In conclusion, the spectroscopic and electron-diffraction results for $C_5H_5Zr(BH_4)_3$ support the suggestion that direct substitution of a cyclopentadienide ring for one of the borohydride groups in $Zr(BH_4)_4$ does not affect the overall structure much: neither the average B–H bond length nor the B·B distance changes significantly, and although the Zr–B bond lengthens and the B–Zr–B angle decreases, these changes are consistent with the changes in steric effects discussed above.

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Supplementary Material Available: Tables of total intensities and final backgrounds from each plate and average molecular intensities (9 pages). Ordering information is given on any current masthead page.

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Phase Transitions in Cesium 7,8-Dicarbaundecaborate(12): A New One-Dimensional Cesium Solid Electrolyte at 210 °C

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The structural study of the three polymorphs of cesium 7,8-dicarbaundecaborate(12) in the temperature interval 20–250 °C is reported. While the low- and medium-temperature polymorphs (γ and β, respectively) present very poor conductivity, the phase transition to the high-temperature form (α) is associated with an increase of 4 orders of magnitude of the conductivity for Cs^+ ($\sigma = 5.5 \times 10^{-5}\ \Omega^{-1}\ cm^{-1}$). The structure of the γ-polymorph has been solved by single-crystal X-ray diffraction methods. Crystal data: $Cs[B_9C_2H_{12}]$, monoclinic, space group $P2_1/c$, with $a = 8.360$ (3) Å, $b = 10.696$ (4) Å, $c = 11.222$ (4) Å, $\beta = 92.62$ (2)°, $V = 1002$ Å^3, $Z = 4$, $D_x = 1.75$ g cm^{-3}, μ(Mo Kα) = 36 cm^{-1}, and $F(000) = 496$. The positions of Cs^+ and of the center of mass of the anion in the β-polymorph have been refined by the rigid-body Rietveld refinement technique starting from the corresponding positions in the γ-phase and assuming a $P2_1/c$ space group. Cell parameters at 140 °C: $a = 6.90$ (2) Å, $b = 12.55$ (2) Å, $c = 12.15$ (2) Å, $\beta = 90.0$ (1)°, $V = 1052$ Å^3, $Z = 4$. The crystal structure of the α-polymorph has been deduced from the indexed powder diffraction pattern and corresponds to an I-centered tetragonal cell [$a = 8.64$ (3) Å, $c = 7.14$ (3) Å, $V = 533$ Å^3], with the anions placed at the corners and the center of the cell and the Cs^+ disordered at the (0, $^1/_2$, $^1/_4$) and (0, $^1/_2$, $^3/_4$) sites. The probable conduction path is along the c axis of the tetragonal cell.

Introduction

It is well-known that certain solids, the so-called solid electrolytes, show an abnormally high ionic conductivity. In general, the crystal structure of such compounds consists of one part that remains rigid and of another that is highly disordered at the experimental temperature, i.e. the mobile ions. If we only consider the thermally induced disorder, then two sorts of solid electrolytes can be distinguished depending on the manner of onset of the disorder: those like CaF_2, where the disorder gradually appears with increasing temperature, and the α-AgI type, where the sudden appearance of the disorder is associated with a phase transition. The main factor[1] favoring the easy motion of Ag^+ in α-AgI is, among others, the large number of crystallographic identical jump sites separated by a low potential barrier available for each Ag^+ ion.

In the course of our research on carborane compounds, we have investigated the alkaline-earth-metal series of the nearly spherical $B_9C_2H_{12}^-$ anion. The Cs salt shows a certain parallelism with AgI. First, the ratio of the ionic radii is similar, i.e. $R(Cs^+)/R(B_9C_2H_{12}^-) \cong 1.69/3.43 = 0.49$ and $R(Ag^+)/R(I^-) \cong 1.26/2.16 = 0.58$, and second, the ions are monovalent in both compounds. This parallelism prompted us to further study this compound, specifically the structural characterization and conductivity response. In this paper, we report the conductivity data as a function of the crystallographic form of the compound.

Experimental Section

Synthesis of $B_9C_2H_{12}^-$ and Precipitation of the Cs Salt. The *o*-carborane was partially degraded with KOH in a reaction flask according to Plešek et al.[2] and was precipitated with cesium acetate. The precipitate was filtered out in air and recrystallized from hot water. The subsequent analyses and the spectroscopic results are in agreement with the literature data for this compound. The crystals used in the X-ray diffraction experiments were grown from a solution of the salt in a 1/1 mixture of water and dimethyl formamide.

Table I. Crystallographic Data for γ-$Cs[B_9C_2H_{12}]$ at 26 °C

$a = 8.360$ (3) Å	fw 266.1
$b = 10.696$ (4) Å	space group $P2_1/c$ (No. 14)
$c = 11.222$ (4) Å	cryst dimens 0.20 × 0.12 × 0.15 mm
$\beta = 92.62$ (2)°	$\rho_{calcd} = 1.75$ g cm^{-3}
$V = 1002$ Å^3	$\mu = 36$ cm^{-1}
$Z = 4$	transm coeff 0.77–1.36
$F(000) = 496$	$R(F_o) = 0.052$
$\lambda = 0.71069$ Å	$R_w(F_o) = 0.057$

Electrical Conductivity Measurements. The sample was finely ground, pressed into a cylindrical pellet (6.5 mm in diameter and 4–5 mm thick) under a pressure of 6 atm, and heated in an oven (150 °C) for 2 h but not sintered. Both faces of the sample were coated with evaporated gold, which served as the electrodes. The technique of complex plane impedance analysis was employed to measure the conductivity of the sample in air in the temperature interval 25–350 °C. A Hewlett-Packard impedance analyzer (Model 4192A LF) was used at frequencies ranging between 5 and 13 MHz. The time between consecutive measurements was 20 min.

Differential Scanning Calorimetry. Measurements were done on a DSC2 Perkin-Elmer automated analyzer system in Ar atmosphere (heating rate = 20 K/min).

Crystallography and Structure Determination of $Cs[B_9C_2H_{12}]$ at 26 °C. A colorless fragment of a prismatic crystal was selected for single-crystal X-ray diffraction analysis. Crystal data and relevant structure refinement parameters are given in Table I.

Data were collected on an Enraf-Nonius CAD4 four-circle diffractometer (graphite-monochromatized Mo Kα radiation); 1483 independent reflections with $\theta \leq 25°$ were measured, from which 1176 were observed with $I > 2.5\sigma(I)$. The hkl ranges were $-9 \leq h \leq 9$, $0 \leq k \leq 11$, and $0 \leq l \leq 12$. No significant decay of standard reflection intensities

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† CSIC.

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Table II. Lattice Parameters for the $Cs[B_9C_2H_{12}]$ Polymorphs Obtained from the Least-Squares Refinement from Powder Diffraction Data with Esd's in Parentheses

polymorph	*T*, °C	*a*, Å	*b*, Å	*c*, Å	β, deg	*V*, Å^3
γ	26	8.360 (3)	10.696 (4)	11.222 (4)	92.62 (2)	1002
β	140	6.90 (2)	12.55 (2)	12.15 (2)	90.0 (1)	1052
β	180	6.88 (3)	12.60 (3)	12.21 (3)	90.0 (1)	1059
α	250	8.64 (3)		7.14 (3)		533

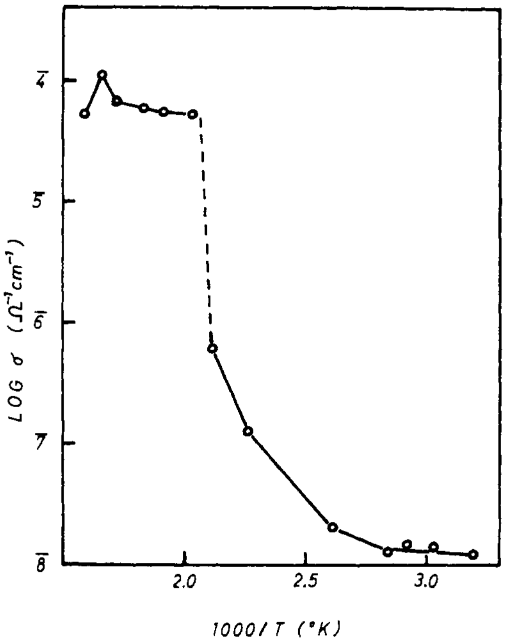

Figure 1. Arrhenius plot of conductivity of Cs in $Cs[B_9C_2H_{12}]$ from room temperature up to 350 °C.

was observed (0.9%). The data were also corrected for Lorentz–polarization effects and for absorption by using the DIFABS program.[3]

The structure was solved by multisolution direct methods with the Ω tangent formula.[4] All refinements were carried out with the least-squares full-matrix method.[5] Eleven H atoms were located in a subsequent difference Fourier syntheses and held fixed, with a global isotropic temperature parameter ($U = 0.05$ Å^2). The final R and R_w values are 0.052 and 0.057, respectively, with $w = 1/[\sigma^2(F) + 0.0018F^2]$. Maximum and minimum heights in the final difference Fourier are 0.55 and −1.0 e Å^{-3}. Scattering factors were taken from ref 6.

Measurement of Powder Diffraction Patterns. Powder diffraction patterns at 26, 140, 180, 220, and 250 °C were collected in air on a temperature-controlled attachment on a conventional Siemens D500 diffractometer using monochromatized Cu Kα radiation (measured 2θ range 5–50°, step size 0.02° 2θ, integration time 10 s).

The diffraction pattern measured at 140 °C was selected to determine the crystal structure of the β-polymorph of $Cs[B_9C_2H_{12}]$. The pattern was smoothed by FT low-pass filtering, and the Cu Kα_2 contribution was subtracted according to the stripping procedure of Keating.[7] The unit cell indexing was performed with the program TREOR.[8] All the refinements necessary for determining the structure were performed with the rigid-body Rietveld refinement method.[9] The function minimized was $\sum w_i[y_i(\text{obs}) - (1/c)y_i(\text{calc})]^2$, with i representing all points of the diffraction pattern where a reflection is expected to appear, with y_i being the net intensity at $2\theta_i$, with c being a scale factor, and with $w_i = 1/Lp(2\theta_i)$. Due to the large volume increases associated with the $\gamma \rightarrow \beta \rightarrow \alpha$ transitions, the sample tends to arch in the sample holder. To compensate for this, a zero shift parameter was also included in the refinement of the unit cell parameters.

Table III. Final Fractional Atomic Coordinates (×10^4) of γ-$Cs[B_9C_2H_{12}]$ with Esd's in Parentheses

atom	*x*	*y*	*z*
Cs	7572 (0.6)	2409 (0.5)	4894 (0.5)
B1	3110 (9)	4218 (7)	8864 (8)
B2	4321 (9)	4014 (8)	7627 (8)
B3	3532 (10)	2681 (7)	8305 (10)
B4	1614 (8)	3042 (7)	8755 (7)
B5	1130 (9)	4595 (7)	8314 (7)
B6	2856 (9)	5213 (7)	7569 (7)
C7	3376 (8)	2884 (7)	6803 (8)
C8	1869 (10)	2384 (6)	7384 (8)
B9	415 (9)	3358 (7)	7431 (7)
B10	1100 (10)	4757 (7)	6720 (7)
B11	3118 (9)	4308 (7)	6279 (8)

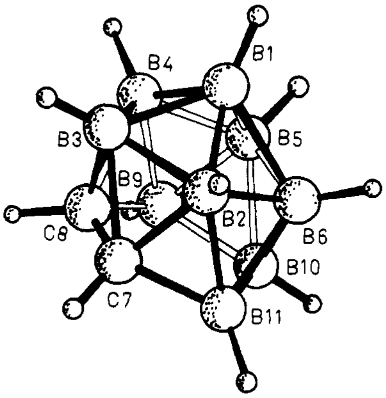

Figure 2. View of the $B_9C_2H_{12}^-$ anion with the corresponding atom labeling.

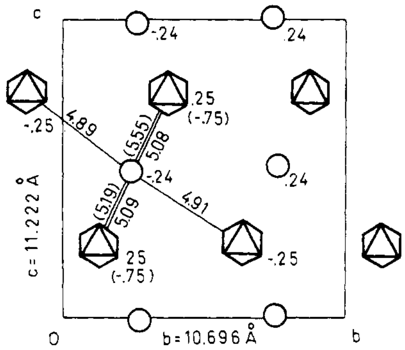

Figure 3. Schematic projection of the structure of the γ-polymorph on (010). For simplicity, the anions are symbolized by octahedra; small circles are Cs^+. The x coordinates are fractional ones.

Results and Discussion

Figure 1 shows the Arrhenius plot of the conductivity of Cs^+ in $Cs[B_9C_2H_{12}]$. As can be seen, an abrupt increase in conductivity with temperature ends at about 205 °C. Above this temperature, the sample shows the highest conductivity ($\sigma = 5.5 \times 10^{-5}$ Ω^{-1} cm^{-1}) with an estimated activation energy of 0.08 eV. This value is comparable to that in α-AgI (0.05 eV) or $RbAg_4I_5$ (0.07 eV).[10] The DSC measurement indicates the existence of two sharp endothermic peaks. The first one ranges from 91.2 to 115.8 °C

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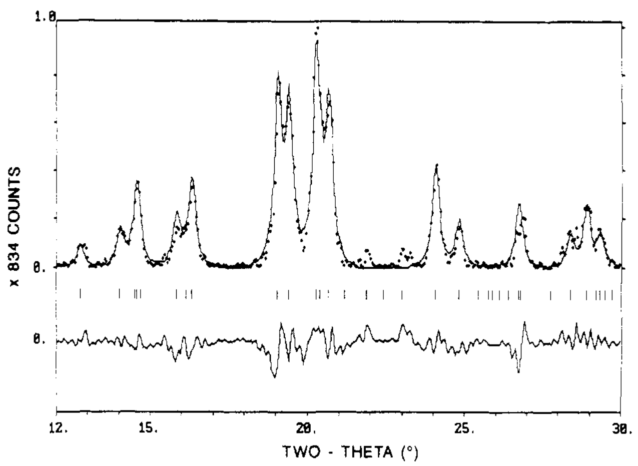

Figure 4. X-ray powder diffraction data for α-Cs[$B_9C_2H_{12}$]. The points are the observed intensities (only the Kα_1 contribution), and the line is the Rietveld fit. The small vertical bars indicate the positions of allowed *hkl* reflections. The difference between the observed and the calculated profiles is plotted below the diffraction pattern.

(enthalpy of transition 10408 J mol^{-1}) with the maximum at 101.52 °C; the second one ranges from 198.8 to 222 °C with the maximum at 209.8 °C and with an enthalpy of transition of 5397 J mol^{-1}. The compound is stable in air up to 260–270 °C. Above this temperature, the oxidation of the $B_9C_2H_{12}^-$ anion begins. To confirm the existence of three polymorphs in the temperature interval 26–250 °C, i.e. polymorph γ up to 102 °C, polymorph β between 102 and 210 °C, and polymorph α above 210 °C, the corresponding crystal structures have been determined from single-crystal or powder X-ray diffraction data. Table II summarizes their refined unit cell parameters.

Polymorph γ (at 26 °C). Final atomic parameters are listed in Table III. The $B_9C_2H_{12}^-$ anion is shown in Figure 2. The average B–B distance is 1.787 (27) Å (18×), the C–B average is 1.68 (5) Å (6×), and C7–C8 is 1.55 (1) Å. These average bond lengths agree well with literature values, e.g. B–B = 1.78 (3) Å and C–B = 1.69 (7) Å in Na[$B_9C_{10}H_{25}O_3S_2$].[11] Figure 3 schematically represents the unit cell contents. The coordination polyhedron of Cs^+ is an octahedron (average length to the centers of mass of the six nearest anions 5.12 (24) Å). The shortest distance from Cs^+ to B is 3.712 Å, and the shortest Cs···H contact is 3.02 Å. This structure can be described as a slightly distorted hexagonal close-packed arrangement of anions with Cs^+ at the two octahedrally coordinated sites (Figure 9a).

Polymorph β (at 140 °C). Since the metric is pseudoorthorhombic, several attempts of refining the structure were first performed by assuming orthorhombic space groups compatible with the observed extinctions (0*k*0 with $k = 2n + 1$) and with packing considerations, but all of them resulted in high final R_{wp} values. Consequently, the structure was assumed monoclinic with Cs^+ and the center of mass of the anion still following the $P2_1/c$ symmetry of the γ-phase. The presence of the (003) reflection clearly evidences that the *c*-glide plane present in the γ-phase is lost. However, its weak intensity and the absence of the ($\bar{1}03$) reflection suggest that the departure from the $c/2$ translation is rather small. The good agreement achieved in the subsequent refinement indicates that this assumption is valid. Since the anion is introduced with an arbitrary orientation, only the low-angle portion of the diffraction data, i.e. with 2θ ranging from 12 to 30°, was used in the Rietveld refinement. This portion is less sensitive to the anion orientation errors. The starting positional parameters were those of the γ-phase at 26 °C. Number of parameters refined: the three positional parameters of Cs^+, the three coordinates of the center of mass of the anion, a scale factor, the peak width parameter (assumed as constant in the 12–30° 2θ interval), and an occupation factor for Cs^+ that represents the

Table IV. Results of the Rigid-Body Rietveld Least-Squares Refinement of the β-Polymorph at 140 °C with Esd's in Parentheses

atom or group	*x/a*	*y/b*	*z/c*
Cs^+	0.889 (3)	0.259 (6)	0.492 (8)
[$B_9C_2H_{12}$]$^-$	0.35 (1)	0.439 (6)	0.72 (1)

scale factor: 4.6 (5) × 10^{-5}
fwhm (2θ): 0.27 (1)
occ factor of Cs^+: 0.80 (4)
R_p, %: 19.4
R_{wp}, %: 13.7

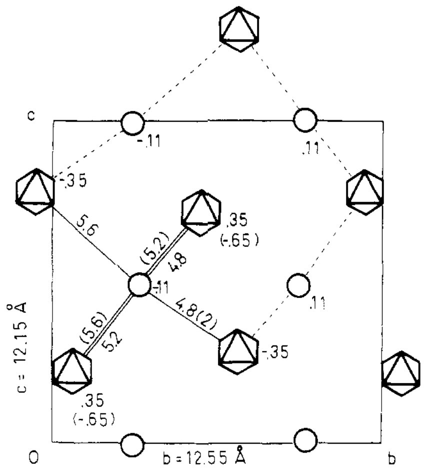

Figure 5. Schematic (010) projection of the structure of the β-polymorph. The symbology is the same as in Figure 3.

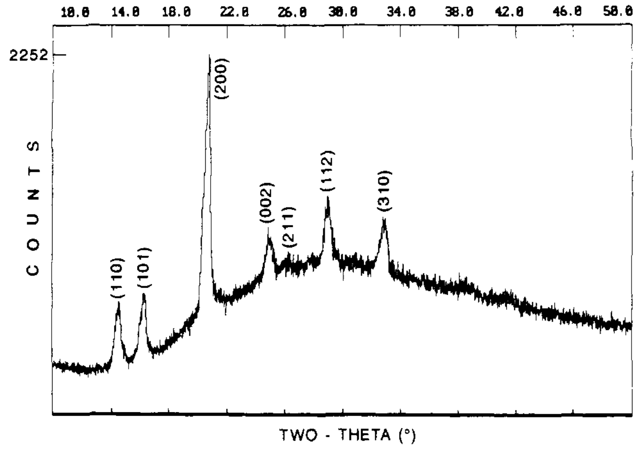

Figure 6. Indexed powder X-ray diffraction pattern of the α-polymorph at 250 °C (see Table V).

average value $\langle \exp[-2(B_{Cs} - R_{anion})(\sin^2\theta)/\lambda^2] \rangle$. Table IV summarizes the results of the Rietveld refinement. Figure 4 shows the observed and calculated powder diffraction patterns. Although not given here, the agreement between observed and calculated patterns between 30 and 40° is also good. Figure 5 represents a schematic (010) projection of the structure. The crystal structure can be described as an intermediate stage toward a CsCl-like structure (with cell parameters $a' = 6.898$ Å, $b' = b/2 = 6.276$ Å, and $c' = c/2 = 6.077$ Å). The coordination polyhedron of Cs^+ is still a distorted octahedron (average bond length 5.20 Å) (Figure 9b). A CsCl-like structure is indeed found in the salt of the monovalent anion 7,8-dimercapto-7,8-dicarbaundecaborate(10) with the larger tetramethylammonium cation.[12] However, the formation of a CsCl-like structure in Cs[$B_9C_2H_{12}$] would imply a coordination number (CN) 8 for Cs^+. This CN would violate Buerger's rule[13] referring to polymorphic modifications, which states that high-temperature modifications tend to possess a smaller CN than the respective low-temperature ones. According to this,

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Table V. X-ray Powder Diffraction Pattern of $Cs[B_9C_2H_{12}]$ (250 °C) Indexed by Assuming a Tetragonal *I*-Centered Cell[a]

hkl	$1/d_{obs}^2$	$1/d_{calc}^2$	Δ	I_{meas}
110	0.0268	0.0270	−0.0002	25
101	0.0336	0.0333	0.0003	27
200	0.0540	0.0539	0.0001	100
002	0.0790	0.0790	0.0000	16
211	0.0867	0.0870	−0.0003	3
112	0.1057	0.1058	0.0001	25
310	0.1348	0.1344	0.0004	19

[a] Refined cell parameters: $a = b = 8.64$ (3) Å, $c = 7.14$ (3) Å, zero shift (2θ) = 0.07 (8)°.

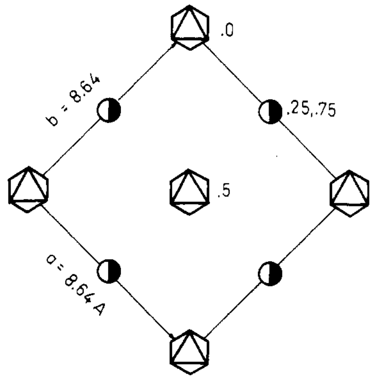

Figure 7. (010) projection of the α-polymorph. The symbology is the same as in Figure 3.

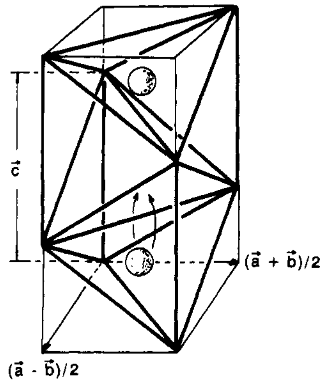

Figure 8. View of one column of face-sharing tetrahedra of the α-polymorph showing the one-dimensional conduction path. The anions occupy the corners of the tetrahedra.

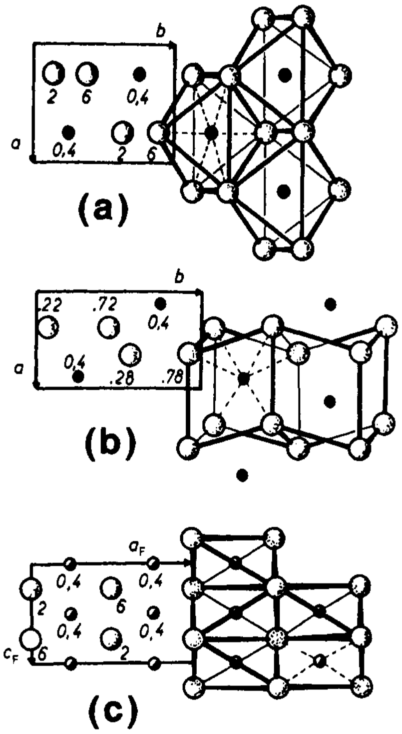

Figure 9. Environment of Cs^+ in the different polymorphs (large circles = anions, small circles = Cs^+): (a) γ-polymorph: (b) β-polymorph: (c) α-polymorph. The integers in the unit cells refer to one-eighth of the cell parameter normal to the plane of the paper. For clarity, the unit cell outline given here refers to the tetragonal *F* lattice ($a_F = a\sqrt{2}$, $c_F = c$).

it may be assumed that the coordination polyhedron of Cs^+ becomes more unfavorable with increasing temperature, thus leading to the observed $\beta \rightarrow \alpha$ transition. The reorganization that occurs during the $\gamma \rightarrow \beta$ transition involves a shortening of the *a* axis (≅−17.5%) and a lengthening by approximately 17.3% and 8.3% of the *b* and *c* axes, respectively.

Polymorph α (250 °C). Figure 6 shows the powder diffraction pattern corresponding to the α high-temperature form, indexed according to a tetragonal I cell (Table V). The model of the structure is represented in Figure 7. The anions occupy the (0, 0, 0) and ($^1/_2$, $^1/_2$, $^1/_2$) sites, and the Cs^+ ions are disordered at (0, $^1/_2$, $^1/_4$) and (0, $^1/_2$, $^3/_4$) with an occupation factor of 0.5. This arrangement explains the strong magnitude of the (200) reflection, for which the whole cell content scatters in phase. The most probable conduction mechanism is depicted in Figure 8. It represents one column along *c* of face-sharing tetrahedra. Notice that not all the tetrahedron faces are alike. Since *c* is shorter than *a*, the three-coordinated sites of the tetrahedron faces parallel to *c* are smaller (3.8 Å vs 4.5 Å). Consequently, the migration of Cs predominantly occurs along the *c* direction through the three-coordinated sites of the tetrahedron faces not parallel to *c* (Figure 9c). Moreover, the low activation energy (0.08 eV) as well as the measured entropy of the $\beta \rightarrow \alpha$ transition (11.2 J mol^{-1} K^{-1}), which is of the same order as the entropy of the $\beta \rightarrow \alpha$ transition for AgI at 146 °C (14.5 J mol^{-1} K^{-1}),[14] seems to confirm that this transition may be effectively regarded as a one-dimensional quasi-melting of the Cs cations in the anion lattice. The present results lead to the conclusion that there exists a high-temperature polymorph of $Cs[B_9C_2H_{12}]$ with a very high conductivity of Cs^+ in one direction. For most practical applications the fast-ion conductors are employed in powdered form, and since, as shown in Figure 1, the resulting averaged conductivity is rather low, the practical utility of the present phase seems to be rather limited. However, the low activation energy, as well as the structural type observed in this phase, suggests the possibility of finding three-dimensionally disordered phases in closely related compounds, e.g. by replacing the $B_9C_2H_{12}^-$ anion by a more symmetrical one.

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Supplementary Material Available: Tables SI–SIII, listing thermal parameters, found hydrogen positions, and bond angles and lengths of γ-$Cs[B_9C_2H_{12}]$ at 26 °C (6 pages); a listing of calculated and observed structure factors (7 pages). Ordering information is given on any current masthead page.

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