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Crystal structures and electronic properties of BaC_2 isomers by theoretical study based on DFT

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Band structures and electronic properties of two BaC_2 isomers were calculated by using density functional theory (DFT) properly. The ionic bond features are all typical between cation (Ba) and anion clusters (C_2) in both structures of the isomers. However, a much stronger covalent bond exists in anion clusters which can be seen by inspecting the electron distribution contour that has a dull bell like shape between two carbon atoms. The shortest distance between Ba^{2+} and C_2^{2-} and the bond length in anion clusters are different in these isomers of BaC_2, which are 0.2945 nm and 0.1185 nm for the structure with the I4/mmm space group and 0.2744 and 0.1136 nm with the C2/c type, respectively. Band structures were clarified by combining the DOS to indicate the ionic bonding features more clearly. Population analysis provided further evidence on these ideas. Thermodynamical calculation results reveal that the transition temperature of these two polymorphs of BaC_2 locates near 132 K, which is consistent with the recent experimental results.

functional materials, metal diaries, phase transition, electron density, first principle calculation, orbital bonding state

Recently, metal carbides and related compounds have received considerable attention due to potential applications as functional materials[1]. The first dicarbide of alkaline earth metal (AEM), BaC_2, was synthesized by the reaction between BaO and $BaCO_3$ in 1892. After that, several researchers have been devoted to investigating the crystal structures and thermodynamical properties of XC_2 (X=AEM), but the properties of these compounds are still not clear[2−5]. Refs. [6, 7] reported the bond lengths of C_2 anion clusters, tetrahedrons and octahedrons formed in CaC_2 in a tetragonal crystal class. In 1990s, Long et al. investigated the bonding features of C_2 anions which aligned along the z direction in BaC_2 crystals. Ruiz and Alemany[8] have applied Hartree-Fock calculations to studying the stability of BaC_2 polymorphs and concluded that the most stable structure of BaC_2 is tetragonal. More recently, the thermal- chemical parameters of several dicarbides including BaC_2 were investigated by Gingerich et al.[9]. It was found that the heat of formation for BaC_2 (g) via Ba (g) +2 C (graphite) = BaC_2 (g) is (252.5±11.5) kJ/mol and the bonding energy is (581.7±14.8) kJ/mol. Temperature effects on the crystal structure of BaC_2 have also been studied in the reference. The exact crystal structure and atomic configurations of BaC_2 polymorphs were analyzed by Vohn[10] using neutron diffraction results. In this work, we used first principles calculations to study the electronic and stability of two BaC_2 polymorphs with space groups of I4/mmm and C2/c (see Figure 1).

1 Methods and details

The whole research was carried out using first principles calculations based on density functional theory as

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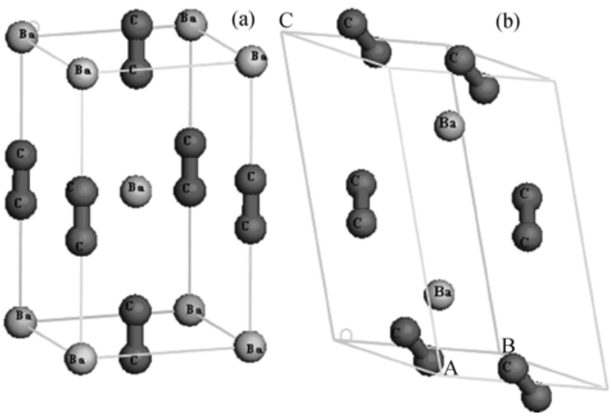

Figure 1 Crystal structure of BaC_2 polymorphs. (a) I4/mmm; (b) C2/c.

implemented in the CASTEP code which uses a plane wave expansion technology. We employed both the normal conserving pseudopotential (NCPP) and the ultrasoft pseudopotential (USPP) to represent the interactions between the ionic core and valence electrons. The valence electron configurations considered in this paper are $5s^2 5p^6 5d 6s^2$ and $2s^2 2p^4$ for Ba and C, respectively. The exchange-correlation energy was approximated at the GGA level of the PBE scheme[11]. The kinetic energy cut-off value was chosen as 660 eV for plane wave expansions. A special ***k*** point sampling method was used for the integration in the first irreducible Brillouin zone with the Monkhorst-Pack scheme[12] and was set as 6×6×4 for bulk crystals. The Pulay density mixing scheme was used for the electronic minimization process. The BFGS algorithm was applied to relaxing the whole crystal to reach the ground state configuration. The average of forces acting on the atom was reduced to 0.001 eV/nm. In order to evaluate the binding energy and the formation enthalpy of BaC_2 polymorphs, the total energy of isolated atoms and binding energies of Ba and graphite were also calculated. All of these calculations are converged and the related parameters are eliminated in the present paper.

2 Results and discussion

2.1 Reliability test

Results obtained by first principles calculations are highly dependent on many parameters, such as plane wave cut-off values, exchange-correlation energy schemes, the ***k*** point mesh, etc. Due to the above reasons, it is better to test the reliability of our calculations first. It is well-known that the total energy is not very sensitive to the variations of calculation parameters mentioned above, but the binding energy and the heat of formation are opposite. In this paper we fixed the ***k*** point mash and the exchange-correlation energy scheme, and then we calculated the binding energy and formation enthalpy as a function of plane wave cut-off values by applying different pseudopotentials. The final results are shown in Table 1. It can be seen that the oscillation of these two energy values decreases by increasing the energy cut-off values, and this trend has been observed by many other researchers. We compared the calculated cell parameters that agreed with Vohn's experimental results. The calculated binding energy (E_{binding}) of BaC_2 is –20.25 eV (–3.375 eV/atom) and –20.05 eV (–3.342 eV/atom) for I4/mmm and C2/c space group types, respectively, and this indicates that I4/mmm crystals are more stable than the C2/c type at 0 K. This is consistent with the results obtained by Vohn[10]. The formation enthalpy is –0.50 eV/uint and –0.69 eV/unit for I4/mmm and C2/c, which implies that the C2/c structure is the ground state of BaC_2 at 0 K.

2.2 Band structure

In this section we will analyze the band structure of BaC_2 in detail and discuss the bonding features that are closely related to the band structure (BS). The symbols of high symmetry points in the first irreducible Brillouin zone were first proposed by Seitz. In the CASTEP code these special ***k*** points were presented by another group of letters of G—Z. In this paper, the band structure expansion path is Z—A—M—G—Z—R—X—G for I4/mmm and L—M—A—G—Z—V for C2/c. The coordination number of Ba atoms in I4/mmm is 10, which is larger than that in the C2/c type of BaC_2. Indicating that great distortions exist in C2/c crystals. When we consider the electron-gravity value of Ba and C in the Pauling scale and atomic configurations in crystal structures, we may expect two dominate interactions: ionic bonding between Ba and C_2 anion clusters, and strong covalent bonding in anion clusters. The calculated bond length of C≡C is 1.185 and 0.1136 nm in I4/mmm and C2/c crystals, respectively. These values in both structures are very close to the length of the triple bond of C_2H_2 molecules. When comparing the atomic positions of the I4/mmm type of BaC_2 before and after optimization, we can observe small derivations from neutron diffraction results and especially the decrease of the distance between carbon atoms in C_2 clusters. The shortest distance between Ba and C_2 clusters has a large value, and

Table 1 Reliability tests of this study by using different pseudopotentials and energy cut-off values

E_{cut} (eV)	600.0		660.0		700.0		280.0		360.0		Exp.	
pseudopotential	NCPP		NCPP		NCPP		USPP		USPP		–	
Space group	I4/mmm	C2/c	I4/mmm	C2/c	I4/mmm	C2/c	I4/mmm	C2/c	I4/mmm	C2/c	I4/mmm	C2/c
a (nm)	0.4318	0.4432	0.4360	0.4446	0.4360	0.4446	0.5672	Module is unsuccessfully	0.4338	0.4441	0.43599	0.44464
c (nm)	0.7175	0.8801	0.7177	0.8806	0.7177	0.8806	0.8255		0.7178	0.8801	0.71773	0.80861
E_g (eV)	2.4	3.3	2.2	3.0	2.2	3.0	1.9		2.2	2.9	–	–
E_{total} $(eV \cdot cell^{-1})$	–2034.56	–2034.29	–2034.42	–2034.04	–2034.31	–2034.00	–2035.66		–2034.49	–2034.27	–	–
$E_{binding}$ $(eV \cdot atom^{-1})$	–3.371	–3.340	–3.375	–3.342	–3.382	–3.347	–		–	–	–	–
ΔH $(eV \cdot atom^{-1})$	–0.43	–0.56	–0.50	–0.69	–0.57	–0.71	0.09		–0.59	–0.76	—	—

the interactions among them are dominated by pi bonding. The dispersion relations of band structures are determined by chemical interactions in crystal and topological properties of atomic orbitals. The calculated BS is shown in Figure 2. We can see that the semi-core orbital of Ba atoms is located very deeply in energy and mainly consist by 5s and 5p bands of metal. These bands show a rather flat shape in the ***k*** space, which indicates the localized nature in a real space. Near the Fermi level the main ingredients are attributed to C_2 anion clusters. Below the 5p bands of Ba atoms, we can also see the sigma bonded state of C≡C. Another anti-sigma band locates at −3 eV and it is very close to 2p bands of C atoms. In the energy range of −3 eV—0 eV, pi and anti-pi bonds formed by 2p bands of C atoms dominate the interactions in this type of crystals. The calculated band gap values of these two polymorphs are different; for I4/mmm this value is 2.2 eV and for C2/c that is 3.0 eV. The “gap problem” of standard DFT calculations made us conclude that both of these two structures are insulators. The conduction band mainly consists of 5d and 6s bands of metal atoms and anti-bonds of C_2 anions. These bands are high in energy and overlapped significantly among different cells which lead to Fermi free electron like dispersion relations in the ***k*** space and also are dispersed in a very large energy range.

2.3 Electron density distributions

In this part, we want to discuss the electron density map of BaC_2 polymorphs. Electron density can be used to illustrate the chemical bond type and bond strength qualitatively. Figure 3(a) and (b) depict the calculated results for I4/mmm and C2/c, respectively. We can see that the ionic bond between metal cations and C_2 anion clusters dominate both of these two polymorphs of BaC_2. Spherical like density contours around the cations are mainly attributed to the semi-core orbital of Ba atoms. Strong covalent interactions of C_2 clusters can be clearly seen, which are shown by the elongated contours around carbon atoms. A very low electron density value can be observed in the interstitial regions of the crystal which correspond to ionic bonds. In fact, the average electron density value around C_2 anion clusters is 10 times larger than the value between C_2 and Ba, and almost 100 times greater than that in interstitial regions of octahedrons in the crystal. Bond lengths and Mulliken population re-

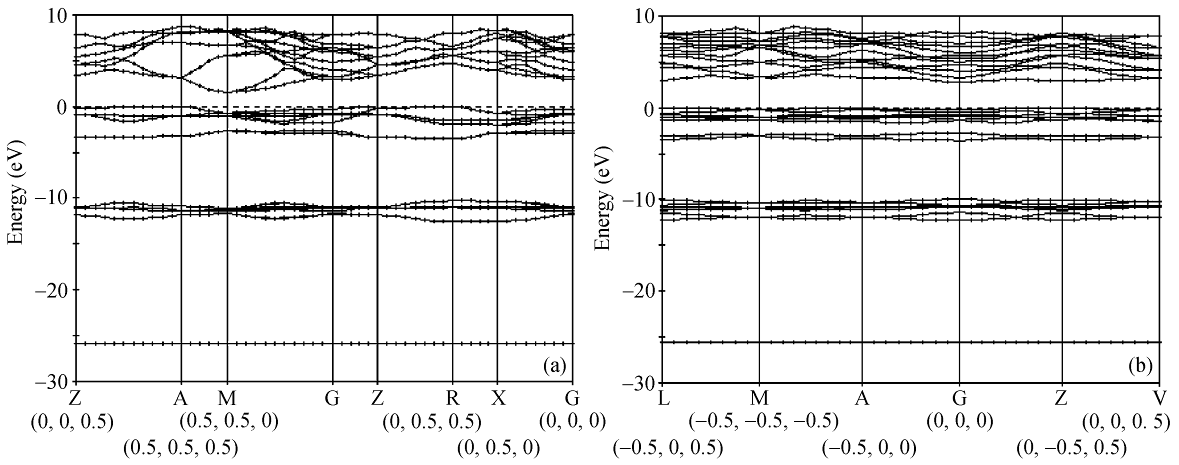

Figure 2 Band structures of BaC_2 polymorphs. (a) I4/mmm; (b) C2/c.

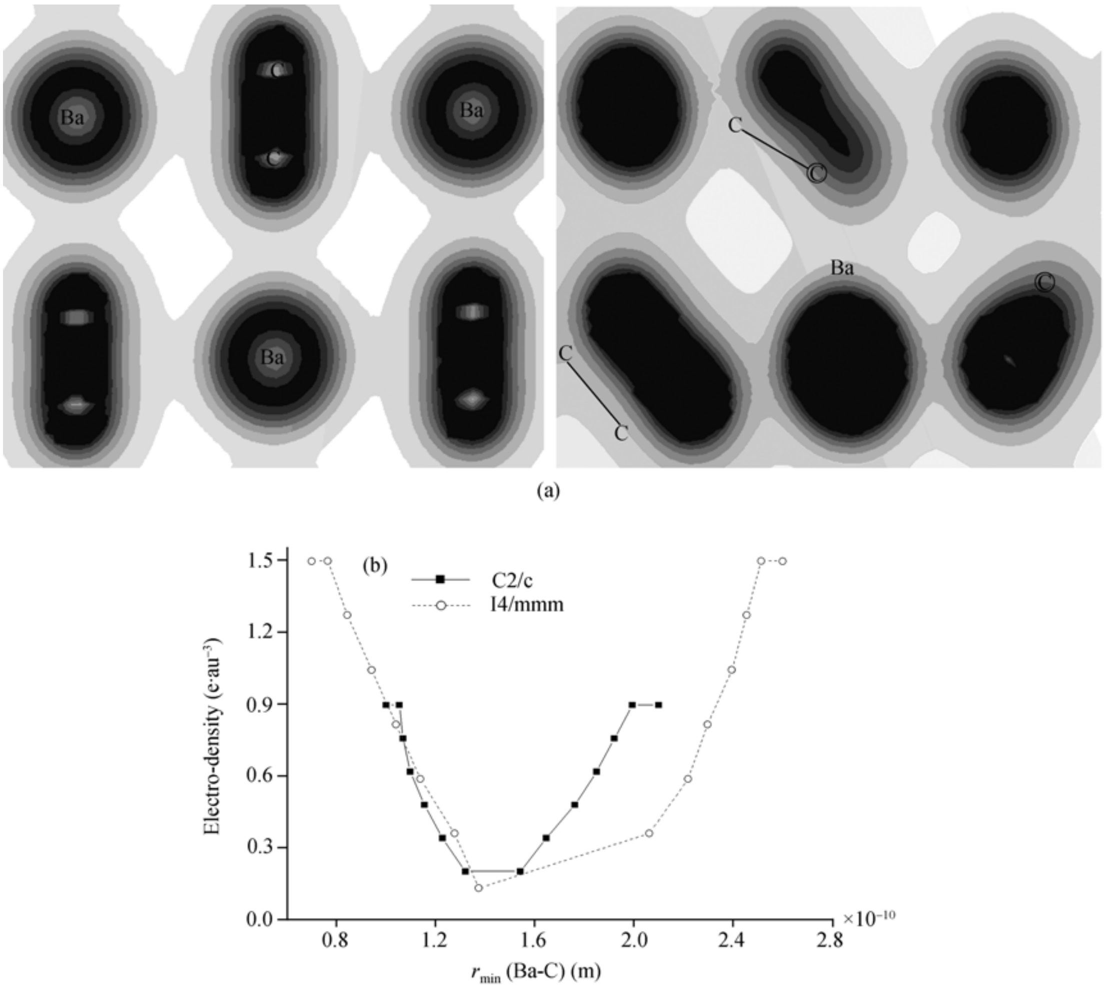

Figure 3 Total electron density distribution maps of BaC_2 polymorphs (left panel: I4/mmm, right panel: C2/c) (a) and density values as a function of distance between C_2 and Ba (b).

sults of C_2 anions clearly demonstrate the existence of triple bonds, and dumbbell like electron density contours verify this conclusion. In the I4/mmm type of BaC_2, Ba atoms are located in the center of octahedrons formed by C_2 anion clusters. The nearest distance between C_2 and Ba is 0.2945 nm and 0.2744 nm for I4/mmm and C2/c, respectively. Due to exceeding positive charge carried by Ba atoms and the very large distance among each other, we may expect a repulsion force between them, though it is very weak. Figure 3(b) shows that the electron density value for both of these two polymorphs of BaC_2 decreases rapidly when increasing the distance between Ba and C_2, and ionic interactions could be the reasonable reason. The population analysis results are listed in Table 2. Since the electronegative values of Ba and C are quite different, a significant charge transfer process from Ba to C can be observed after bonding. We can see that total charges carried by Ba and C in these two structures are very similar. The valence electrons of Ba almost completely transfer to 2p bands of C, and the semi-core orbital of Ba has little effect on the chemical bonding and remains unchanged.

Table 2 Population analysis of BaC_2 polymorphs

Space group	Species	s	p	d	Total (e)	Charge (e)	Bond	Population
I4/mmm	C	1.48	3.09	0	4.58	–0.58	C—C	1.62
	Ba	2.18	6	0.67	8.85	1.15	C—Ba	0.11
C2/c	C	1.49	3.08	0	4.57	–0.57	C—C	1.60
	Ba	2.18	5.98	0.70	8.86	1.14	C—Ba	0.22

2.4 Density of states (DOS) and bonding states

In this section, we want to open a discussion of DOS and chemical bonding states of BaC_2 polymorphs. Figure 4 shows the chemical bonding states and the corresponding DOS predictions in a purely theoretical way. We can see that 5s bands of Ba locate at the lowest

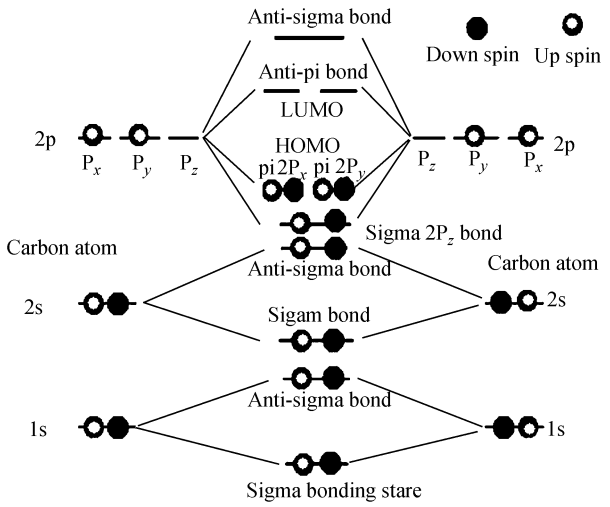

Figure 4 Theoretical prediction of bonding states of C_2^{2-} in BaC_2 molecules.

energy. Near the Fermi level, the DOS mainly consists of 2s and 2p bands of C atoms. A conduction band is dominated by metal's valence orbitals and anti-bonds of C_2 anions. We are very interested in the chemical bonding state of C_2 anions. Based on the classic molecular orbital theory, the triple bond of C_2 molecules contains one Sigma bond and two pi bonds, while these bonds are completely determined by the combinations of 2p orbitals of C atoms. The other two Sigma-like bonds formed by 2s orbitals can also be deduced, and we may observe two sharp peaks in DOS due to the splitting of Sigma and anti-Sigma bonds. On the other hand, one may also recall the orbital hybridization theory proposed by Pauling. In Pauling's theory, a triple bond in C_2 molecules is composed of a sp hybridized Sigma bond and two p-Pi bonds. This means 2s bands of C may overlap to 2p bands. The calculated DOS of these two polymorphs are illustrated in Figure 5. We can see several remarkable peaks in DOS which are typical for ionic crystals. In the energy range of –25 eV, it consists of the 5s band of Ba. Above this peak there is a double peak locates near –12 eV while the large peak corresponds to the 5p band and the small peak can be designated as the Sigma bonding state of C_2 anions. At the top of valence bands, the DOS is dominated by pi bonds of C atoms. The 2s and 2p bands of C atoms also overlap to each other in some degree and this is consistent with the Pauling's bonding theory. As shown in Figure 5, the calculated DOSes of these two structures are almost identical. Vohn et al.[10] has used X-ray diffraction analysis to investigate the temperature effect on the crystal structure and phase transition of BaC_2, and it is found that the transition of I4/mmm to C2/c occurs be-

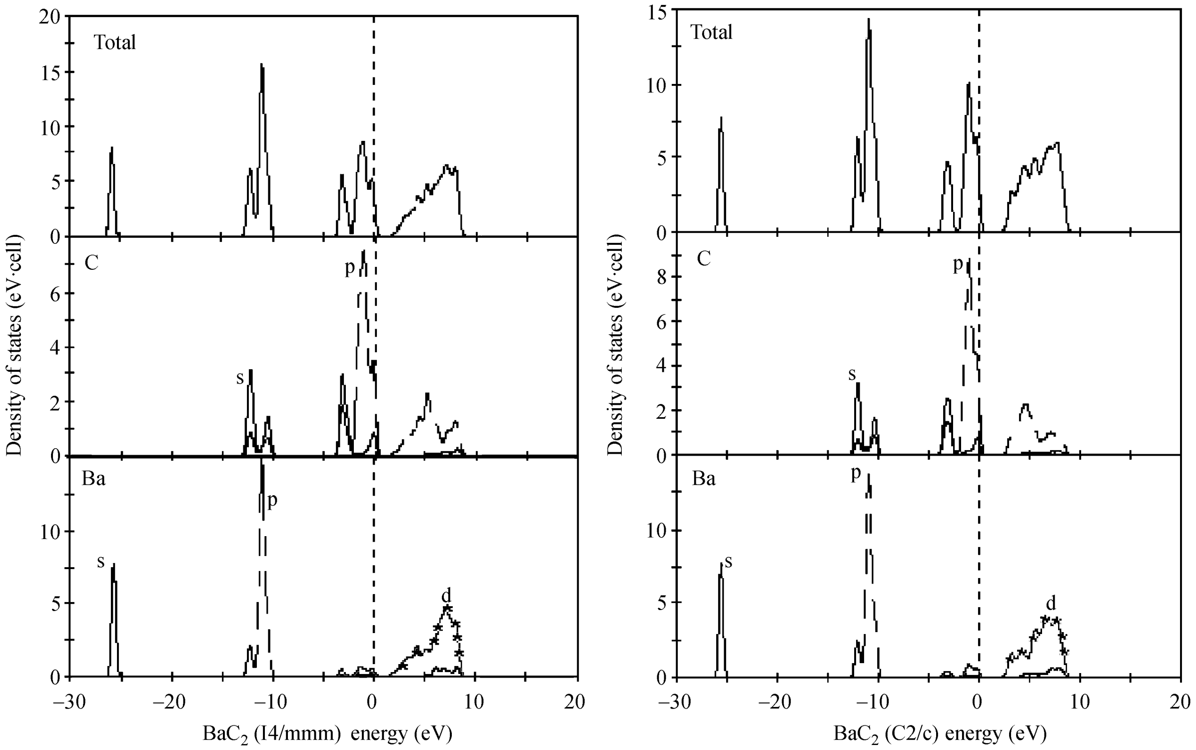

Figure 5 Total density of states and partial DOS of BaC_2 polymorphs.

low 170 K at ambient pressure. At the end of this paper, we will also evaluate the free energy of these two crystals as functions of temperature using DFT. From the results shown in Figure 6, we can clearly see the transition temperature locates near 132 K, which agrees well with the experimental prediction.

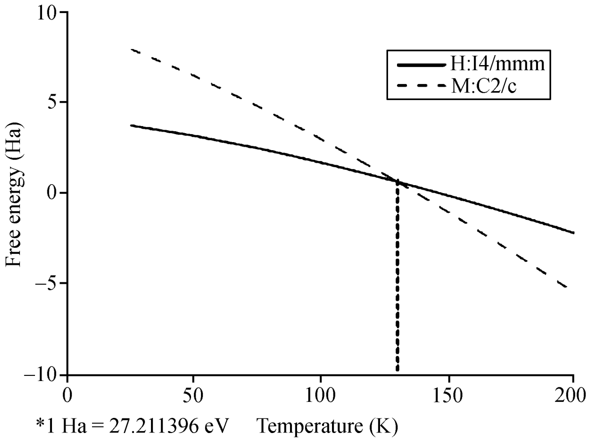

Figure 6 The calculated free energy of BaC_2 polymorphs as a function of temperature.

3 Conclusions

We used *ab initio* calculations to investigate the electronic structure of two BaC_2 polymorphs, and the bands structure and chemical bonding states of these two polymorphs were concerned. The whole crystal of BaC_2 consists of Ba cations and C_2 anion clusters. Ba atoms are located in the center of octahedrons formed by C_2 anions in the I4/mmm type of BaC_2. The chemical bonding state of anions can be designated as one Sigma bond and two Pi bonds. The shortest distance between Ba^{2+} and C_2^{2-} and the bond length in anion clusters are different in these isomers of BaC_2, which are 0.2945 and 0.1185 nm for the structure with the I4/mmm space group and 0.2744 and 0.1136 nm with C2/c, respectively. A much stronger covalent bond exists in anion clusters, which can be seen by inspecting the electron distribution contour that has a dull bell like shape between two carbon atoms. The calculated free energy curve as a function of temperature reveals that these two phases can be transformed to each other near 132 K at ambient pressure.

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