Physica B 407 (2012) 509–514

Contents lists available at SciVerse ScienceDirect

Physica B

journal homepage: www.elsevier.com/locate/physb

About crystal structures of packed double-ions or linear molecules in a FCC lattice

W.J.A. Maaskant*

Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands

ARTICLE INFO

Article history:
Received 13 September 2011
Received in revised form
15 November 2011
Accepted 15 November 2011
Available online 21 November 2011

Keywords:
Inorganic
FeS_2 (pyrite)
N_2
CO_2
Electrostatic quadrupole–quadrupole interaction

ABSTRACT

We derive the crystal-structures of FeS_2 (pyrite), N_2 and CO_2 and similar species, where the double-ions or molecules can be regarded as linear entities, placed in a face-centred cubic (FCC) lattice. The interaction between two of these elongation directions is determined by three constants. A minimum is reached by orienting the elongations of neighbouring ions or molecules in a perpendicular way, which points to electrostatic quadrupole–quadrupole interactions and which has been noted before in ortho-hydrogen and para-deuterium. For several points in the Brillouin zone the interaction is calculated. Especially the X-points are of interest and determine the space group $Pa\overline{3}$, which is a subgroup of $Fm\overline{3}m$, the original group of the fcc lattice. We derive also an alternative setting for $Pa\overline{3}$. The conclusion is made that for all these compounds with a $Pa\overline{3}$-structure an electrostatic quadrupole–quadrupole interaction is present.

1. Introduction

Tabulated in Crystal Structures Vol. 1 by Wyckoff [1] are about 30 inorganic solids with the structure of FeS_2 (pyrite) as well as bi- and triatomic solidified gases such as N_2 and CO_2. All these have the space group (SG) $P2_1/a\overline{3}$ shorter ($Pa\overline{3}$, T_h^6, no. 205 of The International Tables of Crystallography [2]). Both the mentioned molecules and the S_2^{2-} groups lie on a site with S_6 ($\overline{3}$) point group symmetry and carry electric quadrupole moments. For CO_2 and N_2 these have experimentally been determined by Graham et al. [3]. In view of the next paragraph we call these solids: classical solids.

There is, however, still another research area, for which the SG $Pa\overline{3}(=T_h^6)$ is important. This is for ortho-H_2 and para-D_2, which both have a $J=1$ for the nuclear moments. This research started in the years ≈ 1960. A review paper is from Silvera [4]. These solids are called quantum solids, as there is a large zero point motion and also freely rotating molecules in the solid state. Below the melting point these substances have a hcp lattice. At lower temperature, the lattice becomes fcc, probably through the anisotropic intermolecular interactions, which are predominantly electrostatic quadrupole–quadrupole (EQQ) interactions. An orientational order–disorder phase transition occurs if they contain a minimum critical concentration $x \simeq 0.55$, where x is the mole fraction of $J=1$ molecules. For ortho-H_2 this structure is $Pa\overline{3}$ below 2.8 K, and for para-D_2 below 3.8 K. (Previously one used the designation Pa3 for this structure. Nowadays $Pa\overline{3}$ is preferred [2].) From Jochemsen et al. [5], it appears that this structure remains up to 6 kbar and T_c scales as the density to the 5/3 power, which indicates an EQQ-coupling. According to James and Raich [6] these quantum solids have their quantization axes along the four directions, which are also found in the structure of α-N_2 (see Fig. 1). Silvera [4] shows in fig. 22 the spatial distributions (Y_{10}) of the molecular axes of the four inequivalent molecules. In addition the EQQ energy in these quantum solids is a factor 4/25 smaller than what one expects for a classical solid with the $Pa\overline{3}$-structure. We do not intend to give a full description of the research done on quantum solids. We only demonstrate how their structure is connected to the structures of pyrite and the solidified gases N_2 and CO_2.

There is in addition a paper by van der Avoird et al. [7] called "An improved Intermolecular Potential for Nitrogen", in which ab initio calculations for the multipole and short range interactions and the dispersion interactions in solid α-N_2 have been performed. This is an important paper, since it describes quantitatively the interactions in such a solid. In the discussion we will compare these results.

There are as far as we know no solid phases where the N_2-molecules or CO_2-molecules or S_2^{2-}-ions are not oriented. Since all these structures have a FCC-structure as supergroup, it seems plausible to consider orientational ordering with the lowest energy of anisotropic interactions (mainly EQQ) on a FCC lattice.

In this paper we will concentrate on FeS_2 (pyrite) with space group T_h^6. The cell is simple cubic with lattice constant

---

* Tel.: +31 172 509394; fax: +31 71 5274537.
E-mail addresses: maaskant@chem.leidenuniv.nl, wja.maaskant@quicknet.nl

0921-4526/$ - see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.physb.2011.11.025

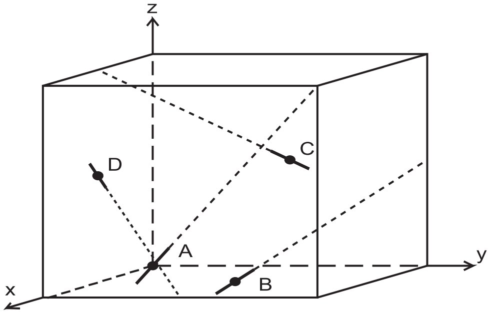

Fig. 1. The orientations of molecules in α-N_2 or S_2^{2-} in Pyrite. The lettering corresponds to Eq. (2).

a_0=5.40667 Å [13]. The Fe-ions as well as the centres from the S_2^{2-}-ions lie at the sites 4a and 4b both with site symmetry S_6 ($\overline{3}$). The individual S-ions lie at site 8c:

$$\pm(u,u,u;\,u+1/2,\,1/2-u,-u;\,-u,u+1/2,\,1/2-u;\,1/2-u,-u,u+1/2)$$
$$u=0.386 \tag{1}$$

(Here the values for u and a_0 determined by Elliot [13] and cited by Wyckoff [1] have been used.) One can regard the structure of pyrite as a superposition of a rocksalt structure with the positive ions Fe^{2+} and a negative charge of $-2e$ at the centre of the accompanying S_2^{2-}-ions. A compensating $+2e$-charge at the same place together with the two $-e$-charges on the S-ions lead to the linear quadrupoles along the S–S-directions. However, a quantitative estimate of these quadrupoles has not been made, as far as we know. Each S_2^{2-}-ion is surrounded octahedrally by Fe-ions. But the direction of the S_2-axes are not pointing towards these Fe-ions, but along the directions of the body-diagonals of the surrounding cubes. As in Fig. 1 there are four elongation directions.

We describe the Pa$\overline{3}$ structures as subgroups of Fm$\overline{3}$m, the SG of a FCC-structure of monoatomic van der Waals crystal, or a rocksalt-like crystal of say FeO. Cell enlargements can be described by wave vectors. Those which can be considered as essential to the change in symmetry have to fit the simple cubic cell of T_h^6. Its basic axes are: $\mathbf{u_1}=a(1,0,0)$, $\mathbf{u_2}=a(0,1,0)$ and $\mathbf{u_3}=a(0,0,1)$. These correspond exactly to the three X-points in the Brillouin zone (BZ) of rocksalt (O_h^5, Fm$\overline{3}$m). The groups of $\mathbf{k}$ are D_{4h} for the three directions. The three $\mathbf{k}$-vectors of the X-points are respectively: $(\mathbf{b_2}+\mathbf{b_3})/2$, $(\mathbf{b_1}+\mathbf{b_3})/2$ and $(\mathbf{b_1}+\mathbf{b_2})/2$. The index of the subgroup T_h^6 with respect to O_h^5 is a factor 4 for the lattice and a factor 2 for the reduction from O_h to T_h. The index is therefore 8.

In 1978 Thomas with his coworkers [8] published a three-states Potts model in order to describe structural phase transitions caused by the cooperative $E\otimes\epsilon$ Jahn–Teller effect in cubic perovskites. We used a similar approach for the same type of Jahn–Teller problems in hexagonal perovskites [9,10]. Similarly, we will use here a four states Potts model, where the favourable directions lie along trigonal axes. We introduce three quadrupole moments: $Q_1=yz\cdot f(r)$; $Q_2=zx\cdot f(r)$; $Q_3=xy\cdot f(r)$, where the $f(r)$-functions keep these quadrupole moments localized. The four states can be expressed as

$$A:(Q_1+Q_2+Q_3)/\sqrt{3},\quad B:(Q_1-Q_2-Q_3)/\sqrt{3}$$
$$C:(-Q_1+Q_2-Q_3)/\sqrt{3},\quad D:(-Q_1-Q_2+Q_3)/\sqrt{3} \tag{2}$$

We assume a steep rise of the potential, such that the system is perfectly localized in one of these valleys, corresponding to a rigid orientation of the connection line between the two S-ions in each S_2^{2-}-double ion. The positions of these elongations are according to the 8c-sites [2] respectively 0,0,0; 1/2,1/2,0; 0,1/2,1/2 and 1/2,0,1/2. All minima have the same third order term $\propto Q_1Q_2Q_3$. We expect therefore a first order phase transition, as has also been observed in the mentioned quantum solids (Silvera [4], Cullen et al. [11]). We will restrict ourselves for pyrite to structures at $T=0$ K, so that we do not enter the area of phase transitions.

Since there are only three quadrupole components on each site, we can consider the following interaction Hamiltonian:

$$\mathcal{H}^{int}=(1/2)\Sigma'_{l,l}\mathbf{Q}^{l}\cdot\mathbf{V}^{l,l'}\cdot\mathbf{Q}^{l'} \tag{3}$$

This quadrupole–quadrupole interaction Hamiltonian consists of a 3×3 tensor $\mathbf{V}$. The sites are numbered by l and l'. The factor 1/2 avoids double counting and the prime at the summation sign means that an interaction between a site with itself is excluded. When we can minimize this interaction energy, we can expect that this leads to a possible structure at $T=0$ K.

In Section 2 we discuss the interactions between nearest neighbours on the same fcc lattice. We explain that three scalar quantities are involved and that one of them is by far the most important. In Appendix A this interaction is described over all 12 nearest neighbours as well as their Fourier transforms.

In Section 3 the resulting interactions for several points in the first BZ of Fm$\overline{3}$m are derived. In Section 4 we choose those possibilities with the lowest energy. A different setting of the Pa$\overline{3}$ structure is derived in Appendix B. Section 5 contains the discussion.

2. The interaction between linear quadrupoles

In this section the interaction of linear quadrupoles of double-ions or linear molecules, which are placed in an fcc lattice will be discussed. According to Bradley and Cracknell [12] the basic vectors for the real and the reciprocal lattice of the fcc cell are, with a the cubic lattice constant:

$$\mathbf{a}_1=a(0,1/2,1/2),\quad \mathbf{a}_2=a(1/2,0,1/2),\quad \mathbf{a}_3=a(1/2,1/2,0) \tag{4}$$

$$\mathbf{b}_1=2\pi/a(-1,1,1),\quad \mathbf{b}_2=2\pi/a(1,-1,1),\quad \mathbf{b}_3=2\pi/a(1,1,-1) \tag{5}$$

First we discuss the interaction between the sites at (0,0,0) and at $a(1/2,1/2,0)$. By means of symmetry the 3×3 matrix $\mathbf{V}$ can be simplified. Later we treat the effects of the other 11 next-nearest neighbours. According to Eq. (4), the vector which connects these points is $\mathbf{a}_3$. Consider those group elements of the point group O_h, the point group before distortion, which do not change the vector $\mathbf{a}_3$. These form a group, which is said to form the group of the vector $\mathbf{a}_3$. It appears to be the point group C_{2v}. The four elements that form this group are in Jones' faithful notation [12] [(xyz), $(yx\bar{z})$, $(xy\bar{z})$, (yxz)]. These can also be denoted as [E,C_{2a}, σ_z, σ_{db}]. This set of elements applies also to the vector which points in the $-\mathbf{a}_3$ direction. For the other five directions and their opposites, the point group is always C_{2v}, but the elements differ. The character table belonging to the vector $\mathbf{a}_3$ is given in Table 1. The single coordinates have a right-handed sense.

The three double products which are of interest belong to three different irreducible representations (IRREPS). Non-diagonal matrix elements of $V_{i,j}$ correspond to energy terms $V_{i,j}\Gamma_i\Gamma_j$. But

Table 1
Character table C_{2v}, the group of $\mathbf{a}_3$.

C_{2v}	E	C_{2a}	σ_z	σ_{db}		
A_1	1	1	1	1	$(x+y)/\sqrt{2}$	xy
A_2	1	1	−1	−1		$z(y-x)/\sqrt{2}$
B_1	1	−1	1	−1	$(y-x)/\sqrt{2}$	
B_2	1	−1	−1	1	z	$z(x+y)/\sqrt{2}$