

Calculated structural, elastic and electronic properties of SrCl₂

V. Kanchana^{a,1}, G. Vaitheeswaran^{a,1}, A. Svane^{b,*}

^a Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, 70569 Stuttgart, Germany

^b Department of Physics and Astronomy, University of Aarhus, DK-8000 Aarhus C, Denmark

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Abstract

Density functional calculations have been performed to obtain the structural and electronic properties as well as elastic constants of cubic SrCl₂. The compound is found to be an insulator with an indirect band gap of 5.18 eV. The band gap initially increases and then decreases as a function of pressure. Calculated equilibrium properties such as lattice constant, bulk modulus and elastic constants are in good agreement with experimental studies. The calculated C_{44} value agrees well with experiment only when the chlorine atoms are allowed to displace under strain, indicating the importance of inner strain relaxation. From the elastic constants theoretical values of the Young's modulus, shear modulus, Poisson's ratio, sound velocities, and Debye temperature of SrCl₂ are obtained.

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1. Introduction

There is a growing interest in the study of alkaline-earth halides due to their technological importance in the field of solid state ionics. Crystals with fluorite structure, e.g. CaF₂, SrF₂, BaF₂, SrCl₂, and PbF₂ exhibit fast-ion conduction at high-temperatures [1]. These compounds have ionic conductivities at temperatures well below the melting temperature which finds potential application as solid state electrolytes. From the experimental side several interesting properties of alkaline-earth halides such as electronic structure and optical spectra, elastic constants, lattice dynamics and high-pressure structural phase transitions have been studied [2–9]. From the theoretical point of view the electronic structure, structural phase stability, equation of state, elastic constants, ionic conductivity, and temperature dependence of elastic parameters have been determined [10–19].

Strontium dichloride has the unique distinction of being the only divalent metal chloride crystallizing in the cubic $Fm\bar{3}m$ symmetry without an established temperature depen-

dent phase transition [20]. The smaller alkaline earth calcium has the orthorhombic $Pn\bar{m}$ structure in CaCl₂ [21]. MgCl₂ also occupies an interesting position in the sequence of crystal structure formed by groups II–VII elements with the AB₂ stoichiometry. Fluorite packing where A-coordination is eight, is usually preferred if the radius ratio (r_A/r_B) is greater than 0.73 (CaF₂ and SrCl₂). For smaller ionic radius ratio, the A-coordination decreases to six and the compounds adopt rutile or distorted rutile structures (MgF₂, CaCl₂, CaBr₂) first, and then layered structures (MgCl₂, MgBr₂, CaI₂) are adopted [22]. Barium dichloride crystallizes in the orthorhombic $Pnam$ symmetry [23]. The high-pressure structural phase transformation of BaX₂ (X = Cl, Br, I) has been reported by Leger et al. [24,25]. Like all the other fluorite type dihalides, SrCl₂ is also expected to undergo a high-pressure structural phase transition to orthorhombic structure [26]. On the other hand, there are no theoretical studies available explaining the ground state and elastic properties of this compound at ambient conditions. From the experimental side, sound velocity measurements on the single crystal SrCl₂ has been carried out by Lauer et al. [27]. Hence, in the present work we investigate the electronic structure of SrCl₂ with emphasis on the ground state properties and elastic properties. Section 2 deals with the computational details. Results are discussed in Section 3. Finally, conclusions are presented in Section 4.

* Corresponding author. Tel.: +45 8942 3678; fax: +45 8612 0740.

E-mail addresses: kanch@kth.se (V. Kanchana), vaithee@kth.se (G. Vaitheeswaran), svane@phys.au.dk (A. Svane).

¹ Present address: Department of Materials Science and Engineering, Royal Institute of Technology (KTH), Stockholm, Sweden.

2. Computational details

2.1. The electronic structure method

In this work, we have used the all-electron full-potential linear muffin-tin orbital (FP-LMTO) method to calculate the total energies as well as the basic ground state properties [28]. Here, the crystal is divided into two regions: non-overlapping muffin-tin spheres surrounding each atom and the interstitial region between the spheres. We used a double κ spdf LMTO basis (each radial function within the spheres is matched to a Hankel function in the interstitial region) for describing the valence bands. The following basis set Sr(4s, 5s, 4p, 4d), Cl(3s, 3p, 3d) were used in the calculations. Within the spheres, the potential is expanded in terms of spherical harmonics, while in the interstitial region, it is expanded in terms of plane waves. The exchange correlation potential was calculated within the generalized gradient approximation (GGA) scheme [29]. The charge density and potential inside the muffin-tin spheres are represented by spherical harmonics up to $l_{\max} = 6$, while in the interstitial region, 12,050 plane waves with the energies up to 112.56 Ry were included in the calculation. Total energies were calculated as a function of volume, for a (32, 32, 32) k -mesh and are fitted to the Birch equation of state [30] to obtain the ground state properties.

2.2. The elastic constants

A cubic system has three independent elastic constants C_{11} , C_{12} and C_{44} . The bulk modulus B of this system can be expressed as a linear combination of C_{11} and C_{12} . The condition for elastic stability is that B , $C_{11} - C_{12}$, and C_{44} are positive [31]. The elastic constants can be obtained by calculating the total energy as a function of volume conserving strains that break the cubic symmetry. For calculating C_{11} and C_{12} , we apply the tetragonal strain [32,33] that transforms the lattice vectors as

$$\mathbf{R}' = \epsilon \mathbf{R}, \quad (1)$$

where \mathbf{R} and \mathbf{R}' are the old and new lattice vectors, respectively, and ϵ is the strain tensor expressed in terms of the tetragonal deformation parameter δ as

$$\epsilon_{\text{tet}} = \begin{pmatrix} 1 + \delta & 0 & 0 \\ 0 & 1 + \delta & 0 \\ 0 & 0 & \frac{1}{(1 + \delta)^2} \end{pmatrix}. \quad (2)$$

Furthermore, the connection between the increase in total energy per unit cell volume, U , and the distortion, δ , is given by

$$U(\delta) = 6C'\delta^2 + O(\delta^3), \quad (3)$$

where C' is the tetragonal shear constant, which is also given by

$$C' = \frac{1}{2}(C_{11} - C_{12}). \quad (4)$$

By calculating C' and the bulk modulus

$$B = \frac{1}{3}(C_{11} + 2C_{12}) \quad (5)$$

from the Birch equation of state, the C_{11} and C_{12} parameters can be extracted.

Similarly, the following volume conserving monoclinic strain [34] is applied to calculate C_{44} :

$$\epsilon_{\text{mon}} = \begin{pmatrix} 1 & \frac{\delta}{2} & 0 \\ \frac{\delta}{2} & 1 & 0 \\ 0 & 0 & \frac{4}{(4 - \delta^2)} \end{pmatrix} \quad (6)$$

In this case, the strain energy density is even in the strain parameter and given by

$$U(\delta) = \frac{1}{2}C_{44}\delta^2 + O(\delta^4) \quad (7)$$

The strain energy density is the increase of the energy density of a distorted system, which is proportional to the corresponding change in total energy. The accuracy of the total energy differences needed for calculating the elastic constants is of the order of microRydberg, and one needs a highly accurate computational method, like the FPLMTO, to obtain a good agreement with experimental data.

C_{11} , C_{12} , and C_{44} comprise the complete set of elastic constants for a cubic system, and the shear modulus G , Young's modulus E , and the poisson's ratio ν can be derived using the following standard relations:

$$G = \frac{1}{5}(3C_{44} + C_{11} - C_{12}), \quad (8)$$

$$E = \frac{9BG}{3B + G}, \quad (9)$$

$$\nu = \frac{1}{2} \left(\frac{1 - E}{3B} \right) \quad (10)$$

2.3. The Debye temperature

Once we have calculated the Young's modulus E , bulk modulus B , and shear modulus G , we may obtain the Debye temperature, which is an important fundamental parameter closely related to many physical properties such as specific heat and melting temperature. At low temperatures the vibrational excitations arise solely from acoustic vibrations. Hence, at low temperatures the Debye temperature calculated from elastic constants is the same as that determined from specific heat measurements. One of the standard methods to calculate the Debye temperature, Θ_D , is from elastic constants data, since Θ_D may be obtained from the average sound velocity, v_m by the following relation [35]:

$$\Theta_D = \frac{h}{k} \left[\frac{3}{4\pi} \left(\frac{N_A \rho}{M} \right) \right]^{1/3} v_m, \quad (11)$$

where h is Planck's constant, k the Boltzmann's constant, N_A the Avagadro's number, M the molecular weight, and ρ is the density. The average wave velocity is approximately given as

[35]:

$$v_m = \left[\frac{1}{3} \left(\frac{2}{v_s^3} + \frac{1}{v_l^3} \right) \right]^{-1/3} \quad (12)$$

where v_l and v_s are the compressional and shear wave velocities, respectively, which are obtained from Navier's equation [37]:

$$v_l = \sqrt{\frac{(B + (4/3)G)}{\rho}}, \quad v_s = \sqrt{\frac{G}{\rho}}, \quad (13)$$

3. Results

3.1. Structural and elastic properties

The calculated ground state properties such as equilibrium lattice constant and the elastic constants are tabulated in Tables 1 and 2, where they are compared with the available experimental results [27]. The calculated lattice constant overestimates the experimental (RT value) by 0.8%, while the local density approximation (LDA) calculation of Ref. [42] is 2.5% too low, a behavior typical for the accuracy of LDA and GGA. The calculated bulk modulus at the theoretical equilibrium volume is in excellent agreement with the experimental value, however when evaluating the bulk modulus at the experimental volume, the theoretical value is 15% too large.

For the elastic constants, tabulated in Table 2, one observes excellent agreement with the experimental values. The calculated C_{11} is 5% lower than the experimental value. For C_{12} two experimental values are derived (providing an estimate of experimental uncertainty), and the C_{12} value calculated in the present work is 13 and 20% larger than these, respectively. For the monoclinic strain, applied for the calculation of C_{44} (Eq. (6)), the

Table 1
Calculated GGA values of lattice constant, a , expressed in Angstrom, bulk modulus, B_0 , in gigaPascal for SrCl₂, compared with experiment

	a	$B_0(V_0^{\text{th}})$	$B_0(V_0^{\text{exp}})$
Present	7.032	35.3	39.5
Experimental	6.9744 ^a		34.3 ^b
Other theory	6.80 ^c	–	

The bulk modulus has been calculated both at the experimental and theoretical equilibrium volume ($B_0(V_0^{\text{exp}})$ and $B_0(V_0^{\text{th}})$, respectively.)

^a Room temperature value from Ref. [22].

^b From elastic constants of Ref. [27].

^c LAPW calculations using LDA of Ref. [42].

Table 2
Calculated elastic constants, shear modulus G , Young's modulus E , all expressed in gigaPascal, and Poisson's ratio ν for SrCl₂

	C_{11}	C_{12}	C_{44}	G	E	ν
Present	66.9	19.6	9.9 (21.7)	15.4	40.3	0.310
Experimental ^a	70.2	16.4, 17.3	9.72	16.6	42.9	0.292

For C_{44} the value obtained without relaxation of chlorine positions is given in parentheses (see text for discussion). Results from the present study refer to the calculated equilibrium volume.

^a Data at 195 K, from Ref. [27].

Table 3

Calculated longitudinal, shear, and average wave velocity (v_l , v_s , and v_m , respectively) in 10³ m/s and the Debye temperature Θ_D in kelvin, from the average elastic wave velocity for SrCl₂

	v_l (10 ³ m/s)	v_s (10 ³ m/s)	v_m (10 ³ m/s)	Θ_D (K)
Present	4.30	2.25	2.52	170
Experimental ^a average	4.30	2.25	2.52	173
Experimental ^b (1 0 0)	4.79	1.78	2.02	–
Experimental ^b (1 1 1)	3.93	2.58	2.83	–

Results from the present study refer to the calculated equilibrium volume.

^a Averaged data at 195 K (Eq. (14)), from Ref. [27].

^b Directional sound velocities at 195 K, from Ref. [27].

crystal symmetry allows for additional optimization of the anion positions, which constitutes an important effect in ionic fluorites [15,43]. For SrCl₂, the calculated C_{44} is approximately twice too large when chlorine relaxation is not allowed for, while the value calculated including relaxations agrees within 2% with the experimental value. We mention as one point of caution the fact that the calculated values pertain to 0 K temperature, while experiments are performed at $T = 195$ K. Finite temperature generally tends to reduce the elastic constants. Consequently, we would expect the experimental values at low temperature to be somewhat larger than the values quoted in Table 2.

The sound velocities and Debye temperature of SrCl₂ were obtained from the calculated elastic constants of Table 2, as outlined in Section 2. The results are listed in Table 3 together with experimental results from Ref. [27]. A substantial anisotropy is found for the sound velocities in the experiment, which the theory of Section 2.3 does not take into account. Therefore, we have chosen to compare our calculated sound velocities and Debye temperatures with those obtained from experimental values averaged like:

$$v_{\text{av}} = \frac{3}{7}v^{(100)} + \frac{4}{7}v^{(111)}, \quad (14)$$

for both the longitudinal and transversal sound velocities. This leads to a very fine agreement, with a calculated Debye temperature of $\Theta_D = 170$ K, while the experimental value (obtained in a similar fashion from (11) and (14)) is 173 K, the deviation mainly stemming from the slightly different equilibrium volumes in theory and experiment.

3.2. Electronic structure

Though there are many experimental studies available regarding the rare-earth doping and ionic conductivity for SrCl₂, very few studies directly address the electronic structure. The Cl K β absorption and emission as well as L_{2,3} absorption was used by Sugiura [38] to investigate the valence bands and conduction bands of SrCl₂, and a fundamental band gap of 7.5 eV was determined. The charge density profile of SrCl₂ was studied experimentally [36] and theoretically [41], the latter using the Hartree–Fock method. Furthermore, as already mentioned, the LDA total energy was reported in Ref. [42] for the determination of the equilibrium volume. Hence, we study the electronic structure of SrCl₂, displaying in Fig. 1 the band structure along main

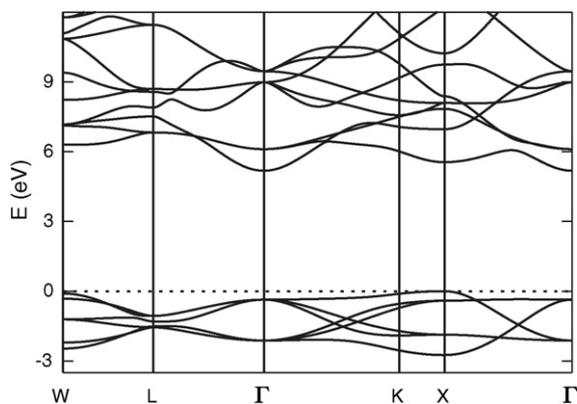


Fig. 1. Band structure of SrCl₂ at the theoretical lattice constant (GGA). The energy is set to zero at the valence band top.

symmetry lines of the fcc Brillouin zone, and in Fig. 2 the density of states. This compound is found to be a large gap insulator, with an indirect band gap of 5.18 eV. This is substantially lower than the 7.5 eV found experimentally [38], but in accord with the general underestimation of gaps by the Kohn–Sham eigenvalues of GGA and LDA [39,40]. The top of the valence band is found at the X point, while the bottom of the conduction bands is situated at the Γ point. The direct gap at Γ is 5.54 eV, while the direct gap at X is only marginally higher, 5.55 eV. From the density of states one observes that the valence bands are predominantly Cl p-like with a total width of 2.75 eV. The deep-lying Cl s-states in this compound are not shown (their GGA position is at ~ 12.7 eV below the valence band maximum). The states in the conduction band are dominated by the d-like states of strontium, with some hybridization with Sr s.

The variation of the band gap of SrCl₂ with compression is shown in Fig. 3. As observed in many insulators, the band gap initially increases with pressure and subsequently decreases upon compression. From the figure, this behavior is seen to originate from the crossing of levels at the conduction band between the Γ and X points. At large volumes, the conduction edge at the Γ point is the lowest, while with compression the X edge

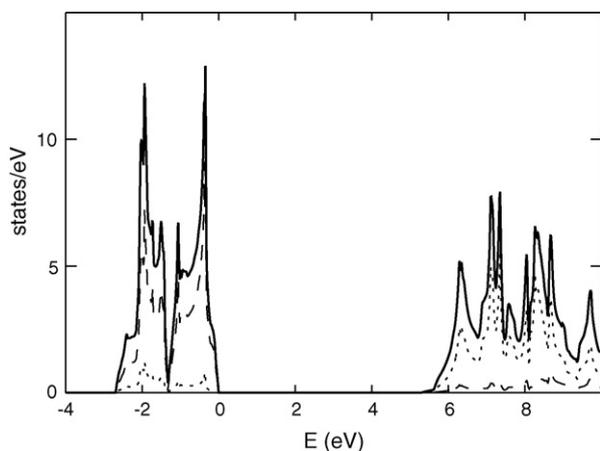


Fig. 2. Density of electronic states of SrCl₂ at the theoretical lattice constant (GGA). The energy is set to zero at the valence band top. The total density of states is shown with a full line, while projected density of states for Sr is given with a dotted line, and for Cl with a dashed line.

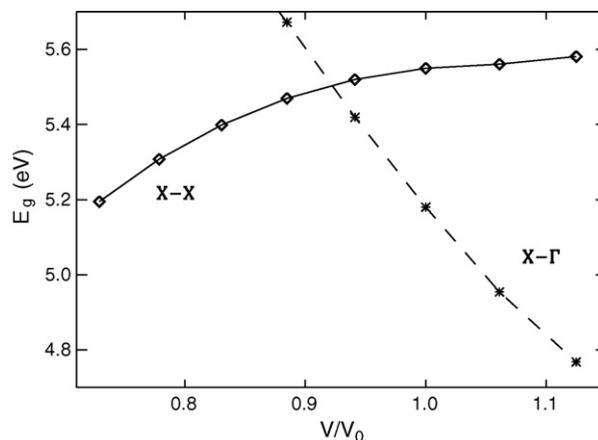


Fig. 3. The fundamental gap of SrCl₂ (in eV) as function of compression. Volume is given relative to the theoretical equilibrium volume. The conduction band minimum at Γ is shown with diamonds and a dashed line to guide the eye, while the minimum at X is shown with asterisks and full line.

moves below. The valence band maximum is always at the X point. The crossing occurs at $V/V_0 = 0.92$, where the gap has increased by 0.3 eV compared to the equilibrium value. At compressions larger than this threshold SrCl₂ is found to be a direct gap insulator, the gap being located at the X point of the Brillouin zone boundary.

4. Conclusions

Electronic structure calculations were reported for the first time for the compound SrCl₂, which is found to be a wide band gap insulator with an indirect gap of 5.18 eV. The equilibrium lattice constant, bulk modulus and elastic constants were evaluated from the GGA total energy and found to agree quite well with experimental information.

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References

- [1] L.E. Nagel, M. O'Keeffe, in: W. Van Gool (Ed.), *Fast Ion Transport in Solids*, North Holland, Amsterdam, 1973, p. 165.
- [2] R.T. Poole, J. Szajman, R.C.G. Leckey, J.G. Jenkin, J. Liesegang, *Phys. Rev. B* 12 (1975) 5872.
- [3] J. Barth, R.L. Johnson, M. Cardona, D. Fuchs, A.M. Bradshaw, *Phys. Rev. B* 41 (1990) 3291.
- [4] C.R.A. Catlow, J.D. Comins, F.A. Germano, R.T. Harley, W. Hayes, *J. Phys. Matter* 11 (1978) 3197.
- [5] M.O. Manasreh, D.O. Pederson, *Phys. Rev. B* 31 (1985) 3960.
- [6] D.H. Kühner, H.V. Lauer, W.E. Bron, *Phys. Rev. B* 5 (1972) 4112.
- [7] J.R. Kessler, E. Monberg, M. Nicol, *J. Chem. Phys.* 60 (1974) 5057.
- [8] L. Gerward, J.S. Olsen, S. Steenstrup, M. Malinowski, S. Asbrink, A. Waskowska, *J. Appl. Crystallogr.* 25 (1992) 578.
- [9] R.J. Angel, *J. Phys. Condens. Matter* 5 (1993) L141.
- [10] V. Kanchana, G. Vaitheeswaran, M. Rajagopalan, *J. Alloys Compd.* 352 (2003) 60.

- [11] V. Kanchana, G. Vaitheeswaran, M. Rajagopalan, *Physica B* 328 (2003) 283.
- [12] V. Kanchana, G. Vaitheeswaran, M. Rajagopalan, *J. Alloys Compd.* 359 (2003) 66.
- [13] V. Kanchana, Ph.D Thesis, Anna University, India (2002).
- [14] M. Catti, R. Dovesi, A. Paves, V.R. Saunders, *J. Phys. Condens. Matter* 3 (2003) 4151.
- [15] M. Mérawa, M. Llundell, R. Orlando, M. Gelize-Duvignau, R. Dovesi, *Chem. Phys. Lett.* 368 (2003) 7.
- [16] Z.H. Levine, J.H. Burnett, E.L. Shirley, *Phys. Rev. B* 68 (2003) 155120.
- [17] S. Ghosh, S. Dasgupta, *Phys. Rev. B* 35 (1987) 4416.
- [18] R.K. Singh, C.N. Rao, S.P. Sanyal, *Phys. Rev. B* 39 (1989) 13493.
- [19] S. Dasgupta, A.N. Basu, A. Basu, *Phys. Rev. B* 30 (1984) 7255.
- [20] H. Mark, S. Tolksdorf, *Z. Phys.* 33 (1925) 681.
- [21] A.K. Van Bever, W. Nieuwenkamp, *Z. Krist.* 90 (1935) 374.
- [22] R.W.G. Wyckoff, *Crystal Structures*, vol. 1, 2nd ed., Interscience Publishers, New York, 1982.
- [23] E.B. Brackett, T.E. Brackett, R.L. Sass, *J. Phys. Chem.* 67 (1963) 2132.
- [24] J.M. Leger, J. Haines, A. Atouf, *J. Appl. Crystallogr.* 28 (1995) 416.
- [25] J.M. Leger, A. Atouf, *J. Phys. Condens. Matter* 4 (1992) 357.
- [26] L.H. Brixner, *Mater. Res. Bull.* 11 (1976) 1453.
- [27] H.V. Lauer, K.A. Solberg, D.H. Kühner, W.E. Bron, *Phys. Lett.* 35A (1971) 219.
- [28] S.Y. Savrasov, *Phys. Rev. B* 54 (1996) 16470.
- [29] J.P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* 77 (1996) 3865.
- [30] F. Birch, *J. Appl. Phys.* 9 (1938) 279.
- [31] D.C. Wallace, *Thermodynamics of Crystals*, Wiley, New York, 1972.
- [32] M. Dacorogna, J. Ashkenazi, M. Peter, *Phys. Rev. B* 26 (1982) 1527.
- [33] N.E. Christensen, *Solid State Commun.* 49 (1984) 701.
- [34] A.Y. Liu, D.J. Singh, *Phys. Rev. B* 47 (1993) 8515.
- [35] O.L. Anderson, *J. Phys. Chem. Solids* 24 (1996) 909.
- [36] M.V.H. Linkoaho, *Acta Crystallogr. A* 35 (1978) 140.
- [37] E. Schreiber, O.L. Anderson, N. Soga, *Elastic Constants and their Measurements*, McGraw-Hill, New York, 1973.
- [38] C. Sugiura, *Phys. Rev. B* 9 (1974) 2679.
- [39] J.P. Perdew, M. Levy, *Phys. Rev. Lett.* 51 (1983) 1884.
- [40] L.J. Sham, M. Schlüter, *Phys. Rev. Lett.* 51 (1983) 1888.
- [41] D.R. Jennison, A.B. Kunz, *Phys. Rev. B* 13 (1976) 5597.
- [42] J.A. Válgoma, J.M. Perez-Mato, A. Garcia, K. Schwarz, P. Blaha, *Phys. Rev. B* 65 (2002) 134104.
- [43] V. Kanchana, G. Vaitheeswaran, A. Svane, A. Delin, *J. Phys. Condens. Matter* 18 (2006) 9615.