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## The crystal energy of pyrite

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**Abstract.** The crystal energy of iron pyrite, ideally of composition  $\text{FeS}_2$ , is evaluated with an ionic model, assuming atoms in the solid to be ionized as  $\text{Fe}^{2+}$  and  $\text{S}^{2-}$ . To calculate the proper crystal energy, terms accounting for the static electric dipole moments of the sulphur ions have to be included. For this purpose, so-called electrostatic lattice constants are introduced, with Madelung's constant being the first term of a Taylor expansion for the electrostatic interaction energy. Following these considerations, a theoretical crystal energy of  $-2835$  kJ per mole of pyrite is calculated. The formalism gives a first estimation of the strength of the sulphur dipole moment in the  $\text{FeS}_2$  lattice:  $\mu_{\text{S}} = 12.3 \times 10^{-30}$  C m (3.7 D). The thermodynamic Born–Haber cycle is generalized to include polarized species, yielding an 'experimental' value for the crystal energy of  $-2893$  kJ per mole of pyrite, which differs only by 2% from the theoretical one.

### 1. Introduction

For many years the structural, optical, electronic and other properties of semiconducting iron pyrite, ideally of composition  $\text{FeS}_2$ , have been investigated by solid-state physicists and chemists (for recent reviews see [1, 2]). However, until now no information concerning the crystal energy of the material has been reported, although its structure is cubic and the summation should be done easily. Because of the high absorption coefficient for electromagnetic radiation in the visible range and its non-toxic constituents, pyrite has gained interest as a potential solar-cell material in the recent decade [3–7]. Therefore it seems important to understand the basic properties of the material. Here, crystal energy calculations are presented for iron pyrite and compared with an experimental value derived from the Born–Haber cycle.

The theoretical crystal energy  $W_{\text{th}}$  consists of different terms, describing interactions of attractive and repulsive nature between the atoms in the crystal lattice. Most important are the electrostatic interaction  $W_{\text{e}}$  and the core–core repulsion  $W_{\text{r}}$ , the latter accounting for the interaction between electronic cores of the ions. The parts of the internal energy due to thermal vibrations and van der Waals attraction are usually small compared with the other terms. For alkali halides and compounds in the sphalerite structure, the electrostatic interaction  $W_{\text{e}}$  is sufficiently described by a point-charge model, leading to a sum of lattice points, which is well known as the Madelung constant. But for the evaluation of pyrite's crystal energy it is important to incorporate dipole terms, too. Owing to the crystal's geometry, dipole moments are only located at sulphur atoms, as was first pointed out in [8]. Because the strength of those dipole moments,  $\mu$ , is unknown at present, the crystal energy calculation will

be used to find a first approximation of it. A  $\mu$ -dependent expression for the crystal energy will be derived and solved with equations describing equilibrium bond lengths and compressibility of pyrite.

The Born-Haber cycle computes the crystal energy by dividing the formation reaction of the solid into its chemical subprocesses and balancing the energies (heat of sublimation, electron affinity, ionization energy, etc.). The summation procedure is based on an ionic model, which, as is well known, was successfully used to calculate the crystal energy of ionic alkali halides [9]. For the case considered here, atoms are imagined to be ionized as  $\text{Fe}^{2+}$  and  $\text{S}^-$ . It will be shown that the ionic model leads to reliable results for the crystal energy of pyrite, if the Born-Haber cycle is slightly extended, to account also for the occurrence of polarized ions within the lattice.

## 2. The pyrite structure

The pyrite structure is often compared with that of NaCl, because metal atoms in both crystals span a face-centred cubic (FCC) sublattice in which the anions are embedded. In NaCl the halogen FCC sublattice is shifted by a translation vector  $\tau = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$  relative to that of Na atoms. In pyrite (space group  $Pa\bar{3}$ , No. 205) sulphur atoms are grouped as  $\text{S}_2$  dimers with their centre of mass occupying Cl positions of the NaCl structure (see figure 1). The dimers are directed along  $\langle 111 \rangle$  directions with S atoms on symmetry-related coordinates. To arrive at  $\text{FeS}_2$  the unit cell with four irons must contain eight S atoms in the ideally stoichiometric compound. Their  $8 \times 3$  coordinates are described by one sulphur positional parameter  $u$ . The atoms' coordinates are compiled in table 1.

There are two inter-ionic distances in the pyrite crystal, accounting for the sulphur-iron and sulphur-sulphur distances respectively. If they are abbreviated in fractional coordinates by  $d_1$  and  $d_2$ , it can be shown that they depend on the sulphur positional parameter  $u$  as

$$d_1 = [u^2 + 2(\frac{1}{2} - u)^2]^{1/2} \quad (1a)$$

$$d_2 = \sqrt{3}(1 - 2u). \quad (1b)$$

To get their absolute values,  $d_1$  and  $d_2$  are to be multiplied by the cubic cell length  $a$ . The positional parameter  $u$  was measured [10] to be 0.38505(5), whereas the unit-cell edge  $a$  is slightly less than 5.41870 Å, depending on the degree of sulphur deficiency [11].

**Table 1.** The pyrite unit cell contains four formula units  $\text{FeS}_2$ . The ion positions are specified in fractional coordinates of the cube edge  $a$ ;  $u$  stands for the sulphur positional parameter ( $u = 0.385$ ). The directions of S dipole moments are specified with unit vectors  $n_s$ .

Fe	0,0,0	$0, \frac{1}{2}, \frac{1}{2}$	$\frac{1}{2}, 0, \frac{1}{2}$	$\frac{1}{2}, \frac{1}{2}, 0$
S	$\pm(u, u, u)$	$\frac{1}{2} \pm u, \frac{1}{2} \mp u, \pm u$	$\pm u, \frac{1}{2} \mp u, \frac{1}{2} \pm u$	$\frac{1}{2} \pm u, \pm u, \frac{1}{2} \mp u$
$n_s$	$\pm[111]/\sqrt{3}$	$\pm[\bar{1}11]/\sqrt{3}$	$\pm[1\bar{1}1]/\sqrt{3}$	$\pm[11\bar{1}]/\sqrt{3}$

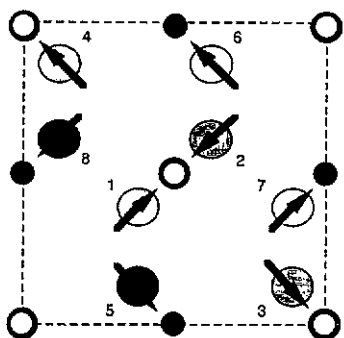


Figure 1. Projection of the cubic pyrite structure (space group  $Pa\bar{3}$ ), with broken lines indicating borders of the unit cell. Iron atoms build up an FCC sublattice and are indicated at the height  $0, \frac{1}{2}$  and 1 by small white and black circles. The eight sulphur atoms in the unit cell are differently shaded according to their different heights. They are all marked with an arrow, indicating the direction along which the dipole moment unit vector  $\mu_S$  is oriented (compare with table 1). Because sulphur atoms occupy equivalent crystallographic positions, the strength of the dipole moment is the same for all of them. It is evaluated to be  $\bar{\mu} = 0.141ea$ ,  $e$  being the elementary charge and  $a$  the unit cell length.

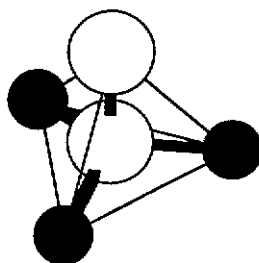


Figure 2. Sulphur coordination tetrahedron. The sulphur atoms in the pyrite lattice are linked to three Fe and another S atom (black and white circles, respectively). If the atoms are assumed to be ionized, such a charge configuration must lead to an electric field  $F(\mathbf{u})$  at the central sulphur position, polarizing the atom in the direction of the sulphur-sulphur bond. This is in sharp contrast to atoms in NaCl or ZnS structure, where electric field vectors of other lattice points cancel one another.

The local coordination of the iron atoms is an octahedron with a slight tetrahedral distortion of  $4^\circ$  (point group  $C_{3i}$ ) and can be approximated for most considerations as octahedral (point group  $O_h$ ). The local coordination of sulphur atoms is a compressed tetrahedron, with three corners occupied by Fe atoms and the fourth by the other S atom of an  $S_2$  dimer (point group  $C_3$ ). The sulphur atoms do not occupy centres of inversion in the lattice. It is easy to see that the sum of electric fields from the next point-charge neighbours does not cancel at the S position—as it does in the case of Cl atoms in NaCl. On the contrary, the next-neighbour interaction results in a net electric field along the same direction in which  $S_2$  dumbbells are oriented, i.e.  $\langle 111 \rangle$  (see figure 2).

Also the summation over all point charges of the lattice yields a non-vanishing component of the electric field oriented along  $\langle 111 \rangle$  axes at the sulphur positions. This must cause a static polarization of the atom. To account for this, the ionic model must be extended, so that the electrostatic potential of the sulphur ions is described by two terms: its charge  $z_S$  and its dipole moment  $\mu_S$ . Because the  $\langle 111 \rangle$  axes are of threefold rotational symmetry, it is easy to understand from a crystallographic point of view that the dipole moment has to be oriented along this direction. Every other orientation of the dipole vector would come into conflict with the point symmetry of the sulphur position. For each of the eight S atoms in the unit cell, the dipole's direction is specified in table 1. The sum of all dipole moments ( $P = \sum \mu_i$ ) does not manifest itself in a macroscopically measurable polarization of the crystal, since two dipole moments of an  $S_2$  dimer are directed antiparallel and sum to zero.

At the Fe position the sum of electric fields from all other lattice points is zero because the iron atoms occupy centres of inversion, i.e. for every field vector arising

from a charge  $q$  at  $r$  there is another charge  $q$  at  $-r$ , so that their fields cancel. This argument does not hold for the potential, as is well known from the non-vanishing Madelung constant. But the dipole moment associated with iron atoms is assumed to be zero because there is no exciting field.

### 3. The theoretical crystal energy

The calculation of the theoretical crystal energy  $W_{th}$  is done by summing two terms describing the electrostatic interaction  $W_e$  and the core-core repulsion  $W_r$ . They will be developed now. The thermal energy and van der Waals attraction are neglected. Most generally, the electrostatic interaction between a source at a point in space  $r_k$  and a charge distribution at  $r_i$  can be written as a Taylor expansion, of which the first two terms are:

$$q_i \Phi(r_{ik}) - \langle \mu_i | F(r_{ik}) \rangle \quad (2)$$

where  $q_i$  and  $\mu_i$  are the first and second moments of the charge distribution (i.e. net charge and dipole moment),  $r_{ik} = r_i - r_k$  is the distance vector, and  $\Phi$  and  $F$  are the potential and field with which the interaction is to be evaluated. Because considerations are limited to a situation described by point charges and point dipoles, the potentials and fields associated with them have to be taken:

$$q_i (\Phi^{mon} + \Phi^{dip}) - \langle \mu_i | F^{mon} + F^{dip} \rangle. \quad (3)$$

The potential of a point charge is simply  $q/r_{ik}$ . So the first term has to be extended over all point charges in the crystal and be multiplied by  $\frac{1}{2}$  to avoid double summation when the energy per mole is added. This term is the Madelung constant  $\alpha^m$ :

$$q_i \Phi^{mon} = \frac{q_i}{4\pi\epsilon_0 a^2} \sum_{k, k \neq i} \frac{q_k}{r_{ik}} = \frac{e^2}{4\pi\epsilon_0 a} \frac{z_i}{2} \sum_{k, k \neq i} \frac{z_k}{\rho_{ik}} = \frac{e^2}{4\pi\epsilon_0 a} \alpha_i^m \quad (4)$$

with  $e$  being the elementary charge and  $\epsilon_0$  the vacuum dielectric constant. Using fractional coordinates  $\rho$  and writing  $r_{ik} = a\rho_{ik}$ , the unit-cell length  $a$  can be placed before the sum. In contrast to the situation in the alkali halides,  $\alpha^m$  in pyrite yields differing values for the iron and sulphur sites, respectively;  $i = 1$  or  $2$  should therefore indicate the Fe or the S atom ( $z_1 = +2$ ,  $z_2 = -1$ ).

To evaluate the second term in (3) the sum is to extend over the electrostatic potential of all dipoles, yielding a new geometric sum of lattice points abbreviated by  $\alpha^d$ :

$$q_i \Phi^{dip} = \frac{e\mu}{4\pi\epsilon_0 a^2} \frac{z_i}{2} \sum_{k, k \neq i} \frac{\langle n_k | \rho_{ik} \rangle}{\rho_{ik}} = \frac{e\mu}{4\pi\epsilon_0 a^2} \alpha_i^d \quad (5)$$

where  $\mu$  stands for the strength of the dipole and the unit vector  $n$  for its direction (see table 1). With the notation developed before, the two last terms in (3) give

$$\begin{aligned} & - \langle \mu_i | E^{mon} + E^{dip} \rangle \\ &= - \frac{e\mu}{4\pi\epsilon_0 a^2} \frac{n_i}{2} \sum_{k, k \neq i} \frac{z_k \rho_{ik}}{\rho_{ik}^3} - \frac{\mu^2}{4\pi\epsilon_0 a^3} \frac{n_i}{2} \sum_{k, k \neq i} \frac{3 \langle n_k | \rho_{ik} \rangle \rho_{ik} - \rho_{ik}^2 n_k}{\rho_{ik}^5} \\ &= - \frac{e\mu}{4\pi\epsilon_0 a^2} \beta_i^m - \frac{\mu^2}{4\pi\epsilon_0 a^3} \beta_i^d \end{aligned} \quad (6)$$

where the electric fields of point charges and dipoles have been inserted. The sums  $\alpha^m$ ,  $\alpha^d$ ,  $\beta^m$  and  $\beta^d$  will be referred to as electrostatic lattice constants. The notation is chosen such that  $\alpha$  always indicates a sum of potentials, whereas  $\beta$  accounts for fields, and superscripts  $m$  and  $d$  are abbreviations for monopoles and dipoles. In the pyrite space group  $Pa\bar{3}$  the distances of ions  $\rho_{ik}$  are dependent on the positional parameter  $u$  (see equations (1a,b)) and therefore all electrostatic lattice constants are dependent on it ( $\alpha = \alpha(u)$ ,  $\beta = \beta(u)$ , etc.).

Adding all the electrostatic energy terms for one molecular unit  $\text{FeS}_2$  gives ( $N_L$  being Loschmidt's number)

$$W_e = \frac{N_L}{4\pi\epsilon_0} \left( \frac{e^2}{a} (\alpha_{\text{Fe}}^m + 2\alpha_{\text{S}}^m) + \frac{e\mu}{a^2} (\alpha_{\text{Fe}}^d + 2\alpha_{\text{S}}^d - 2\beta_{\text{S}}^m) - \frac{\mu^2}{a^3} 2\beta_{\text{S}}^d \right) \quad (7)$$

where  $i = 2$  terms (subscript S) occur twice because there are twice as many sulphur as iron atoms per mole of pyrite. The  $\beta_{\text{Fe}}$  terms are missing because they all vanish at a lattice site with inversional symmetry.

Let us consider the terms describing the core-core repulsion. The repulsive interaction is described with a hardness parameter  $n$  and a proportionality constant  $B$ . The core-core repulsion is assumed [12] to be inversely proportional to the distance between atoms to the power  $n$ . Expressing bond lengths again in fractional coordinates (see equations (1a,b)), and taking into account only repulsion between nearest neighbours, yields

$$W_r = \frac{N_L e^2}{4\pi\epsilon_0} \left( \frac{6B_1}{d_1^n a^n} + \frac{B_2}{d_2^m a^m} \right) \quad (8)$$

with  $B_1$ ,  $B_2$  and  $n$ ,  $m$  being the parameters for the iron-sulphur and the sulphur-sulphur bond, respectively. There are six times more Fe-S than S-S bonds in  $\text{FeS}_2$ , so the first term is multiplied by 6.

For a heteropolar bond  $n$  is assumed to be the geometric mean of the hardness parameter of both sorts of atoms [13], with  $n = (n_{\text{S}} n_{\text{Fe}})^{1/2}$  in the case considered here, if  $n_{\text{Fe}}$  and  $n_{\text{S}}$  are assumed to be the hardness parameters of the iron and sulphur ions, respectively. The same rule yields for the sulphur-sulphur bond  $m = n_{\text{S}}$ . Pauling proposed [14] values of 9 for ions with an electronic configuration as in Ar,  $3p^6$ , or as in  $\text{Cu}^+$ ,  $3d^{10}$ . The Fe ions in pyrite have  $3d^6$  configurations and the hardness parameters can therefore be assumed to be smaller, so  $n_{\text{Fe}} = 8$  is taken. In the case of  $n_{\text{S}}$  the calculations were done with  $n_{\text{S}} = 9$ , but it could be smaller, because the  $\text{S}^-$  configurations are also not that of a filled electron shell. Furthermore, Goldschmidt recommended to reduce  $n_{\text{S}}$  by a correction term  $k$ , because sulphur atoms are not sixfold, but only fourfold coordinated,  $k$  being 0.935 in this case (after [14]). To simplify the calculation it is assumed that  $n = m$ . An arithmetic mean is evaluated for  $n$  weighted by the number of bonds:

$$n = [6(kn_{\text{S}} n_{\text{Fe}})^{1/2} + kn_{\text{S}}] / 7 \quad (9)$$

which gives for the values specified  $n = m = 8.23$ . With this value all the following calculations were performed.

The final expression for the crystal energy of one molecular unit of pyrite then becomes

$$W_{\text{th}} = \frac{N_L}{4\pi\epsilon_0} \frac{e^2}{a} \left( \alpha_{\text{Fe}}^m + 2\alpha_{\text{S}}^m + \bar{\mu} (\alpha_{\text{Fe}}^d + 2\alpha_{\text{S}}^d - 2\beta_{\text{S}}^m) - 2\bar{\mu}^2 \beta_{\text{S}}^d + \frac{6B_1}{d_1^n a^{n-1}} + \frac{B_2}{d_2^n a^{n-1}} \right) \quad (10)$$

where the abbreviation  $\bar{\mu} = \mu/ea$  is introduced to provide the 'natural' energy unit  $e^2/4\pi\epsilon_0 a$  of the system. This expression contains only the dipole moment  $\mu$  and the repulsion constants  $B_1$  and  $B_2$  as unknowns. Their solution is accomplished with three equations, two of them describing the equilibrium of the crystal:

$$(dW_{th}/d\alpha)|_{\alpha=a_0} = 0 \quad (11a)$$

$$(dW_{th}/du)|_{u=u_0} = 0 \quad (11b)$$

where  $a_0$  and  $u_0$  represent the measured unit-cell length and sulphur positional parameter as mentioned above. Whereas equation (11a) was first used successfully for the calculation of the crystal energy of alkali halides, there is no equivalent of (11b) for that case. But it is intuitively clear that the system will minimize its energy also with respect to this free parameter and that both equations will hold, if the new parameter occurs. The third equation comes from the measurement of the bulk modulus  $K$ , which, in cubic crystals with four formula units per unit cell (as NaCl, ZnS, FeS<sub>2</sub>, etc.), is related to the equilibrium cell edge  $a_0$  as

$$\frac{4}{9\alpha} \frac{d^2 W_{th}}{d\alpha^2} \frac{1}{N_L} \Big|_{\alpha=a_0} = K. \quad (12)$$

The bulk modulus of pyrite was measured [15] to be  $1.18(4) \times 10^{11}$  N m<sup>-2</sup>. Equation (12) accounts for the physical situation of shortening all bonds in the unit cell, because S-Fe and also S-S bonds are dependent on  $\alpha$ . In alkali halides this equation is normally formulated as dependent on the interatomic distance (being  $a/2$ ), which is not possible for pyrite owing to two different bond lengths in the crystal.

The solution of this system of equations is shown in the appendix. A solution is also given for the case when the existence of dipoles within the lattice is denied, i.e. if  $\mu = 0$  is assumed. Then the hardness parameter  $n$  may be regarded as the third unknown instead of  $\mu$ . The results of both solutions will be given and compared. One difficulty arises in connection with equation (11b), because the derivatives of the electrostatic lattice constants  $\alpha$  and  $\beta$  with respect to  $u$  have to be evaluated numerically, which is a computer-time-consuming task. Details concerning the calculation of the electrostatic lattice constants of pyrite and their derivatives will be given elsewhere [16].

#### 4. The electric field at the sulphur position

As was shown above, there is a net electrical field acting at the sulphur position. The occurrence of such a field is in sharp contrast to crystal lattices where only the electric *potential* of all other point charges gives a non-vanishing sum as in the rock salt or sphalerite structure. The field will be abbreviated  $F(u)$ , with  $u$  accounting for the sulphur positional parameter. The strength of this electric field can be calculated with the tools developed above. For this one makes use of the fact that both vectors  $\mu$  and  $F(u)$  must be oriented along the  $\langle 111 \rangle$  axes. Every other orientation would be incompatible with the symmetry requirements of the crystal's structure. From equation (6) the field strength may be written as

$$F(u) = (2e/4\pi\epsilon_0 a^2)(\beta_S^m + \bar{\mu}\beta_S^d) \quad (13)$$

where the factor 2 reappears to cancel its inverse that was introduced to avoid double summation of energies. This equation allows the determination of  $F(u)$  as a function of known values. Because S atoms occupy equivalent positions in the pyrite structure, this holds for all the eight S positions in the unit cell.

The significance of an electric field within an ionic model of the crystal may not be easily understood. It may be argued that ions in electric fields would move in the field's direction, which would indeed be the case for a true point charge. But charge distributions of atoms and ions are described by more complicated solutions of the wave equation. An applied electric field will cause a deformation of such a kind that it is neutralized at any point within the charge distribution. It is clear that such quantum-mechanical considerations would go beyond the scope of the ionic model of crystals, however far it may be extended to higher electrical moments. We deal with this seeming contradiction by assuming the ions to be fixed at their lattice sites and assign a dipole moment to them, whenever they occupy positions with non-vanishing electrostatic lattice constants of the  $\beta$  type.

### 5. The Born-Haber cycle

To determine an experimental value of the crystal energy, which can be compared with the theoretical one as calculated with formulae above, one usually evaluates the Born-Haber cycle (see figure 3). It makes use of the fact that the sum of energies of all steps in a thermodynamic cycle should be equal to zero [9, 17]. The first step stands for the inverse formation of the solid from the elements, which is accounted for by the negative heat of formation ( $-H_F$ ). Then follows the sublimation of the elements at standard temperature and pressure (energy of sublimation  $Sub$ ). In the case of iron this produces monatomic gaseous species; however, with sulphur the sublimation produces higher-order gaseous species. These must then dissociate (dissociation energy  $D$ ). The next step promotes the monatomic species to their proper charges: the iron atoms must be ionized (first and second ionization potential  $I$ ) and the sulphur must accept one electron (electron affinity  $EA$ ).

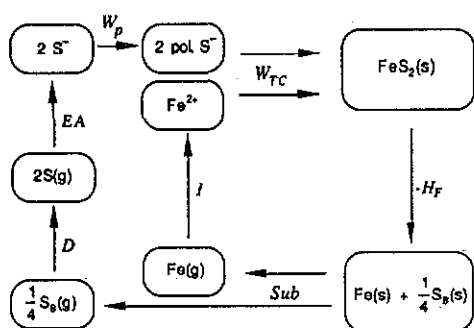
For the Born-Haber cycle developed for crystals containing only unpolarized ions, it is the combination of the gaseous charged species into the crystal that releases the crystal energy  $W_{BH}$ . Its value can be extracted if others are known. For this case of pyrite, a modification of the cycle is necessary, because we have to account for the work  $W_p$  done on S ions by polarizing them. We assume this process to happen after the ionization of the S atom (see figure 3). A new thermodynamic cycle energy  $W_{TC}$  therefore is introduced, which is linked with the old one by  $W_{BH} = W_{TC} + W_p$ . If  $W_p$  is not counted separately, it remains hidden within a too-large value obtained for  $W_{BH}$ .

The work for inducing a dipole moment to a charge distribution is  $\mu \cdot F/2$ , where  $\mu$  accounts for the resulting dipole strength and  $F$  is the exciting field. But if a field is applied the relaxation of the dipole within it must also be considered [17], which is given by the potential energy of the system  $-\mu \cdot F$ . The polarization work  $W_p$  done for the sulphur ion is the sum of both

$$W_p = \mu \cdot F/2 - \mu \cdot F = -\mu \cdot F/2. \quad (14)$$

The polarization of S ions therefore is an energy-releasing process, as was the acceptance of an electron by the neutral S atom. Its value may not be drawn easily





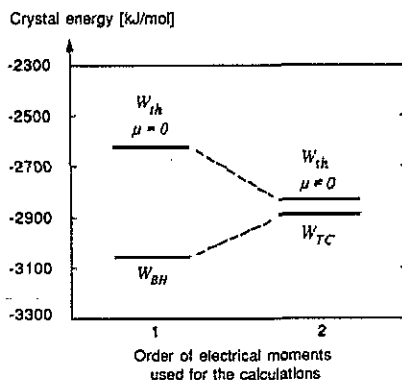
**Figure 3.** Energy-consuming and -releasing processes of the generalized Born-Haber cycle for the pyrite system. All steps of the cycle must sum up to zero:  $-H_F + Sub + D + I + EA + W_P + W_{TC} = 0$ . To account for the polarization of S ions (pol  $S^-$ ) within the lattice, a polarization process is inserted after the ionization of the S atoms, which releases the energy  $W_P = -\mu \cdot F/2$ . The value of  $W_P$  can only be calculated with the help of formulae developed for the theoretical crystal energy.

from thermodynamic or atomic data books as the other parameters of the cycle. But the formalism developed for the theoretical crystal energy provides equations to calculate  $\mu$  of the sulphur ion (equation (A4)) and  $F(u)$  (equation (13)), from which  $W_P$  can be calculated. It should be emphasized that one should discriminate between the field acting at the S ions in the gas phase as a part of the thermodynamic cycle and  $F(u)$ , which appears within the crystal. But their strengths are assumed to be equal, because in both cases the same polarization is achieved. A correction of the Born-Haber cycle, as proposed above, changes its character from relying purely upon experimental data to being a thermodynamic cycle that is also dependent on theoretical considerations.

## 6. Results and discussion

Table 2 shows the calculated electrostatic lattice constants and their derivatives with respect to the S positional parameter  $u$ . It can be seen that the newly introduced constants such as  $\alpha^d$  and  $\beta$  are in the typical range of Madelung constants calculated for other types of crystals;  $\alpha_{Fe}^m$  and  $\alpha_S^m$  are negative and indicate a bonding energy. They are in agreement with the only values to be found in the literature [18]. The physical meaning of the  $u$  derivatives can be understood by regarding only the first bonding sphere around the atom under consideration. For the Madelung constant they are positive, i.e. the monopole interaction energy is decreased. This is in agreement with lowering of the Coulomb attraction with increasing  $u$ , which causes the S-Fe bond to become stretched.

The terms  $\alpha_{Fe}^d$ ,  $2\alpha_S^d$  and  $-2\beta_S^m$ , which account for the interaction between dipoles and point charges, are negative. But the share of the crystal energy represented by



**Figure 4.** Schematic drawing of the crystal energies due to theoretical and thermodynamic cycle considerations as a function of order of electric moments used. Taking into account only monopole interactions causes the difference of both to become as large as 15%. This is reduced to 2% if for the crystal energy evaluations second-order electric moments are included.

Table 2. Electrostatic lattice constants for iron and sulphur positions in the pyrite lattice and their derivatives with respect to the sulphur positional parameter  $u$  (both evaluated at  $u_0 = 0.385$ ).

	$\alpha_{\text{Fe}}^m$	$\alpha_{\text{S}}^m$	$\alpha_{\text{Fe}}^d$	$\alpha_{\text{S}}^d$	$\beta_{\text{S}}^m$	$\beta_{\text{S}}^d$
Electrostatic lattice constant	-7.458	-1.957	-2.898	-1.184	2.632	-2.561
Derivative $d/du$	5.05	6.64	-27.2	-53.7	67.3	-558.3

them is obtained by multiplying them with the dipole moment  $\bar{\mu}$ , see formula (10). Whether they stand for attractive or repulsive forces depends on the sign of  $\mu$ , i.e. its direction along  $\langle 111 \rangle$  axes. The term  $(-\beta_{\text{S}}^d)$  describing the dipole-dipole interaction is positive and stands for a repulsive force because it is proportional to  $\mu^2$ . Increasing  $u$  means—in terms of first bonding sphere considerations—that antiparallel dipole moments are becoming closer and the repulsion is enhanced. From this it is understandable that  $d(-\beta_{\text{S}}^d)/du$  is also greater than zero.

Inserting the values of the electrostatic lattice constants into equation (A4) gives a dipole moment associated with the sulphur atom in the pyrite lattice of  $\bar{\mu} = 0.141$  in units of  $ea$  or  $12.3 \times 10^{-30}$  C m (3.7 D). The positive sign indicates that the dipole vector points to the S dumbbell neighbour. It also means that the negatively polarized part is directed towards the centre of mass of the iron neighbours, which could have been expected by simple electrostatic considerations. The sign of  $\bar{\mu}$  causes the term  $\bar{\mu}(\alpha_{\text{Fe}}^d + 2\alpha_{\text{S}}^d - 2\beta_{\text{S}}^m)$  to become negative. The associated forces therefore are attractive, i.e. the S dipole in pyrite strengthens the bonding. The electric field at the sulphur position is obtained by equation (13) to amount to  $2.23 \times 10^{10}$  V m $^{-1}$ , whose significance and consequences will be discussed elsewhere.

With these values the theoretical crystal energy can now be calculated, which will first be discussed for the assumption of zero polarization,  $\mu = 0$ . As is shown in the appendix, the system of equations (11a,b) and (12) can be solved under this assumption with the hardness parameter  $n$  as the new variable instead of  $\mu$ . The results obtained will not be given here in full detail; instead it should only be mentioned that a negative repulsion constant  $B_2$ , a hardness parameter of  $n = 9.72$  and  $W_{\text{th}} = -2617$  kJ mol $^{-1}$  are calculated. It is clear that a negative  $B_2$  does not make sense physically and  $n$  is implausibly large. Table 3 gives the energies for the Born-Haber cycle of the pyrite system and references for the values. A compilation was attempted with only thermodynamic data that were measured for  $T = 298$  K. The sum of the normal Born-Haber cycle energy per mole of FeS $_2$  is added to be  $W_{\text{BH}} = -3058$  kJ. This differs by 15% from the monopole solution crystal energy  $W_{\text{th}}$  as mentioned above.

The solution with  $\mu \neq 0$  gives much more reliable results. For this case, use is made of the hardness parameter as estimated above,  $n = 8.23$ . Then, both repulsion constants  $B_1$  and  $B_2$  become positive and can be calculated with the help of formula (A6) and (A7)

$$B_1/d_1^n a^{n-1} = 0.262 \quad B_2/d_2^n a^{n-1} = 0.134.$$

Comparing them with the electrostatic lattice constants (table 2), it can be seen that these terms are an order of magnitude smaller and therefore determine the associated

Table 3. Generalized Born-Haber cycle for the pyrite system with the energy values given for each process. The sum of the energies should equal zero. Therefore the unknown experimental crystal energy  $W_{\text{BH}}$  or  $W_{\text{TC}}$  can be calculated with the help of the other thermodynamic and atomic data. Symbols (s) and (g) indicate solid and gaseous state;  $\alpha$  stands for the  $\alpha$  modification of sulphur; for other symbols see text.

Step	Process	Energy (kJ mol <sup>-1</sup> )	Ref
$-H_{\text{F}}$	$\text{FeS}_2(\text{s}) \rightarrow \text{Fe}(\text{s}) + \frac{1}{4}\text{S}_8(\text{s}, \alpha)$	174.6	[2]
$Sub$	$\frac{1}{4}\text{S}_8(\text{s}, \alpha) \rightarrow \frac{1}{4}\text{S}_8(\text{g})$	$\frac{1}{4}(106) - \frac{1}{4}RT$	[20] <sup>a</sup>
	$\text{Fe}(\text{s}) \rightarrow \text{Fe}(\text{g})$	$416.3 - RT$	[21] <sup>a</sup>
$D$	$\frac{1}{4}\text{S}_8(\text{g}) \rightarrow \text{S}_2(\text{g})$	$\frac{1}{4}(387) - \frac{3}{4}RT$	[22] <sup>a</sup>
	$\text{S}_2(\text{g}) \rightarrow 2\text{S}(\text{g})$	425	[23]
$I$	$\text{Fe} \rightarrow \text{Fe}^{2+}$	2324	[24]
$EA$	$2\text{S} \rightarrow 2\text{S}^-$	$2(-200.2)$	[25]
$W_{\text{p}}$	$2\text{S}^- \rightarrow 2\text{pol}(\text{S}^-)$	$2(-82.4)$	This work
$W_{\text{TC}}$	$\text{Fe}^{2+} + 2\text{S}^- \rightarrow \text{FeS}_2$	-2893	This work

$$W_{\text{BH}} = H_{\text{F}} - Sub - D - I - EA = -3058 \text{ kJ mol}^{-1}$$

$$W_{\text{TC}} = W_{\text{BH}} - W_{\text{p}} = -2893 \text{ kJ mol}^{-1}$$

<sup>a</sup> These values account for enthalpies and have to be corrected by  $RT$  ( $R$  = universal gas constant,  $T$  = 298 K) to give energies.

energy to be roughly only 10% of the total crystal energy. This is the same situation as for alkali halides [9]. Table 4 shows the different parts of which the crystal energy is composed. The monopole interaction is almost as strong as the whole sum. The core-core repulsion leads to a reduction of  $\approx 10\%$ , but this is balanced by the interaction of dipoles with point charges. Being smaller than 1% of the whole crystal energy, the dipole-dipole interaction is negligible. The whole crystal energy is added to give  $W_{\text{th}} = -2835 \text{ kJ mol}^{-1}$ .

Table 4. Composition of the theoretical crystal energy due to single terms of equation (10) accounting for electrostatic interaction (4)–(6) and core-core repulsion (8), setting the hardness parameter  $n = 8.23$ . Values are given in kJ mol<sup>-1</sup>.

(1)	$N_{\text{L}}e^2(\alpha_{\text{Fe}}^{\text{m}} + 2\alpha_{\text{S}}^{\text{m}})/4\pi\epsilon_0 a$	-2917
(2)	$N_{\text{L}}e\mu(\alpha_{\text{Fe}}^{\text{d}} + 2\alpha_{\text{S}}^{\text{d}} - 2\beta_{\text{S}}^{\text{m}})/4\pi\epsilon_0 a^2$	-382
(3)	$N_{\text{L}}\mu^2(-2\beta_{\text{S}}^{\text{d}})/4\pi\epsilon_0 a^3$	+26
(4)	$N_{\text{L}}e^2(6B_1/d_1^n + B_2/d_2^n)/4\pi\epsilon_0 a^n$	+438
$\Sigma =$		-2835

If this is compared with the value obtained by the normal Born-Haber cycle, we still have to state a difference of 7% between them. This is clear progress compared to the situation as given above. But if the polarization work  $W_{\text{p}}$  is inserted as a new step within the cycle, and  $\mu$  and  $F(u)$  are calculated as given in equations (A4) and (13), the thermodynamic cycle energy  $W_{\text{TC}}$  yields a value of  $-2893 \text{ kJ mol}^{-1}$ , which is in even closer agreement with the theoretical value. It may be concluded that the difference of 15% regarding the monopole crystal energies is reduced to 2% if dipole corrections are made for both the theoretical and the Born-Haber crystal energy. These developments are visualized in figure 4, where the crystal energies are given

as a function of the order of electrical moments used for the calculation. The result strongly favours the assumption of static polarized S ions within the pyrite lattice.

The errors of the values calculated for  $\mu$  and  $W_{th}$  are in the few per cent range as they were for the experimental data used (bulk modulus,  $\Delta K = 3.4\%$ ; sulphur dissociation energy,  $\Delta D = 3\%$ ; heat of sulphur sublimation,  $\Delta S(S) = 4\%$ ).  $B_1$  and  $B_2$  depend greatly upon the choice of  $n$ , whereas the solution is stable for  $\mu$  and  $W_{th}$ . The van der Waals attraction and the (repulsive) phonon part of the crystal energy are probably of the same magnitude, so that they cancel. It also should be remembered that the hardness parameters for the iron-sulphur bond was approximated to be equal to the one of the sulphur-sulphur bond. Without this assumption there would have been more unknowns than equations. Another approximating assumption was that repulsion terms can be taken into account by adding only nearest-neighbour interactions. In the alkali halides the anion-anion and cation-cation repulsions have to be considered to reach an agreement between theoretical and experimental crystal energy of less than 2% [14]. Further, the  $1/r^n$  law for the core-core repulsion was substituted later by an exponential expression by Born and Mayer. Regarding all these possible sources of error, the difference between  $W_{th}$  and  $W_{TC}$  is astonishingly small.

For the time being it may not be excluded that there are electric quadrupole moments associated with the iron and sulphur ions, which may cause further terms in the theoretical crystal energy. At least, the point symmetry of both crystallographic sites allows for non-vanishing electric field gradients, which might excite quadrupoles in the same way as the electric field caused a polarization. But if there is any third-order interaction, it will probably not be very significant. As could have been seen, the interaction energy is closely linked with the radial exponent on which it acts: whereas the  $1/r$  dependent monopole-monopole term was almost as strong as the sum of the whole crystal energy, the interaction between point charges and dipoles, following a  $1/r^2$  law, made up only 10% of it. Any  $1/r^3$  monopole-quadrupole term will probably be in the few per cent range, as was the dipole-dipole energy. Also the close agreement between theoretical and thermodynamic cycle energy indicates that any further electrostatic order would contribute only little to the sum of energies.

Altogether, the extended ionic model, which regards ions in the pyrite lattice as point charges and point dipoles, gave useful results. The good agreement between the crystal energies due to theoretical and thermodynamic cycle considerations emphasizes the usefulness of the newly introduced electrostatic lattice constants and supports the assumption of a static electric dipole moment associated with the sulphur atoms in pyrite. Their strength is almost twice as strong as the dipole moment of the water molecule, which must have important consequences for the physical properties of the material. There is no obvious reason why the considerations presented here should not be applicable on other crystal lattices with atoms on positions that are not centres of inversion, e.g. other pyrite compounds, chalcopyrites, rutiles, perovskites, etc. To solve the system of equations, the number of unknown dipole moments and repulsion constants must equal the number of equations describing the crystal's equilibrium and compression.

## 7. Conclusions

It has been shown that the crystal energy of pyrite cannot be described with an ionic model that accounts for electrical monopoles alone but leads to physically meaningless

results. Only by introducing dipole moments, associated with the S atoms, it was possible to calculate proper values of the electrostatic interaction, the core-core repulsion and the crystal energy, the latter being in accordance with an extended Born-Haber cycle. The dipole moment of the sulphur atom must be of importance for the physical properties of the solid. The electrostatic lattice constants introduced here, accounting for the generalization of the Madelung constant, have proven their usefulness. They are pure geometric sums of crystal lattice points and it should be possible to apply the presented concept to other structures with polarized atoms occupying positions that are not centres of inversion.

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### Appendix

Equations (11) and (12) are rewritten by inserting (10) as

$$E + 2\bar{\mu}L + 3\bar{\mu}^2C + \frac{6nB_1}{d_1^n a^{n-1}} + \frac{nB_2}{d_2^n a^{n-1}} = 0 \quad (\text{A1})$$

$$\frac{dE}{du} + \bar{\mu} \frac{dL}{du} + \bar{\mu}^2 \frac{dC}{du} + (L + 2\bar{\mu}C) \frac{d\bar{\mu}}{du} + \frac{6B_1}{a^{n-1}} \frac{d}{du} \frac{1}{d_1^n} + \frac{B_2}{a^{n-1}} \frac{d}{du} \frac{1}{d_2^n} = 0 \quad (\text{A2})$$

$$2E + 6\bar{\mu}L + 12\bar{\mu}^2C + \frac{6n(n+1)B_1}{d_1^n a^{n-1}} + \frac{n(n+1)B_2}{d_2^n a^{n-1}} = \frac{9Ka^4\pi\epsilon_0}{e^2} \quad (\text{A3})$$

where the abbreviations

$$\bar{\mu} = \mu/ea \quad E = \alpha_{\text{Fe}}^m + 2\alpha_{\text{S}}^m$$

$$L = (\alpha_{\text{Fe}}^d + 2\alpha_{\text{S}}^d - 2\beta_{\text{S}}^m) \quad C = -2\beta_{\text{S}}^d$$

are used and the other constants have their usual meaning. Writing the dipole moment in this dimensionless form, it is not affected by taking the derivatives with respect to  $a$ , whereas  $u$  derivatives have to be evaluated. The system of equations can be solved for the unknowns  $\mu$ ,  $B_1$  and  $B_2$ . Multiplying (A1) with  $(n+1)$  and subtracting it from (A3) yields a quadratic equation for  $\mu$  that is solved to give

$$\bar{\mu}_{1,2} = \frac{-(2n-4)L \pm \{(2n-4)^2L^2 - 4C(3n-9)[E(n-1) + 9Ka^4\pi\epsilon_0/e^2]\}^{1/2}}{2C(3n-9)} \quad (\text{A4})$$

In this form  $\bar{\mu}$  is dependent only on the electrostatic lattice constants, the hardness parameter  $n$  and a dimensionless form of the bulk modulus. Fortunately, one is able

to solve for  $\bar{\mu}$  only by a combination of (A1) and (A3), so the  $\bar{\mu}$  derivative may be evaluated from the quadratic equation for  $\bar{\mu}$  to be

$$\frac{d\bar{\mu}}{du} = -\frac{\bar{\mu}^2 C'(3n-9) + \bar{\mu} L'(4n-2) + E'(n-1)}{L(2n-4) + 2\bar{\mu} C(3n-9)} \quad (\text{A5})$$

where primed constants indicate derivatives with respect to the sulphur positional parameter  $u$ . By calculating  $d\bar{\mu}/du$ , use was made of the fact that  $dK/du = 0$ , as has been determined experimentally [15]. With the help of

$$\frac{d}{du} \frac{1}{d_1^n} = \frac{n(1-3u)}{d_1^{n+2}} \quad \frac{d}{du} \frac{1}{d_2^n} = \frac{2\sqrt{3}n}{d_2^{n+1}} \quad (\text{A6})$$

the other two unknowns are evaluated by isolating  $B_2$  from (A1) to give

$$\frac{B_2}{d_2^n a^{n-1}} = -\frac{E + 2\bar{\mu}L + 3\bar{\mu}^2 C}{n} - \frac{6B_1}{d_1^n a^{n-1}} \quad (\text{A7})$$

which inserted in (A2) results in

$$\frac{B_1}{a^{n-1}} = d_1^{n+2} \frac{2\sqrt{3}(E + 2\bar{\mu}L + 3\bar{\mu}^2 C) - d_2[E' + \bar{\mu}L' + \bar{\mu}^2 C' + (\bar{\mu})'(L + 2\bar{\mu}C)]}{6d_2 n(1-3u) - 12\sqrt{3}d_1^2 n} \quad (\text{A8})$$

where primed constants again indicate  $u$  derivatives. These are the solutions of the equilibrium and compression modulus equations setting the hardness parameters of the two sorts of atoms to be equal  $n = m$ .

The system of equations (A1)–(A3) can be solved for  $\mu = \mu' = 0$ , using the three variables  $n, B_1$  and  $B_2$  as the new set of unknowns. Instead of (A4) the new equation for  $n$  then becomes

$$n = 1 - \frac{9Ka^4\pi\epsilon_0}{Ee^2} \quad (\text{A9})$$

whereas the solutions of  $B_1$  and  $B_2$  remain the same as in (A7) and (A8) with the slight change that  $\mu = 0$  is to be inserted. This is the solution for the crystal energy when the dipole moment associated with the sulphur atoms in the lattice is denied. Equation (A9) is usually obtained in the case of lattices with atoms occupying centres of inversion exclusively, as in alkali halides [19]. The solution can be recognized to be the mathematical limit of the two equivalent series  $\mu, \mu' \rightarrow 0$  or  $L, C \rightarrow 0$ .

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