[1] for a nitride ion N^{3-} in Li_3N. A more extreme example of high charge would be the carbide ion C^{4-}. Several of the salt-like binary carbides are in fact acetylides[2] (*e.g.* CaC_2) and the likely candidates for C^{4-} salts are Be_2C and Al_2C_3 which evolve methane rather than acetylene on contact with water and dilute acids. Beryllium carbide is a transparent (colourless when pure) crystalline solid with the antifluorite structure, stable in dry air to >2200 °C and is an electrical insulator.[3,4] Does it therefore 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[5] 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:[6] $n = 2.635(10)$ at a wavelength of $\lambda = 6640$ Å. Using the Lorentz–Lorenz formula (1) and noting[6] that the lattice parameter is 4.342 Å, the polarisability per formula unit is found to be $\alpha_m = 21.9 \pm 0.1\ a_0^3$ ($1\ a_0^3 \simeq 0.14819$ Å^3 $\boxminus$ $1.6488 \times 10^{-41}\ C^2\ J^{-1}\ m^2$). On the ionic hypothesis, 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[7] [$\alpha(Be^{2+}) \simeq 0.052\ a_0^3$] this value implies that

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

carbide ions, if present in Be_2C, have a large polarisability of $21.8 \pm 0.1\ a_0^3$ [*cf.* $\alpha(Ne) = 2.68\ a_0^3$, $\alpha(F^-$ in LiF$) = 5.98\ a_0^3$, $\alpha(O^{2-}$ in MgO$) = 11.35\ a_0^3$, see *e.g.* ref. 8]. In the present communication we report an all-electron *ab initio* calculation of the polarisability of a carbide ion in the Be_2C environment, and from the level of agreement with the experimental result deduce the Be_2C is indeed essentially ionic.

A series of theoretical investigations of ionic solids[9—12] 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 interaction with the infinite lattice of charges, and by overlap interactions, *i.e.* Pauli repulsion from the nearest cationic neighbours. In alkali halides this is primarily a first-shell, isotropic effect.[9] The oxide anion is larger, and for MgO it has been suggested that second-shell oxide–oxide interactions are also significant.[10] The high negative charge of the putative carbide ion and the implied large volume of its electron cloud present an extra challenge to this previously successful theoretical model.

An isolated C^{4-} ion *in vacuo* is unstable with respect to electron loss and is thus effectively infinitely polarisable. How this is reflected in a practical calculation of the electronic structure depends on the particular theoretical method employed: symmetry constraints or basis set limitations in a self-consistent field calculation may force a spurious closed-shell solution as they do for the unbound O^{2-} and S^{2-} ions.[10,12—14] However, the properties of the isolated system are almost irrelevant to the problem of the ion in the crystal. If the ionic description is applicable to Be_2C, the Madelung stabilisation and overlap compression in the crystal must compress the enormously diffuse and polarisable free C^{4-} system into the volume allowed by the Be–C distance [$(\sqrt{3}/4)\ a \simeq 1.88$ Å] and reduce its polarisability to only $\sim 20\ a_0^3$.

In the calculations described here we follow the method established for simple ionic solids[9—12] and build up a simulated crystalline environment step by step. The anion is represented by a large, flexible basis of Gaussian functions; the neighbouring cations are treated first as point charges then as fully polarisable electron clouds 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.[15] A series of different calculations allows the separation of electrostatic and overlap, first- and second-shell, ionic and charge-transfer effects on the polarisability, α, and size (as measured through the second moment $\langle \Sigma_i e_i r_i^2 \rangle$) of the carbide ion.

The basis for carbon is an uncontracted (17s12p6d) set derived from the Huzinaga[16] 11s7p set expanded by the method of Werner and Meyer,[17] further extended by a geometric progression in the *s* and *p* series, and by adding *d* functions with exponent pattern $[32\eta, 9\eta, 3\eta, \eta, 1/3\eta]$ where $\eta = 0.02845\ a_0^{-2}$. Thus augmented, the basis includes highly diffuse functions (the lowest *d* exponent is $\sim 0.009\ a_0^{-2}$) and is suitable for describing anionic carbon. In the octahedral symmetry of the C site in Be_2C the *d* sets act mainly as polarisation functions which account for the distortion of the electron cloud by applied fields.

Three basis sets for beryllium were derived from the 10s set of van Duijneveldt.[18] A coupled Hartree–Fock calculation on Be^{2+} in a (10s8p) basis formed by adding *p* functions with the 8 lowest *s* exponents gave the ground state eigenvector ψ° and its electric field derivative $\psi_\alpha' = (\partial\psi/\partial F_\alpha)$ as the (10s) $\rightarrow$ [1s] linear combinations and (8p) $\rightarrow$ [1p], respectively. Basis A consists of this single *s* contraction on each Be, basis B is [1s1p], and in basis C the *s* set is split into two contractions of equal length. All three sets give the near Hartree–Fock energy of $E(Be^{2+}) = -13.6109\ E_h$; sets B and C give the limiting polarisability of $0.052\ a_0^3$. When used in cluster calculations the progression from A to B to C accounts first for the hard repulsive core of Be^{2+}, then its polarisability, then the possibility of charge transfer into its empty 2s orbital. A cut-off of 10^{-4} a.u. was used to eliminate three near linearly

Table 1. Effects of a point charge lattice on carbide ion properties. N is the total number of centres in the lattice, α is the polarisability of the C^{4-} ion, and $\bar{Q}$ is the unsigned mean second moment of its charge density. The outer faces of the lattice are scaled to preserve electroneutrality. V is the electrostatic potential due to the point charges, evaluated at the carbide site.

N	α/a_0^3	$\bar{Q}/a_0^2$	V/E_h
127	26.95	15.15	2.600
395	27.02	15.15	2.605
885	27.03	15.16	2.607
1673	27.04	15.16	2.608
2837	27.04	15.16	2.609
4431	27.04	15.16	2.609

Table 2. Influence of lattice size on the properties of C^{4-} in a cage of 8 Be^{2+} neighbours. N is the total number of centres and α and $\bar{Q}$ are the net polarisability and second moment for the central ion, obtained from the properties of the full cluster as described in the text. All calculations refer to the [17s12p6d/1s] basis (basis A).

N	α/a_0^3	$\bar{Q}/a_0^2$
9	18.68	12.63
29	18.80	12.65
127	19.42	12.70
395	19.42	12.70
885	19.43	12.71
1673	19.43	12.71
2837	19.44	12.71
4431	19.45	12.72

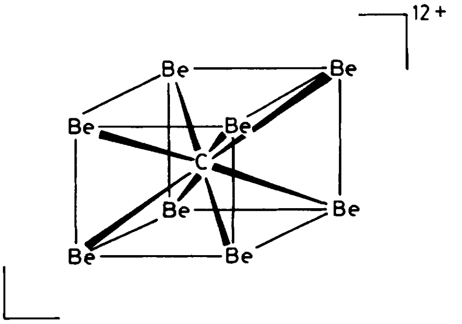

Figure 1. Arrangement of neighbours around the carbon site in Be_2C. This Be_8C^{12+} cluster is used to model the environment of the carbide anion in the solid.

Table 3. Variation of carbide ion properties with improvements in the cation basis set. Basis sets A, B, and C introduce successively core repulsion, cation polarisability, and C(2p) → Be(2s) charge transfer. In all three calculations the lattice contains a total of 127 centres.

	Cluster	C^{4-}	
Basis	α	α	$\bar{Q}$
A [17s12p6d/1s]	19.45	19.42	12.70
B (17s12p6d/1s1p]	19.78	19.41	12.76
C [17s12p6d/2s1p]	19.91	19.54	12.81

dependent eigenvectors of the overlap matrix for the full cluster basis. SCF and CHF calculations were carried out in these basis sets with the Exeter version of the SYSMO program to separate the various physical influences on the carbide properties. The results are now discussed in turn.

(i) Madelung potential. Table 1 shows a series of results for the carbide ion embedded in a point charge lattice. Charges on the outer faces of the cubic lattice fragment are scaled for overall electroneutrality as described in ref. 9. Although the isolated carbide anion would have an effectively infinite polarisability, the Madelung potential of point-charge neighbours reduces this to only ~27 a_0^3. Increasing the lattice size gives rise to very little further change and the infinite lattice limit is estimated to be ~27.1 a_0^3 in this basis. The well depth at the carbide site is more slowly convergent but these results illustrate the important physical point that the radius of the spherical potential rather than its absolute depth determines the polarisability of the compressed anion. Table 1 also shows that the size of the anion, assessed from the radial expectation value $\bar{Q} = 1/3\langle\psi|\Sigma_i r_i^2|\psi\rangle$, is equally stable with respect to lattice size. A value of $\bar{Q} = 15.15\ a_0^2$ corresponds to a root mean square radius of ~1.1 Å per electron.

(ii) Overlap effects. Table 2 explores the effect of adding overlap compression to the model. The gas-phase CBe_8^{12+} cluster (see Figure 1) has a *total* polarisability of 18.71 a_0^3 in basis A. Although the cations are nominally unpolarisable in this basis they can borrow diffuse carbon-centred functions and thus achieve a small, spurious polarisability through a type of basis set superposition error (BSSE).[9] Of several ways to correct for this mathematical artefact the simplest is chosen here. The orbital polarisabilities are evaluated and the contributions from cage-localised molecular orbitals subtracted out. The cage correction is small ($\leqslant 0.03\ a_0^3$).

A similar method is used for the second moment of the charge distribution, and so all values of α and $\bar{Q}$ in Table 2 refer to properties of the carbide ion itself and not the ion cluster. The main trends in the table are as expected: 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 by ~5%, but stabilises to the infinite-lattice limiting value of ~19.5 a_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 ~2/3.

(iii) Cation polarisability. In basis B each cation has a full complement of polarisation functions and the total cluster polarisability is larger than for basis A. On the classical dipole–induced-dipole (DID)[19] model for a cluster of point polarisable ions the cluster polarisability would be given by equation (2), where the DID enhancement is given by equation (3) and $\alpha(Be^{2+})$ is a constant, independent of the ion's environment. Thus we might expect a small enhancement of the effective carbide polarisability on going from basis A to B. As Table 3 shows, this does not give a quantitative description of the changes; in fact a small fall in $\alpha(C^{4-})$ is observed.

$$\alpha(\text{total}) = \alpha(C^{4-}) + 8\alpha(Be^{2+}) + \alpha(\text{DID}) \qquad (2)$$

$$\alpha(\text{DID}) \simeq 16[\alpha(C^{4-})]^2[\alpha(Be^{2+})]/[R(BeC)]^6 \simeq 0.16\,a_0^3 \qquad (3)$$

(iv) Charge transfer/covalency. In the last calculation reported in Table 3 the beryllium s functions were split to allow for the possibility of charge transfer from the anion to the empty 2s orbitals. The Mulliken populations of Be in the cluster show some evidence of such a shift. They are 2.000 (basis A), 2.021 (basis B), and 2.020 (basis C), which correspond to carbon charges of −4.002, −3.829, and −3.841, respectively. The effective size and polarisability of the anion also increase in basis C, but the variation between bases is less than 1%. 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.

(v) Electron correlation. Taken together the results described so far indicate that the carbon centre in Be_2C is associated with charge close to the nominal -4 and a polarisability of 19—20 a_0^3. These predictions are based on SCF calculations on 9-ion clusters and it is necessary to consider how they might change if these restrictions too were lifted in a more extensive calculation. Electron correlation is known to increase the polarisability of p^6 anions, though its effect is quenched in the crystal,[11] and it seems likely that the intra-ionic correlation contributions to $\alpha(Be_2C)$ would add at least 10% to the SCF value and possibly considerably more, to judge from results[10] for O^{2-} in MgO, for example. A Møller–Plesset calculation on a 9-ion cluster in a slightly reduced version of the basis A and using the CADPAC[19] program gives a second-order correlation polarisability of 0.27 a_0^3. However, anion–anion second shell interactions are significant for an extended electron distribution like C^{4-} and they would tend to counteract the correlation increase. A full calculation on a cluster with two shells of carbons would be prohibitively expensive in the present basis.

A final calculation combined the best basis (C) and the largest lattice (4431 centres) to produce our best SCF estimate of $\alpha(C^{4-})$. We found a value of 19.56 a_0^3. Given the likely magnitude of correlation and residual basis set effects this constitutes excellent agreement between the theoretical and empirical (Lorentz–Lorenz) values of $\alpha(C^{4-})$ and our *ab initio* calculations provide theoretical support for the existence of C^{4-} in Be_2C. In-crystal forces are sufficient to bind the diffuse electron cloud of this highly charged anion.

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