

# First-principles study of mechanical, vibrational and thermodynamic properties of magnetic XC compounds (X = Rb, Sr)

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Lattice dynamic and mechanical properties of hypothetical RbC and SrC compounds were investigated using the ab-initio pseudopotential method and a linear response scheme. The lattice dynamics was studied in the framework of the density functional perturbation theory (DFPT). The dynamical and mechanical stability of the hypothetical RbC and SrC compounds was proved in their equilibrium B1 structure. In addition, the same stability was confirmed in the B3 phase. The thermodynamic properties were also investigated. They exhibited the same trend in both phases, and followed the Debye model. These results were confirmed in the ferromagnetic state, which makes the investigated compounds promising candidates in the spintronic field.

Keywords: *alkaline-earth metal carbides; ferromagnetism; elasticity; phonon; thermodynamics*

## 1. Introduction

Ongoing research on current technologies to improve the components speed let us overcome the limitations of the classical electronic. The spintronics has become the most reliable alternative due to the studies already carried. However, the use of electron spin instead of its charge gives rise to a promising approach to overcome the problem of physical limits. Dilute magnetic semiconductors (DMS) have been widely studied due to their localized partially filled transition metal d-shell [1, 2]. The electronic states at the Fermi level induce high spin polarized currents [3, 4] which lead to remarkable magnetic properties. The last few years have seen the emergence of a new class of materials in this field, namely the d<sup>0</sup>-ferromagnets. This new class is based on alkali and alkaline earth metal elements, where the magnetic order is realized by the polarization of p-empty states without any direct contribution of d-electrons. Previous studies on alkali and alkaline earth metals with

V- and VI-elements predicted half-metallicity with ferromagnetic order in various structures [5–16]. The total magnetic moment takes an integer value depending on the empty states at the Fermi level. All these works were focused on the origin of magnetism, whereas the mechanical and dynamical stability question remains unanswered. In our previous paper we proved the stability of RbN and CsN compounds in their equilibrium B1 phase [17]. The main purpose of this work is to provide a comprehensive study of the stability of carbide-based compounds, namely RbC and SrC. We investigate the elastic properties, lattice dynamic and thermodynamic properties emerging from those compounds within first-principles framework.

## 2. Experimental

First-principles calculations have been performed using the plane-wave pseudopotential approach within the density functional theory (DFT) [18] implemented in the Quantum-ESPRESSO package [19]. The exchange

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correlation term was treated using the generalized gradient approximation of Perdew, Burke and Ernzerhof (PBE-GGA) [20]. We used the ultrasoft pseudopotentials with no linear core correction. The main computational parameters have been tested before performing calculations. The plane-wave cutoff was taken up as 45 Ry, where the Gaussian smearing technique has been used due to the metallic character. The Brillouin zone (BZ) was integrated using the Monkhorste-Pack scheme [21] with  $10 \times 10 \times 10$  mesh giving 94 special k-points. For elastic constants determination, we used  $14 \times 14 \times 14$  mesh to improve the accuracy on the energy with respect to strain.

The phonon part of the calculations has been realized within the density functional perturbation theory (DFPT) [22, 23]. It is based on a technique that allows calculation of system responses to external perturbations within the density functional framework with the addition of some perturbing potential. We used  $4 \times 4 \times 4$  uniform q-points mesh of the BZ to obtain real-space interatomic force constants (IFC's). The reciprocal-space dynamical matrices and subsequently vibrational frequencies have been obtained by fast Fourier transform at arbitrary q-vectors of the BZ.

### 3. Results and discussion

#### 3.1. Structural and electronic properties

In the first part of the calculation, we investigated the magnetic ground state in various phases. We performed a spin-polarized and spin-unpolarized calculation in five structures (B1, B2, B3, wurtzite (wz) and NiAs). All the structural parameters have been determined with energy minimization in nonmagnetic (NM), ferromagnetic (FM), and anti-ferromagnetic (AFM) state. Fig. 1 shows the variation of energy as function of volume. As seen in the figure, both compounds have the B1 phase as the most stable one, except that they differ in order between the B2 and NiAs phases. On the other hand, the RbC compound shows the anti-ferromagnetic state as the favorite one in all structures, whereas the SrC seems to be energetically stable in the ferromagnetic state,

except for the B2 phase which is found to be non-magnetic. Numerical results of the energy difference between the AFM and FM state are shown in Table 1 along with other structural parameters. In order to estimate the transition pressure  $P_t$  we calculated the enthalpy of formation with respect to pressure. The results show that three phase transitions, B2, B3 and wurtzite, are possible from the equilibrium B1 phase. As indicated in Table 1 the transition pressure ranges from  $-9.5$  GPa to  $7.1$  GPa.

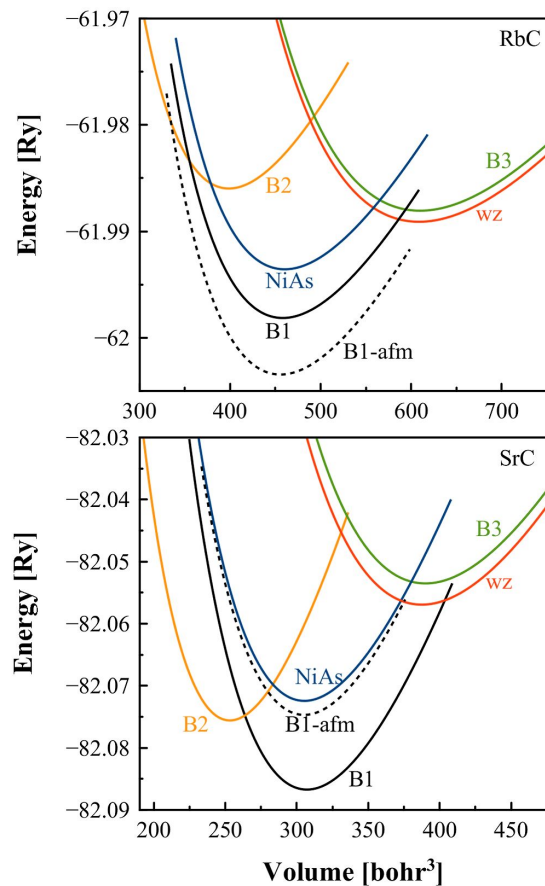


Fig. 1. Total energy as function of volume for both RbC and SrC. Solid lines denote the FM state whereas dotted lines denote the AFM state.

In order to discuss the origin of magnetism, we calculated the total and atomic spin-density of states (spin-DOS). Fig. 2 shows the spin-DOS at the equilibrium lattice constant of both RbC and SrC in the ferromagnetic state. As seen, the RbC

Table 1. Structural parameters for RbC and SrC in the five structures in their magnetic ground state along with the total magnetic moment,  $m_{\text{tot}}$ , in the ferromagnetic state.

Compounds	Phases	a [Å]	c/a	u	B [GPa]	$E_{\text{AFM-EFM}}$ [meV]	$m_{\text{tot}}$ [ $\mu_B$ ]	Magnetic ground state	$P_t$ [GPa]
RbC	B1	6.46	—	—	12.20	-72.25	3.00	AFM	—
		6.49 <sup>a</sup>	—	—	—	—	3.00 <sup>a</sup>	—	—
	B2	3.79	—	—	15.18	-296.18	3.00	AFM	7.1
	B3	7.15	—	—	8.09	-43.66	3.00	AFM	-1.7
	NiAs	4.44	1.75	—	11.38	-74.17	3.00	AFM	—
SrC	wz	5.04	1.61	0.379	8.11	-34.92	3.00	AFM	-1.6
	B1	5.67	—	—	44.9	163.65	2.00	FM	—
		5.68 <sup>a</sup>	—	—	—	—	2.00 <sup>a</sup>	FM	—
	B2	3.35	—	—	57.47	—	0.00	NM	6.4
	B3	6.14	—	—	32.12	242.24	2.00	FM	-9.0
	NiAs	3.88	1.79	—	43.46	86.80	2.00	FM	—
	wz	4.35	1.61	0.382	32.31	220.20	2.00	FM	-9.5

<sup>a</sup>[15]

is found to be semiconductor with fully spin polarized 2p states, whereas SrC is half-metal. These results are in good agreement with previous work on carbides compounds [15]. The total polarization of p-C states at the Fermi level demonstrates the sp-hybridization type. This hybridization involves electrons from the s-cation and p-C states which gives a magnetic moment corresponding to the number of holes in each configuration. It leads to 3  $\mu_B$  and 2  $\mu_B$  per formula unit for RbC and SrC, respectively.

### 3.2. Elastic constants

The elastic constants can be derived from the calculated total ground state energy. They give important information about the mechanical stability and the nature of the forces operating in solids. The elastic constants are calculated to determine the stiffness of a crystal for small deformations. In this section, we focused on the elastic constants of both B1 and B3 structures. To obtain the three constants,  $C_{11}$ ,  $C_{12}$ , and  $C_{44}$ , of the cubic systems, three deformations are needed. We used a uniaxial strain,  $(\delta, 0, 0, 0, 0, 0)$ , a volume strain  $(\delta, \delta, \delta, 0, 0, 0)$ , and a volume-conserving rhombohedral strain along the  $\langle 111 \rangle$  direction,  $(0, 0, 0, \delta, \delta, \delta)$ . Here,  $\delta$  is a single strain variable expressed in Voigt notation.

The calculated elastic parameters are summarized in Table 2. One can see that the value of the principal elastic constants  $C_{11}$ ,  $C_{12}$ , and  $C_{44}$  satisfy the well-known Born elastic stability criteria which, for a cubic system [24, 25], are given by:

$$\begin{aligned} C_{11} + 2C_{12} &> 0 \\ C_{11} - C_{12} &> 0 \\ C_{44} &> 0 \end{aligned} \quad (1)$$

We should, however, keep in mind that these stability criteria are valid only for zero-stress under deformation. Another important condition,  $C_{12} < B < C_{11}$ , is also satisfied, unfortunately the small value of  $C_{44}$ , especially for RbC, indicates the weak resistance to shear deformation. We can deduce the other elastic parameters such as the shear modulus  $G_H$ , the Young modulus  $E$ , the Poisson ratio  $\nu$ , and the Zener anisotropy factor  $A$ .

The Poisson ratio  $\nu$  gives the nature of bonding forces character. The obtained values range from 0.23 to 0.43 for both compounds in B1 and B3 structures. This indicates central interatomic forces [26] according to the standard values which range from 0.25 to 0.5. Another important parameter, which indicates the degree of plasticity [26], is the Young modulus  $E$ . The small values of  $E$  show a better plasticity, and indicate the bond type.

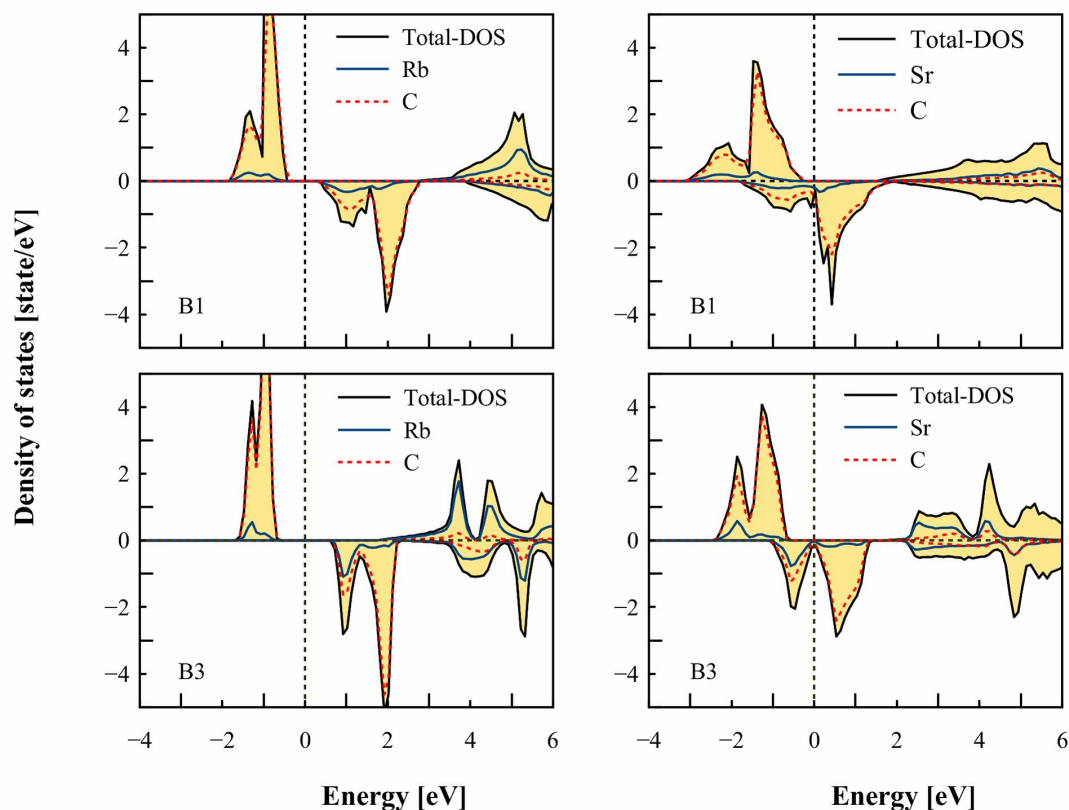


Fig. 2. Spin-density of states of both RbC (left panels) and SrC (right panels) in the B1 and B3 structures.

The predicted values indicate metallic bond in the B1 structure, but ionic in the B3 structure. The Zener anisotropy factor  $A$ , which is equal to unity for isotropic compounds, denotes the extent of elastic anisotropy. According to the obtained values, the compounds exhibit strong anisotropy in the B3 phase. Finally, the B:G ratio confirms the versatile properties of the studied compounds. The critical value between the ductility and the brittleness is 1.75. The obtained values of the B:G ratio indicates a brittle material in the B1 phase but still a ductile one in the B3 phase.

### 3.3. Phonon dispersion

The phonon dispersion curves were calculated in the B1 and B3 structures for both compounds. The calculations were performed with spin-polarization at arbitrary wave vector  $q$  of the Brillouin zone (BZ). The goal of such calculations was to investigate the stability of those compounds

in the ferromagnetic state. As is commonly known, there are two atoms per unit cell in the B1 and B3 structures which lead to six normal modes. The latter are divided into three acoustic modes and three optical ones. Fig. 3 shows the phonon dispersion curves along with the projected phonon density of states (PPDOS) of RbC and SrC in B1 and B3 phases. The general shape of the phonon dispersions can be easily understood with the PPDOS. The gap formed between the acoustical and optical modes is due to the atomic mass difference. The light C atom contributes to the optical modes at high frequencies, and the heavy Rb and Sr atoms contribute to the acoustical modes at low frequencies with a small contribution of carbon. The presence of the gap leads also to weaker electron-phonon interactions. As seen in Fig. 3, the general condition for the stability of RbC and SrC in terms of lattice dynamics is confirmed in both structures. All normal vibration modes have real and finite frequency. The analysis of the dispersion curves

Table 2. The elastic constants ( $C_{ij}$ ), the shear modulus ( $G_H$ ) and the Young modulus  $E$  (in GPa), the Poisson ratio ( $\nu$ ), the Zener anisotropy factor ( $A$ ), and the B:G ratio for RbC and SrC in the B1 and B3 structures.

	$C_{11}$	$C_{12}$	$C_{44}$	$G_H$	$E$	$\nu$	$A$	B:G
RbC								
B1	26.2	5.00	6.60	7.986	19.63	0.23	0.62	1.51
B3	10.1	7.20	4.50	2.862	7.68	0.34	3.10	2.85
SrC								
B1	87.3	26.8	25.6	27.37	68.75	0.26	0.85	1.72
B3	35.0	32.4	9.30	4.39	12.62	0.43	7.15	7.57

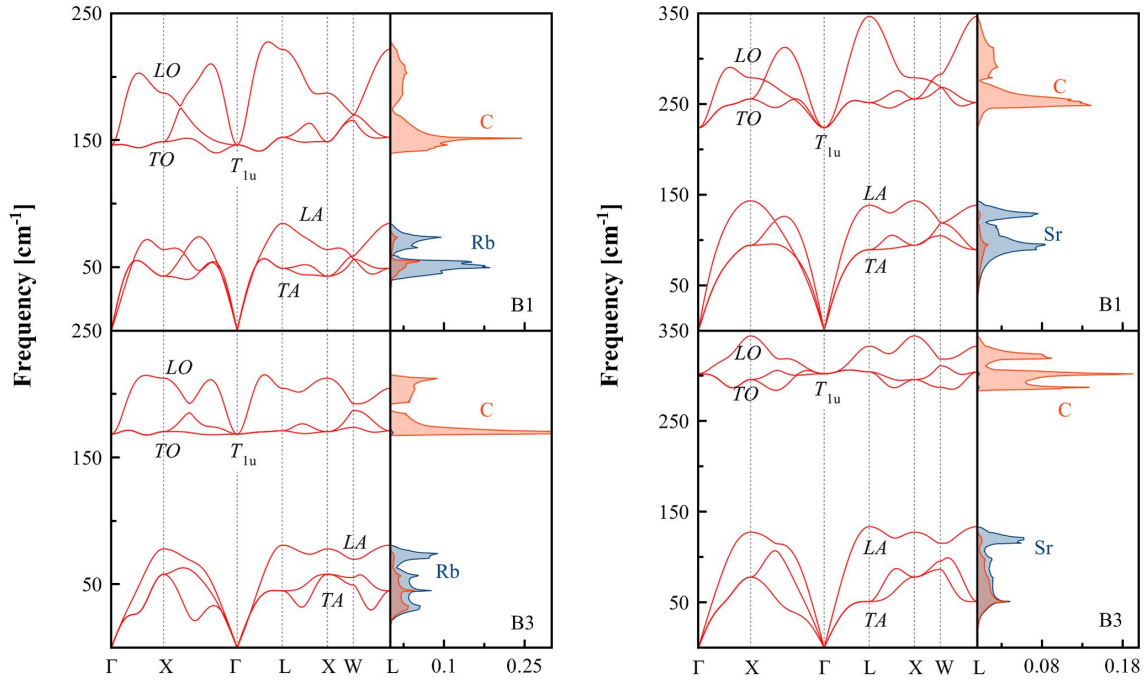


Fig. 3. Phonon dispersion curves along with projected-DOS of RbC (left) and SrC (right), in the B1 and B3 phases.

at the irreducible Brillouin zone center modes gives  $\Gamma = T_{1u}$  (acoustic) +  $T_{1u}$  (optic). For the optical modes,  $T_{1u}$  (optic) mode is infrared (IR) active. In Fig. 3 we see also that the LO and TO phonon modes are degenerated for both compounds and enough dispersive. We summarized the longitudinal and transverse frequencies in Table 3.

### 3.4. Thermodynamic properties

The thermodynamic properties can be derived from the phonon spectrum in the framework of the quasi-harmonic approximation (QHA) [27].

The phonon contribution to the temperature-dependent thermodynamic properties is therefore deduced. Fig. 4a and Fig. 4b show the free energy  $E_{\text{free}}$  and the internal energy  $E_{\text{int}}$  as function of temperature  $T$  for RbC and SrC in the equilibrium B1 structure, respectively. Note that both compounds exhibit similar trend in the B3 structure. The temperature is limited to 1000 K to avoid any influence from anharmonicity. The internal energy increases linearly with increasing temperature, whereas the free energy decreases. The zero temperature values of the internal and free energies do not vanish due to zero point motion. The results show that



Table 3. The longitudinal and transverse frequencies of the optical and acoustical branches at  $\Gamma$ , X and L axis (in  $\text{cm}^{-1}$ ).

	$T_{lu}$	$X_{TA/LA}$	$L_{TA/LA}$	$X_{TO/LO}$	$L_{TO/LO}$
RbC					
B1	146.21	42.74/63.83	49.07/84.42	148.76/187.11	152.22/221.56
B3	168.38	57.94/77.93	44.93/80.88	170.27/212.86	170.96/204.48
SrC					
B1	223.74	94.08/143.12	89.10/138.24	255.47/278.78	251.50/346.61
B3	302.28	77.94/127.50	51.02/133.62	295.94/344.02	304.32/332.72

$E_{\text{free}}^0 = E_{\text{int}}^0$  and take the value of 4.06 kJ/mol and 4.19 kJ/mol for RbC in B1 and B3 phase, respectively, and 6.66 kJ/mol and 6.95 kJ/mol for SrC in B1 and B3 phase, respectively. Fig. 4c and Fig. 4d show the contribution from the lattice vibrations to the entropy  $S$  which describes the disorder of micro-particles in thermodynamic system. It approaches a finite value at low temperature when the magnitude of the mass of the constituents approaches each other, and gradually changes with the temperature. The lattice contribution to the specific heat  $C_v$  is also calculated and shown in Fig. 4e and Fig. 4f. It follows the Debye model with a rapid variation up to  $\sim 200$  K, and converges to a limit value. This value, known as the Debye-Petit limit, is found equal to  $\sim 50$  J/K·mol for both compounds, which corresponds to  $3R \times n \text{ atoms} = 6R$ .

## 4. Conclusions

In summary, we investigated the mechanical and dynamical properties of the hypothetical RbC and SrC compounds. SrC is predicted to be half-metallic ferromagnet in its B1 phase, whereas RbC is a semiconductor and takes the anti-ferromagnetic state. The calculated elastic constants satisfy the mechanical stability conditions. The results on lattice dynamics in the framework of the density functional perturbation theory proof the dynamical stability in both B1 and B3 phases. The thermodynamic properties of both compounds exhibit the same trend and follow the Debye model.

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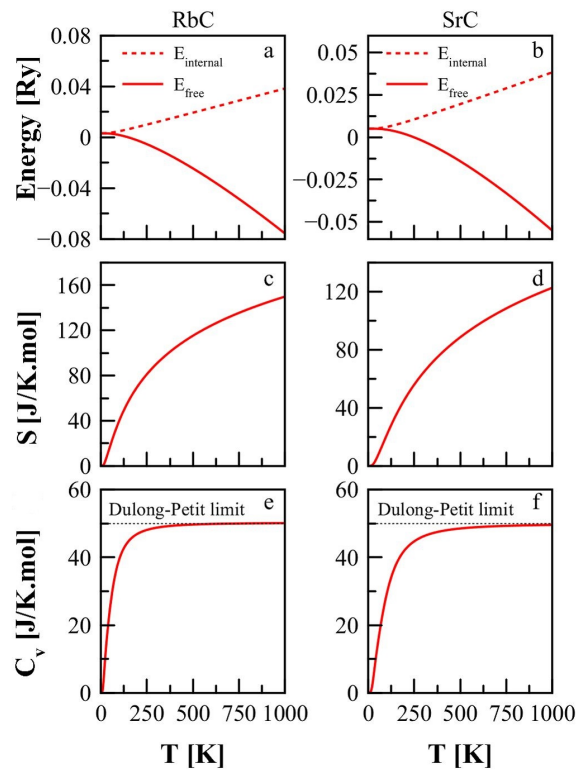


Fig. 4. Thermodynamic properties as function of temperature  $T$  of RbC (left panels) and SrC (right panels); (a) and (b) show the internal and the free energy, (c) and (d) the entropy  $S$ , (e) and (f) the specific heat  $C_v$ .

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