A review of the oxidation–pressure concept (OPC) and extended Zintl–Klemm concept (EZKC), and the emergence of the high-pressure Ni_2In -type phase of lithium sulfide (Li_2S) rationalized by reference to a newly defined stability enhancement ratio (S)

Angel Vegas^{a*} and H. Donald Brooke Jenkins^{b,c}

Received 6 February 2017

Accepted 27 July 2017

Edited by E. V. Boldyreva, Russian Academy of Sciences, Russia

Keywords: lithium sulfide; high pressure; oxidation–pressure concept; alkali metal sulfates; crystal chemistry; stability enhancement ratio (S); extended Zintl–Klemm concept (EZKC).

^aUniversidad de Burgos, Hospital del Rey, s/n, 09001 Burgos, Spain, ^bDepartment of Chemistry, University of Warwick, Coventry, West Midlands CV4 7AL, UK, and ^c'Fieldgate', 3 White Hill, Olney, Buckinghamshire MK46 5AY, UK.

*Correspondence e-mail: avegasmolina@ubu.es

Taking into account new experimental data [Barkalov *et al.* (2016). *Solid State Sci.* **61**, 220–224] on the pressure-induced Ni_2In phase of Li_2S , at 30 GPa, three concepts related to high-pressure phase transitions are reviewed here. This paper firstly reviews evidence that chemical oxidation (by inclusion of oxygen atoms) can produce a similar effect to the application of physical high pressure and temperature, in an effect labelled as the oxidation–pressure concept. Secondly, the pressure-induced Ni_2In phase of Li_2S is the final phase in the double transition antifluorite $\rightarrow$ anticotunnite $\rightarrow \text{Ni}_2\text{In}$, as is observed in other alkali metal sulfides. This new phase for Li_2S could be expected after knowledge of the high-pressure $Cmcm$ phase of Li_2SO_4 , which is a distortion of the hexagonal $I\text{-Na}_2\text{SO}_4$ phase, both having $M_2\text{S}$ subarrays of the Ni_2In -type. Thirdly, in order to clarify these links, a simple methodology is proposed for gauging the level of increased stability (by defining a stability enhancement ratio, S) when the extended Zintl–Klemm concept (EZKC) has been applied. The method uses relative values of the lattice potential energies estimated for Li_2S and for the pseudo-lattice $\Psi\text{-BeS}$ derived by applying the EZKC to Li_2S , after which, Li_2S can be reformulated as $\text{Li}^+[\text{LiS}]^- \equiv \text{Li}^+[\Psi\text{-BeS}]$.

1. Introduction

Many AX_2 compounds with fluorite or antifluorite structures undergo the double transition fluorite $\rightarrow$ cotunnite $\rightarrow \text{Ni}_2\text{In}$ under increasing pressure (Léger *et al.*, 1995). The alkali metal sulfides $M_2\text{S}$ ($M = \text{Li}$ to Cs) belong to such a family of compounds, although the double transition has been experimentally observed only for Na_2S at 7 and 16.6 GPa, respectively (Vegas *et al.*, 2001), and for Rb_2S at 2.6 and 4.5 GPa, respectively (Santamaria-Perez *et al.*, 2011a).

In contrast, K_2S seems to undergo a direct antifluorite $\rightarrow \text{Ni}_2\text{In}$ transition at 6 GPa without the formation of the intermediate anticotunnite structure, although, as reported by Vegas *et al.* (2002), the sample did change colour when ground in a mortar, indicating that an intermediate phase (probably cotunnite) can exist at very low pressures. Cs_2S is the only sulfide that is anticotunnite at ambient pressure, transforming into Ni_2In at 5 GPa (Santamaría-Pérez *et al.*, 2011b).

Finally, Li_2S undergoes the antifluorite $\rightarrow$ anticotunnite transition near 12 GPa (Grzechnik *et al.*, 2000) and, very recently, Barkalov *et al.* (2016) reported the expected anticotunnite $\rightarrow \text{Ni}_2\text{In}$ transition, observed near 30 GPa. The Ni_2In phase of Li_2S is then one of the two missing links which are

required in order to complete the double transition for the alkali metal sulfides, the second being the cotunnite phase of K_2S .

Vegas (2011) reported the complete relationship between these transitions involving both sulfides and selenides. In connection with this, Lazicki *et al.* (2006) provided an illustrative diagram incorporating all transitions observed in alkali sulfides, showing how, according to a general trend, the transition pressures decrease as the atomic number increases from Li to Cs.

Our new approach to describing and understanding inorganic structures is based on two principal concepts. The first is a concept that relates oxidation with pressure and the second is the application of the Zintl–Klemm concept to structures other than those of the Zintl phases for which the concept was originally postulated. In the following sections, both concepts will be reviewed in some detail and also explained are the calculations involving the ionic strength, which will be developed in final sections.

2. The oxidation–pressure concept (OPC)

In 2000, we began an investigation of the high-pressure phases of alkali metal sulfides (Grzechnik *et al.*, 2000; Vegas *et al.*, 2001), aiming to find experimental support for the concept that relates oxidation and pressure. This new concept was formulated by our group (Martínez-Cruz *et al.*, 1994) following the high-pressure experiments reported by Beck & Lederer (1993) on BaSn. The process is represented in Fig. 1 and should be thought of in the light of the double transition $\text{B1} \rightarrow \text{B33} \rightarrow \text{B2}$ which occurs as pressure increases in several

compounds, for example, in the alkali metal halides (Léger *et al.*, 1998).

Under normal conditions, BaSn is a CrB-type (B33) structure, but at 3.5 GPa it undergoes a $\text{B33} \rightarrow \text{B2}$ transition. As in CrB, the Ba atoms form blocks of trigonal prisms (blue spheres in Fig. 1a), centred by the Sn atoms (grey spheres), which when connected, form infinite zigzag chains. When BaSn is compressed at a pressure of 3.5 GPa, it transforms into the B2 structure.

As early as 1946, Megaw (1946) had reported the structure of the cubic BaSnO_3 perovskite and, as in all perovskites, its cationic $[\text{BaSn}]$ substructure is also of the CsCl type (B2). The combination of both results leads on to a simple new concept that can be expressed as follows:

The BaSn alloy can stabilize the CsCl-type structure either by oxidizing the BaSn alloy or by applying an external pressure.

The most surprising result was that the dimensions of the unit cells were almost exactly the same, *viz.* 4.048 Å in BaSn at 4.0 GPa and 4.1085 (15) Å in BaSnO_3 at atmospheric pressure. Fig. 1 shows that ‘the inclusion of three oxygen atoms in the BaSn structure (B33) produces the same effect as does the application of a pressure of 3.5 GPa, resulting in both cases in the occurrence of the $\text{CrB} \rightarrow \text{CsCl}$ phase transition’. In other words, *the insertion of O atoms into the structure of an alloy, such as BaSn, is equivalent to the application of a physical pressure to the alloy structure.*

This means that under the O-atom subarray of any oxide one can discover, within the cationic subarray, structures of high-pressure phases of the parent alloy. This point is important because it means that from the structures of oxides one can infer the existence of new phases for the alloys. Moreover, a comparison of the structures of both alloys and oxides can thus explain the phase transitions which occur either at high temperature or at high pressure. Vegas & Mattesini (2010) explained these structural coincidences in terms of the electron localization function (ELF).

3. The effect of temperature

Yet another example is provided by KCl and the KClO_3 and KClO_4 oxides. KCl possesses the NaCl-type structure under normal conditions but undergoes the double transition $\text{B1} \rightarrow \text{B33} \rightarrow \text{B2}$ when subjected to increasing pressure. Thus, when KCl is oxidized to KClO_3 , the halide transforms into the CrB (B33) structure. Application of an additional pressure of 1.1 GPa to KClO_3 then causes the formation of a rhombohedral distortion of the cubic CsCl (B2) structure, so completing the double transition.

KCl can be oxidized to KClO_4 , a process in which the $[\text{KCl}]$ subarray adopts not the B33 structure but the B27 (FeB-type) structure, which is a stacking variant of the B33 structure. The important outcome is that on heating KClO_4 , one recovers the original NaCl structure of KCl. The process is sketched in Scheme 1, from which one can conclude that temperature can balance the effect of pressure, causing the structure to retrace the path induced by pressure.

Figure 1

Diagram of the transformations undergone by the BaSn (B33) alloy when oxidized and compressed at 3.5 GPa. In the first case, the cubic BaSnO_3 perovskite is obtained. In the second case, the transition $\text{B33} (\text{CrB}) \rightarrow \text{B2} (\text{CsCl})$ takes place. In the perovskite, we have drawn the O_6 octahedra around the Sn atoms. Colour key: Ba blue, Sn grey and O red.

Thus, the effect of temperature can cause the opposite effect to that of pressure in the oxides of Si and Ge, and these provide another example of the robustness of this idea, as is shown in Fig. 2. Both Si and Ge possess diamond-like structures under normal conditions.

Scheme 1

When Si is oxidized under normal conditions, it forms the quartz structure. Its Si subarray is that of the CrSi_2 type (also cinnabar-like). This structure is so far unknown for Si but exists in other II–VI and III–V compounds. An extra pressure is required in order to transform quartz into stishovite (rutile-type), whose Si skeleton is β -Hg, as was determined by O'Keefe & Hyde (1985).

When quartz is heated it undergoes the double transition quartz $\rightarrow$ tridymite $\rightarrow$ cristobalite. In tridymite, the Si subarray recovers the structure of hexagonal (lonsdaleite) and, at higher temperature, in cristobalite, the effect of pressure is balanced, so recovering the original Si structure, as is shown in Fig. 2.

Figure 2

Set of drawings showing the oxidation of elemental Si ($Fd\bar{3}m$) (a) to yield the quartz structure due to the pressure exerted by the O atoms. (b) When high pressure is applied to the quartz structure, SiO_2 becomes rutile-like, forming the stishovite structure drawn in (c), with unit-cell parameters $a = 4.1501(8)$ and $c = 2.6575(8)$ Å at 5.84 GPa (Sugiyama *et al.*, 1987). When the quartz structure is heated, the pressure exerted by the O atoms is released and the cristobalite structure, drawn in (d), is formed, in which the Si subarray recovers a tetragonal distortion of its original $Fd\bar{3}m$ structure.

Germanium, also $Fd\bar{3}m$ under ambient conditions, when oxidized to GeO_2 transforms into a rutile-like structure (as does stishovite) without passing through the intermediate structure of quartz. However, at 1306 K, the rutile GeO_2 overcomes the O-atom pressure and the compound recovers its 'lost' quartz structure, as shown in Scheme 2. The Si/Ge skeletons of quartz and γ -Sn are illustrated in Fig. 2.

Scheme 2

Pursuing this concept, our interest has been directed towards finding new structural relationships between high-pressure phases of the $M_2\text{S}$ sulfides on the one hand and the cationic arrays of their respective sulfites and sulfates on the other. We have reported some of these relationships in previous articles (Vegas & Jansen, 2002; Santamaria-Perez *et al.*, 2011a,b; Vegas, 2011) and, very recently, Barkalov *et al.* (2016) have reported on the Ni_2In -type phase of Li_2S ($P6_3/mmc$). As was stated earlier, this finding represents a missing link in the general scheme of behaviour of alkali metal sulfides under pressure and also conforms to the structural transitions observed to be occurring in the corresponding sulfate at high temperature and/or high pressure. This new Li_2S phase also confirms the validity of the relationship between oxidation and pressure, as will be discussed further below.

4. Lithium sulfide

The three phases of Li_2S are represented in Fig. 3. The $Fm\bar{3}m$ anti-fluorite structure is drawn in Fig. 3(a). It consists of a face-centred cubic subarray of S atoms, with the $2n$ tetrahedra filled with Li atoms. At 12 GPa, this structure transforms into the $Pnma$ anticotunnite phase represented in Fig. 3(b) (Grzechnik *et al.*, 2000) and above 30 GPa this then stabilizes the $P6_3/mmc$ Ni_2In structure, as represented in Fig. 3(c) (Barkalov *et al.*, 2016). In both the $Pnma$ and $P6_3/mmc$ phases, the Li

atoms form chains of trigonal prisms that are centred on the S atoms.

Sommer & Hoppe (1977) described the anticotunnite structure as being a distorted hexagonal close packed array of S atoms, with Li(1) atoms filling the octahedral voids and Li(2) atoms located at tetrahedral voids but displaced towards the centre of trigonal bipyramids. The antiferite $\rightarrow$ anticotunnite transition implies then that a change takes place in the S-atom substructure going from face-centred cubic to a distorted hexagonal close packed array. In the Ni_2In phase, this hexagonal close packed S-atom array becomes more regular ($P6_3/mmc$); Li(1) atoms remain at the octahedral voids and Li(2) atoms now occupy the centred trigonal bipyramids. Vegas & García-Baonza (2007) described both structures in a more complete way in terms of the *extended Zintl–Klemm concept* (EZKC), as discussed below.

5. Lithium sulfates

When the antiferite phase of Li_2S is oxidized to Li_2SO_4 , the sulfate forms a monoclinic ($P2_1/c$) structure (Alcock *et al.*, 1973) that consists of a strongly distorted face-centred cubic S-atom substructure, with the $2n$ tetrahedral voids filled with the Li_2 atoms. This partial structure is represented in Fig. 4(b),

which consists of a rather regular central octahedron inserted into a strongly distorted cube. The Li atoms (blue spheres) form, in turn, a strongly distorted cube. This structure is to be compared with the regular antiferite structure shown in Fig. 3(a).

The description represented in Fig. 4(b) is due to Parfitt *et al.* (2005) and indicates that, according to the oxidation–pressure relationship, the insertion of four oxygen atoms per Li_2S unit provokes an extreme distortion of the antiferite structure of Li_2S . However, the pressure exerted by the oxygen atoms is not high enough to cause the stabilization of any of the two possible high-pressure phases of Li_2S , *i.e.* anticotunnite or Ni_2In .

Only the application of an additional pressure of 6.7 GPa, converts the distorted antiferite into the $Cmcm$ structure (Na_2CrO_4 -type) that is intimately related to that of Ni_2In , as can be seen by comparing Fig. 4(c) with Fig. 3(c). Thus, the transition (that cannot be attained by oxidation alone) is achieved by applying external pressure. The distortion of the Ni_2In structure is not capricious, as it also occurs in $\text{III-Na}_2\text{SO}_4$, one of three high-temperature phases of Na_2SO_4 obtained by heating thenardite ($\text{V-Na}_2\text{SO}_4$), a phase which is stable under normal conditions. The transition sequence caused by increasing the temperature is thenardite ($Fddd$) $\rightarrow$

$Cmcm \rightarrow Pnma \rightarrow P6_3/mmc$ (Rasmussen *et al.*, 1996), which was discussed by Vegas & García-Baonza (2007) and also later by Vegas (2011) within a wider transition scenario.

The existence of the $P6_3/mmc$ phase of Li_2S could have been anticipated for two reasons. Firstly, by virtue of the transitions which are known to be undergone by the heavier sulfide analogues (Na to Cs) and secondly, because, according to the oxidation–pressure concept, the existence of the high-pressure $Cmcm$ phase of Li_2SO_4 (Na_2CrO_4 -type) is indicative of the existence of an isostructural high-pressure phase for Li_2S (Barkalov *et al.*, 2016).

The importance of the oxidation–pressure relationship resides in the fact that in the same way that we can stabilize high-pressure phases of an alloy (sulfide) by oxidation, so, similarly, it is possible to traverse backwards towards the low-pressure phases of the alloy on heating the oxide. Such is the case in Li_2SO_4 , in that, when heated above 848 K, the effect of pressure is compensated for and the distorted structure of Li_2SO_4 (as drawn in Fig. 4b) recovers the regular antiferite structure of Li_2S (as represented in Fig. 3b). This

Figure 3

(a) The antiferite structure of Li_2S , stable under normal conditions. (b) The anticotunnite structure, stable above 12 GPa, projected on the ac plane. (c) The Ni_2In -type structure, stable above 30 GPa, projected onto the (110) plane. Colour key: S yellow and Li blue.

Figure 4

(a) The high-temperature phase of Li_2SO_4 . The SO_4 tetrahedra have rotational disorder and have been represented as small cubes. Colour key: S yellow, O red and Li blue. (b) Partial structure of the Li_2S subarray in the Li_2SO_4 structure, showing the extreme deformation of the S_8 and of the Li_8 cubes of the distorted antiferite structure. (c) The high-pressure phase ($Cmcm$) of Li_2SO_4 , which is a distortion of the Ni_2In structure.

system provides yet a further example of how pressure and temperature can play opposing roles, thus permitting a rational explanation of both the phase transitions observed and the structures themselves.

6. The extended Zintl–Klemm concept (EZKC)

The second concept applied to the structures is the extended Zintl–Klemm concept (EZKC). The word ‘extended’ was added to the original Zintl–Klemm concept (Zintl, 1939) to emphasize that the same concept could also account for the nature of cationic skeletons of oxides, such as aluminates, silicates, germanates, *etc.* (Santamaría-Pérez & Vegas, 2003; Santamaría-Pérez *et al.*, 2005), which do not fit into the compositions of the original Zintl phases. Later, we realised that the application of the Zintl–Klemm concept to other compounds, supposedly ionic, such as alkali metal sulfides, and also alloys, such as Ni_2In (Vegas & García-Baonza, 2007), ternary alkali oxides (Vegas, 2012) or stuffed bixbyites (Vegas *et al.*, 2009), explained structural features by employing the assumption that electron transfer would take place between conventional cations, even when they are of a similar kind.

Such an approach accounted, for example, for the Al substructure in the stuffed Li_3AlN_2 bixbyite. The electron transfer from the three Li atoms to N₂ and Al yields the pseudo-formula $(\text{Li}^+)_3[\Psi\text{-Si } \Psi\text{-O}_2]$, giving sense to the fact that the Al atoms, located at the 16c site and of the space group $Ia\bar{3}$, reproduce the structure of the dense phase of Si and Ge (Vegas *et al.*, 2009). The same structure admitted other interpretations, although these always required the assumption of unexpected (and therefore unlikely) electron transfers between the constituent atoms that yielded a set of resonance structures. This is explained in the articles by Vegas & García-Baonza (2007), Vegas *et al.* (2009) and Vegas (2012). This idea was been applied previously by Vegas & García-Baonza (2007) to the structures of binary alkali metal sulfides and can now be extended further to the structures of Li sulfides and Li sulfates.

7. The structures of Li_2S considered in the light of the EZKC

It is normally assumed that Li_2S is normally formulated as $(\text{Li}^+)_2\text{S}^{2-}$, in which two Li^+ cations neutralize the sulfide anions. This model should be applicable to the three phases of Li_2S represented in Fig. 3. However, if we suppose that, in the light of the EZKC, electron transfer could occur between cations – in this case between the Li atoms – then this would give rise to the pseudo-formula $\text{Li}^+[\text{LiS}]^-$ equivalent to $\text{Li}^+[\text{Li}^-\text{S}]$ and also equivalent to $\Psi\text{-He}[\Psi\text{-BeS}]$. Because real BeS has the zincblende structure, this pseudo-formula should be implicit in the antifluorite structure, as is shown in Fig. 5(a). In other words, a pair of atomic species ($\Psi\text{-BeS}$) can form a four-connected network (ZnS-type) that should be ‘induced’ by the other Li atom. Thus, four of the eight Li atoms forming the cubes (Fig. 3a) would act as donors, while the other four must act as acceptors. The eight Li atoms per cell should form two resonance structures in which the donor–acceptor character of the Li atoms exchanges dynamically.

In the anticotunnite phase, this interpretation seems more plausible because the eight Li atoms in the unit cell are separated into two different Wyckoff positions. Thus, in contrast to antifluorite, in anticotunnite, only one of the Li atoms should be considered as a donor, while the other one should act as an acceptor, which together with the S atoms forms a $\text{II-VI} \equiv \text{IV-IV}$ network. In the case of the antifluorite structure, charge transfer between atoms of the same kind (Li^+ and Li^-) could be questioned because the assigned space group $Fm\bar{3}m$ implies that the eight Li atoms occupy the *same* Wyckoff position. However, if the Li atoms are separated into two families occupying two different Wyckoff positions, then the two Li-atom species can be differentiated. This could be achieved by lowering the symmetry of the assigned space group. We believe that such small differences would be extremely difficult to detect in a standard crystal structure refinement.

Returning again to the anticotunnite structure, the network formed is identical to the $[\text{LiSe}]^- \equiv [\Psi\text{-BeSe}]$ in NaLiSe or to the $[\text{NaS}]^-$ subarray in $\text{K}[\text{NaS}]$. The $[\Psi\text{-BeS}]$ skeleton is drawn with red lines in Fig. 5(b). In the case of ternary sulfides,

Figure 5

(a) The antifluorite structure of Li_2S , in which the eight Li atoms forming the cubes are separated into two families. Li(1) (light-blue spheres) would act as donors and Li(2) (dark-blue spheres) as acceptors. According to the EZKC, the $[\text{Li}(2)\text{S}]^-$ skeleton transforms into a pseudo-anion $[\Psi\text{-BeS}]$ that adopts a diamond-like skeleton, as does real BeS. (b) A stereopair of the anticotunnite structure of Li_2S , in which the Li(1) atoms (dark-blue spheres) convert the pair of $\text{Li}(2)\text{S}$ into the $[\Psi\text{-BeS}]$ skeleton that forms a four-connected network characteristic of tetrels such as the Al^- ($\Psi\text{-Si}$) in the Zintl phase SrAl_2 . (c) The Ni_2In phase of Li_2S , in which donor Li(1) atoms form 3^6 planar nets (connected with green lines) that intercalate with 6^3 planar nets of composition $[\text{Li}(2)\text{S}]^- \equiv [\Psi\text{-BeS}]$ that form graphene-like layers also characteristic of tetrels (carbon).

electron transfer between cations seems more acceptable due to the different electronegativity of the two alkali atoms and, in addition, because the atom that forms the four-connected network with the S atoms is always the most electronegative atom, *i.e.* Li becomes $[\Psi\text{-Be}]$ and Na becomes $[\Psi\text{-Mg}]$. The skeleton formed by the pair $[\Psi\text{-BeSe}]$ is unknown for tetrels, yet appears in Zintl polyanions such as $\text{Al}^- \equiv [\Psi\text{-Si}]$ in the Zintl phase SrAl_2 . The skeletons are represented in Fig. 5(b).

The third phase, the Ni_2In type, can be analysed in a similar manner. This structure, which has been interpreted as a superstructure of the MgB_2 type, can also be interpreted in the light of the EZKC. Also here, the two Li atoms are separated into two families. That located at (0, 0, 0) should act as donor, whereas the Li(1) atoms, together with the S atoms, form a honeycomb-like planar net of pseudo-formula $[\Psi\text{-BeS}]$, where the π -electrons should be delocalized. The structure is drawn in Fig. 5(c) and is to be compared with Fig. 3(c).

8. Ionic strength as a predictor of stability changes resulting from application of the extended Zintl–Klemm concept (EZKC)

We move now to describe how the changes discussed above can easily be shown to bring about an increase in lattice energy and thus lead to a relatively more stable lattice.

The lattice potential energy, *i.e.* U_{POT} (kJ mol^{-1}), of any individual crystal structure is a measure of the energy required to pull the lattice apart into its gaseous ions, separated by infinity. The greater in magnitude the lattice energy, the harder (more energy needed) it will be to separate the structure into these gaseous-ion components and hence the more stable will be the resulting lattice itself. Such a principle will be used here in order to compare the stabilities of the various Li_2S lattices. Two earlier articles (Vegas & Jenkins, 2017; Jenkins & Vegas, 2017) introduced a quantitative approach which predicted that the EZKC, when applied to the $(\text{NH}_4)_2\text{Ge}_7\text{O}_{15}$ lattice (Vegas & Jenkins, 2017) and also to a series of 25 silicate lattices (Jenkins & Vegas, 2017), led to the creation of increasingly stable lattices (and hence represent the thermodynamic driving force behind the changes), hence justifying the use of this extended concept in the new approach currently being developed by Vegas (2017), which offers new rationalizations for the atomic arrangements to be found within crystal structures.

Because both the germanate and the silicate lattices which were considered possessed lattice energies which were larger in magnitude than 5000 kJ mol^{-1} , then the Glasser–Jenkins generalized equation (1), suitable for ionic materials with lattice energies $U_{\text{POT}} > 5000 \text{ kJ mol}^{-1}$ (Glasser & Jenkins, 2000, 2005, 2016), was employed:

$$U_{\text{POT}} = AI(2I/V_m)^{1/3} \quad (1)$$

and used as a practical quantitative means of gauging the effect (change) on lattice stability caused by application of the EZKC. In the equation, $A = 121.4 \text{ kJ mol}^{-1} \text{ nm}$, I is the ionic strength of the lattice which is defined by

$$I = \frac{1}{2} \sum n_i z_i^2, \quad (2)$$

where n_i is the number of ions of type i in the formula unit bearing a charge z_i (with the summation extending over all the ions in the formula unit), and V_m is the formula-unit volume of the lattice. Since the electron migration proposed in the germanate and silicate papers caused as a result of EZKC occurs in both types of lattice, without change of their unit-cell volumes, therefore V_m is constant, so leaving I to be the only variable to be considered in equation (1), hence we can write

$$U_{\text{POT}} \propto I^{4/3}. \quad (3)$$

Thus, when comparing a series of silicate lattices in respect of the EZKC (Jenkins & Vegas, 2017), where the formula-unit volume, V_m , remains constant for each silicate lattice during the electron shifts caused by EZKC, we can further simplify relationship (3) into the truncated form:

$$U_{\text{POT}} \propto I, \quad (4)$$

which requires consideration of only the relative magnitudes of the ionic strength of the lattice when EZKC is imposed.

Since equation (1) is known to reproduce values of $U_{\text{POT}} > 5000 \text{ kJ mol}^{-1}$ to within $\pm 7\%$ of the experimentally known lattice energies, then equation (1) should provide reliable energies for our application made in previous work and so, therefore, should the subset of I values used in our earlier study.

In the case of this study, the lattice energies being considered are $< 5000 \text{ kJ mol}^{-1}$ in magnitude and hence equation (1) is no longer relevant. As part of volume-based thermodynamics (VBT) (Jenkins *et al.*, 1999), equations have been developed for lattices for which $U_{\text{POT}} < 5000 \text{ kJ mol}^{-1}$ (Jenkins *et al.*, 1999, 2002; Jenkins, 2009) and it is to these equations we can now turn in order to consider the quantifying effect of EZKC on the Li_2S lattice transitions.

Applicable for lattice energies in magnitude up to 5000 kJ mol^{-1} , the appropriate VBT equation takes the form:

$$U_{\text{POT}} = 2I[\alpha(V_m)^{-1/3} + \beta] \\ = \sum n_i z_i^2 [\alpha(V_m)^{-1/3} + \beta], \quad (5)$$

where α and β are appropriately fitted constants whose magnitudes depend on the stoichiometry of the lattice [see Table 1 in Jenkins *et al.* (2002)]. The coefficient α is close in value to the general electrostatic conversion factor $A = 121.4 \text{ kJ mol}^{-1}$ which appeared in equation (1).

Accordingly, for Li_2S , the ionic strength, I , takes a value equal to

$$I(\text{Li}_2\text{S}) = \frac{1}{2} \sum n_i z_i^2 = \frac{1}{2} [(2)(+1)^2 + (1)(-2)^2] = 3, \quad (6)$$

and having $\alpha = 165.3 \text{ kJ mol}^{-1} \text{ nm}$ and $\beta = -29.8 \text{ kJ mol}^{-1}$ (corresponding to M_2X stoichiometry), the $Fm\bar{3}m$ (anti- CaF_2) phase of Li_2S , has a cubic unit-cell parameter $a = 5.719 \text{ \AA}$, and hence a cell volume of $V_{\text{cell}} = 186.17 \text{ nm}^3 = 0.18617 \text{ nm}^3$, with $Z = 4$, whereupon $V_m = 0.18617/4 = 0.04654 \text{ nm}^3$ and $V_m^{-1/3} = 2.7799 \text{ nm}^{-1}$. Hence, from equation (5):

Table 1
Relative stabilities of Li₂S lattices.

Structure (Fig. 5)	<i>I</i>	<i>V</i> _{cell} (nm ³)	<i>Z</i>	<i>V</i> _m (nm ³)	(<i>V</i> _m) ^{−1/3} (nm ^{−1})	<i>U</i> _{POT} (kJ mol ^{−1})
Li ₂ S <i>Fm</i> $\bar{3}m$ antifluorite at ambient pressure	3	0.1862	4	0.04655	2.7799	2578
Li ₂ S <i>Pnma</i> anticotunnite at > 12 GPa pressure	3	0.1489	4	0.03722	2.9951	2792
Li ₂ S <i>P6</i> ₃ / <i>mmc</i> Ni ₂ In at > 30 GPa pressure	3	0.1095	4	0.02762	3.3082	3102

Table 2
Relative stabilities of the EZKC (Ψ -BeS) lattices.

EZKC structure (Fig. 5)	<i>I</i>	<i>V</i> _m (nm ³)	(<i>V</i> _m) ^{−1/3} (nm ^{−1})	<i>U</i> _{POT} (kJ mol ^{−1})
(Ψ -BeS) <i>Fm</i> $\bar{3}m$ antifluorite at ambient pressure	4	0.04655	2.7799	3126
(Ψ -BeS) <i>Pnma</i> anticotunnite at > 12 GPa pressure	4	0.03722	2.9951	3331
(Ψ -BeS) <i>P6</i> ₃ / <i>mmc</i> Ni ₂ In at > 30 GPa pressure	4	0.02762	3.3082	3629

$$U_{\text{POT}}(\text{Li}_2\text{S}) = 2(3)[165.3 (2.7799) - 29.8] = 2578. \quad (7)$$

This prediction of the lattice energy is close to the Born–Fajans–Haber experimental value of 2472 kJ mol^{−1} obtained by Jenkins from a thermochemical cycle and further agrees well with the calculated value of Morris (1953) of 2464 kJ mol^{−1}. Both results are quoted by Jenkins in Weast (1988). The good agreement of the total lattice energy values makes it probable that the energetics, which are estimated in connection with the application of the EZKC, are likely to be reasonably close to reality.

We consider now the case of the Li₂S phase transition:

for which the data appears in Table 1. Firstly we see that as the pressure is increased then the cell volume, *V*_{cell}, decreases, as expected, the formula-unit volume, *V*_m becomes smaller and the parameter (*V*_m)^{−1/3} and hence [via equation (5)] the lattice energies of the progressive phases increase and they become relatively more stable. However, once we apply the EZKC, then

so conversion of Li into Be makes it necessary to consider the BeS lattice (Ψ -He is a noble gas, has no charge and so cannot contribute to *I*) and, furthermore, the ionic strength, *I*, is caused by EZKC to increase from 3 to 4:

$$I(\text{BeS}) = \frac{1}{2} \sum n_i z_i^2 = \frac{1}{2} [(1)(+2)^2 + (1)(-2)^2] = 4. \quad (8)$$

The conversion of the Li₂S lattice into the Ψ -BeS lattice causes a small change of *I* (from 3 to 4), indicating that the lattice is further stabilized, since, from equation (5), as *V*_m^{−1/3} is kept constant, *U*_{POT} is proportional to the ionic strength, *I*.

As in the case for Li₂S calculated in equation (7), the lattice energy of BeS, *U*_{POT} (BeS), as calculated from VBT takes the form

$$U_{\text{POT}}(\text{BeS}) = 2 \left\{ 4 [119(V_m)^{-1/3} + 60] \right\} \quad (9)$$

and the VBT value is found to be close to the Born–Fajans–Haber cycle experimental value (see Weast, 1988), giving us confidence concerning the likely realism of the values generated in Table 2. In this table, we see that as the phase changes take place the stability of the lattice increases, which can be attributed to be the thermodynamic *raison d'être* for the transitions to take place, as is suggested in this paper, as stability increases.

9. Stability enhancement ratio, *S*

We have proposed in two previous articles (Vegas & Jenkins, 2017; Jenkins & Vegas, 2017) a stability enhancement ratio (denoted *S*), which measured the ratio of the *I* factor, for the phase resulting from EZKC application, to the original *I* factor for the classical formula. *S* was always greater than 1, denoting increased stability as brought about by EKZC.

$$S[Fm\bar{3}m \rightarrow P6_3/mmc] = 3629/3126 = 1.16 \quad (10)$$

whilst the intermediate *S* values are:

$$S[Fm\bar{3}m \rightarrow Pnma] = 3331/3126 = 1.07 \quad (11)$$

and for *Pnma* → *P6*₃/*mmc* the ratio is:

$$S[Pnma \rightarrow P6_3/mmc] = 3629/3331 = 1.09. \quad (12)$$

10. Concluding remarks

The observation by Barkalov *et al.* (2016) of the existence of the *P6*₃/*mmc* (Ni₂In) phase of Li₂S has now been completely rationalized in this article, showing that it conforms to expectations when compared with the transitions which are found for heavier sulfides and further by employing the oxygen-pressure concept in order to show, in turn, that the existence of the high-pressure *Cmcm* phase of Li₂SO₄ (Na₂CrO₄-type) indicates the existence of an isostructural high-pressure phase for Li₂S. The importance of this observation of the *P6*₃/*mmc* phase (Ni₂In) for Li₂S (Barkalov *et al.*, 2016) is thus considerable.

It is true that Schön *et al.* (2001, 2004) predicted an Ni₂In phase for Li₂S from theoretical calculations, but its existence was not seen within the wider context that has been used here, *i.e.* correlating the structures of sulfides with those of sulfates.

The structures ideally need to be explained in a rational manner – a task that we have undertaken by correlating the structures of the sulfates with those of the sulfides, predicting

their existence by applying the oxidation–pressure concept and the extended Zint–Klemm concept as well. We believe that the interpretations reported here will be most helpful as input information in predicting codes.

In our case, the usefulness of the EZKC has been enhanced by the use of the ionic strength (Glasser & Jenkins, 2005; Jenkins & Vegas, 2017). A quantitative measure, in the form of the enhancement factor S , which is the degree to which stabilization has been created by the EZKC approach, has been introduced and applied. The relevance of this factor is only likely to emerge from a continued study of the relative magnitudes of this property in differing structures. For the moment, at least, we might infer that for Li_2S the overall $Fm\bar{3}m \rightarrow P6_3/mmc$ transition has a slightly greater stabilization effect than have the intermediate phase changes since:

$$S[Fm\bar{3}m \rightarrow P6_3/mmc] > S[Pnma \rightarrow P6_3/mmc] \\ \approx S[Fm\bar{3}m \rightarrow Pnma].$$

Acknowledgements

HDBJ would like to acknowledge the hospitality of his friend and colleague J. M. Recio in the University of Oviedo for inviting him to lecture to the Oviedo group, their post-graduates and undergraduate students, and for making him so very welcome there. HDBJ also wishes to acknowledge the kind assistance given to him by Doña Esperanza Iglesias, the Librarian at the Institute Rocasolano (CSIC, Madrid), who obtained for him some obscure Russian publications in connection with another programme of work being undertaken with his colleague, Professor Catherine Housecroft at the University of Basel, Switzerland. As always, the University of Warwick is thanked for their generous support of this work via the Albright & Wilson Fund and for making these continuing study visits to Spain possible. My colleague, AV, is also thanked for his friendship and continuing collaboration.

References

- Alcock, N. W., Evans, D. A. & Jenkins, H. D. B. (1973). *Acta Cryst.* **B29**, 360–361.
- Barkalov, O. I., Naumov, P. G., Felser, C. & Medvedev, S. A. (2016). *Solid State Sci.* **61**, 220–224.
- Beck, H. P. & Lederer, G. (1993). *Z. Anorg. Allg. Chem.* **619**, 897–900.
- Glasser, L. & Jenkins, H. D. B. (2000). *J. Am. Chem. Soc.* **122**, 632–638.
- Glasser, L. & Jenkins, H. D. B. (2005). *Chem. Soc. Rev.* **34**, 866–878.
- Glasser, L. & Jenkins, H. D. B. (2016). *Phys. Chem. Chem. Phys.* **18**, 21226–21240.
- Grzechnik, A., Vegas, A., Syassen, K., Loa, I., Hanfland, M. & Jansen, M. (2000). *J. Solid State Chem.* **154**, 603–611.
- Jenkins, H. D. B. (2009). *Sci. Prog.* **92**, 91–92.
- Jenkins, H. D. B., Roobottom, H. K., Passmore, J. & Glasser, L. (1999). *Inorg. Chem.* **38**, 3609–3620.
- Jenkins, H. D. B., Tudela, D. & Glasser, L. (2002). *Inorg. Chem.* **41**, 2364–2367.
- Jenkins, H. D. B. & Vegas, A. (2016). *Acta Cryst.* **B72**, 927–927.
- Jenkins, H. D. B. & Vegas, A. (2017). *Acta Cryst.* **B73**. In the press.
- Lazicki, A., Yoo, C. S., Evans, W. J. & Pickett, W. E. (2006). *Phys. Rev. B*, **73**, 184120.
- Léger, J. M., Haines, J., Atouf, A., Schulte, O. & Hull, S. (1995). *Phys. Rev. B*, **52**, 13247–13256.
- Léger, J. M., Haines, J., Danneels, C. & de Oliveira, L. S. (1998). *J. Phys. Condens. Matter*, **10**, 4201–4210.
- Martínez-Cruz, L. A., Ramos-Gallardo, A. & Vegas, A. (1994). *J. Solid State Chem.* **110**, 397–398.
- Megaw, H. D. (1946). *Proc. Phys. Soc.* **58**, 133–152.
- O’Keefe, M. & Hyde, B. G. (1985). *Struct. Bond.* **61**, 77–144.
- Parfitt, D. C., Keen, D. A., Hull, S., Crichton, W. A., Mezouar, M., Wilson, M. & Madden, P. A. (2005). *Phys. Rev. B*, **72**, 054121.
- Rasmussen, S. E., Jørgensen, J.-E. & Lundtoft, B. (1996). *J. Appl. Cryst.* **29**, 42–47.
- Santamaría-Pérez, D. & Vegas, A. (2003). *Acta Cryst.* **B59**, 305–323.
- Santamaría-Pérez, D., Vegas, A. & Liebau, F. (2005). *Struct. Bond.* **118**, 121–177.
- Santamaría-Pérez, D., Vegas, A., Muehle, C. & Jansen, M. (2011a). *Acta Cryst.* **B67**, 109–115.
- Santamaría-Pérez, D., Vegas, A., Muehle, C. & Jansen, M. (2011b). *J. Chem. Phys.* **135**, 054511.
- Schön, J. C., Cančarević, Z. & Jansen, M. (2004). *J. Chem. Phys.* **121**, 2289–2304.
- Schön, J. C., Wevers, M. A. C. & Jansen, M. (2001). *J. Mater. Chem.* **11**, 69–77.
- Sommer, H. & Hoppe, R. (1977). *Z. Anorg. Allg. Chem.* **429**, 118–130.
- Sugiyama, M., Endo, S. & Koto, K. (1987). *Mineral. J.* **13**, 455–466.
- Vegas, A. (2011). *Struct. Bond.* **138**, 133–198.
- Vegas, A. (2012). *Acta Cryst.* **B68**, 364–377.
- Vegas, A. (2017). *New Models in Inorganic Structures. From the Elements to the Compounds*. IUCr/Oxford University Press. In preparation.
- Vegas, A. & García-Baonza, V. (2007). *Acta Cryst.* **B63**, 339–345.
- Vegas, A., Grzechnik, A., Hanfland, M., Mühle, C. & Jansen, M. (2002). *Solid State Sci.* **4**, 1077–1081.
- Vegas, A., Grzechnik, A., Syassen, K., Loa, I., Hanfland, M. & Jansen, M. (2001). *Acta Cryst.* **B57**, 151–156.
- Vegas, A. & Jansen, M. (2002). *Acta Cryst.* **B58**, 38–51.
- Vegas, A. & Jenkins, H. D. B. (2017). *Acta Cryst.* **B73**, 94–100.
- Vegas, A., Martin, R. L. & Bevan, D. J. M. (2009). *Acta Cryst.* **B65**, 11–21.
- Vegas, A. & Mattesini, M. (2010). *Acta Cryst.* **B66**, 338–344.
- Weast, R. (1988). Editor. *Handbook of Chemistry and Physics*, 69th ed. Boca Raton: CRC Press.
- Zintl, E. (1939). *Angew. Chem.* **52**, 1–6.