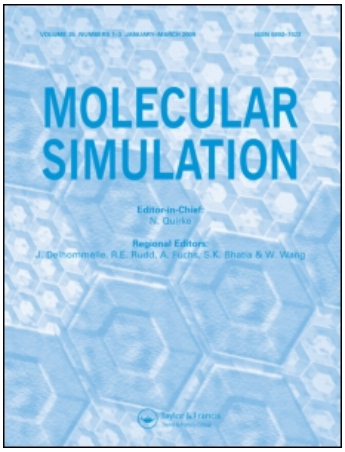

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INTERNAL RELAXATION, BAND GAPS AND ELASTIC CONSTANT CALCULATIONS OF FeS_2

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Full relaxation of volume and internal parameters of iron pyrite and marcasite FeS_2, has been studied using a plane-wave pseudopotential method within the Local Density Approximation to Density Functional Theory (LDA-DFT). We find that the internal parameter u of pyrite decreases with hydrostatic compression. The P-V equation of state falls slightly closer to the experimental curve than a previous unrelaxed Tight-Binding Linear Muffin-Tin Orbital (TB-LMTO) calculation. The optimized parameters are used in a TB-LMTO calculation to predict the electronic structure from which we find a larger band gap on marcasite compared to pyrite. *Ab initio* calculations of elastic constants for pyrite were performed using the Full Potential (FP) LMTO method and agree to within 7% with experiment.

Keywords: Internal relaxation; band gaps; elastic constants; FeS_2

I. INTRODUCTION

Transition metal sulphides are a major group of minerals. The iron disulphides and other pyrites are the most widely occurring of the sulphides being found not only in ore deposits but also as accessory minerals in many common rocks [1]. The mining industry is interested in their electronic, magnetic, optical, structural and thermodynamic properties as these effect ore

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formation, mineral processing and environmental mineralogy. Recently, we made a preliminary study of the equation of state (EOS), the electronic structure, and the optical and bonding properties of pyrite and marcasite [2]. The electronic properties of pyrite [2–5] and marcasite [2, 3] have been calculated earlier by several authors leading to a diversity of band gap values for pyrite and controversy surrounding its origin, mainly ionic or covalent in nature. An early, interesting study using the self-consistent two-centre tight-binding approximation was performed by Bullet [3], who predicted a smaller band gap for marcasite than that of pyrite [3]. A recent *ab initio* study of pyrite has been carried out by Eyert *et al.* [4], using the Augmented Spherical Wave (ASW) method. These authors came to the same conclusion as ourselves [2], that the electronic structure of FeS_2 are dominated by strong hybridization between the Fe $3d$ and S $3p$ states. They also studied the influence of pressure and crystalline distortions on the optical band gap, but under the constraint that the internal parameter u was kept fixed at its experimental equilibrium value. All previous calculations had also not optimized the internal parameters. The purpose of this paper is to perform a full relaxation and pressure dependent calculation of both lattice and internal parameters using CASTEP method [6]. Our relaxed calculations show a slight improvement in the P-V dependence of the EOS, compared to the experimental one. The electronic structures calculated at the optimized internal parameters show a larger band gap for marcasite than pyrite, which contradicts the earlier tight binding calculations [3]. We also present the first ever *ab initio* calculations of the elastic constants of pyrite that are found to accord well with experiment.

II. METHODOLOGY

The lattice constants and the internal parameters of both pyrite and marcasite phases were optimized using LDA version within the MSI-CASTEP programme [7]. The electronic wavefunctions are expanded in plane-waves, the number of which is determined by the cut-off energy of 800 eV for both pyrite and marcasite. This energy cut-off gives a fast Fourier transform (FFT) grid of $40 \times 40 \times 40$ and $30 \times 40 \times 24$ for pyrite and marcasite, respectively. The Monkhorst-Pack scheme was employed to select an optimal set of special k-points of the first Brillouin zone such that the greatest possible accuracy is achieved from the number of points used. In the present calculations a $2 \times 2 \times 2$ Monkhorst-Pack set for pyrite and a $2 \times 2 \times 3$ set for marcasite were used and the finite basis set correction (Pulay correction) was included to compensate the cut-off energy. In all

optimizations, the tolerance in total energy and pressure change before self-consistency was deemed to have been achieved was 2×10^{-5} eV/atom and 0.1 GPa, respectively. Details of our TB-LMTO computations for the pyrite structure have been outlined in [2]. For the orthorhombic marcasite phase (space group Pnnm), the positions of the atoms are generated by Fe: (2a) (0, 0, 0) and S: (4g) (u, v, 0). Additional 14 empty spheres are generated from the three different symmetry points E1: (2d) (0.5, 0, 0); E2: (4g) ($u1$, $v1$, 0) and E3: (8h) (x, y, z). 140 irreducible **k** points were used to generate the band structure and density of states for marcasite FeS_2. Finally, for the elastic constant calculations of FeS_2 we have used the FP-LMTO method which makes no shape approximation to the one-electron potential and provides the smallest possible basis for obtaining the necessary precision of about 10^{-5} Ry per atom in the total energy. More details about the FP-LMTO computations can be found in [8].

III. RESULTS

A. Internal Parameters and Bond Lengths

Figure 1a shows the dependence of the internal parameter u for the pyrite structure as a function of the applied hydrostatic pressure. It is found that the optimized value of u decreases with increasing in pressure due to the Fe—Fe bond length decreasing more rapidly than the S—S bond length, as seen in Figure 1b. The predicted equilibrium value of u is 0.385 compared to the experimental value of 0.384. The optimized bond lengths at equilibrium pressure are 2.145 Å for S—S, 2.249 Å for Fe—S and 3.806 Å for Fe—Fe bonds compared to the experimental values of 2.177 Å, 2.262 Å and 3.831 Å, respectively. At a high pressure of 25 GPa the corresponding bond lengths are reduced to 97.2%, 96.3% and 96.4%, respectively. For the marcasite structure, we have found at equilibrium the lattice parameters a = 4.373 Å (a_{exp} = 4.436 Å), b = 5.381 Å (b_{exp} = 5.414 Å), c = 3.407 Å (c_{exp} = 3.381 Å) and internal parameters u = 0.203 (u_{exp} = 0.200), v = 0.380 (v_{exp} = 0.378) for the S position. This corresponds to predicted bond lengths of 2.195 Å for S—S, 2.229 Å for Fe—S and 3.863 Å for Fe—Fe compared to the experimental values of 2.212 Å, 2.230 Å and 3.886 Å, respectively.

B. Equation of State

Figure 2 compares the equation of state in which the internal parameter u is allowed to relax within CASTEP with our previous TB-LMTO calculation

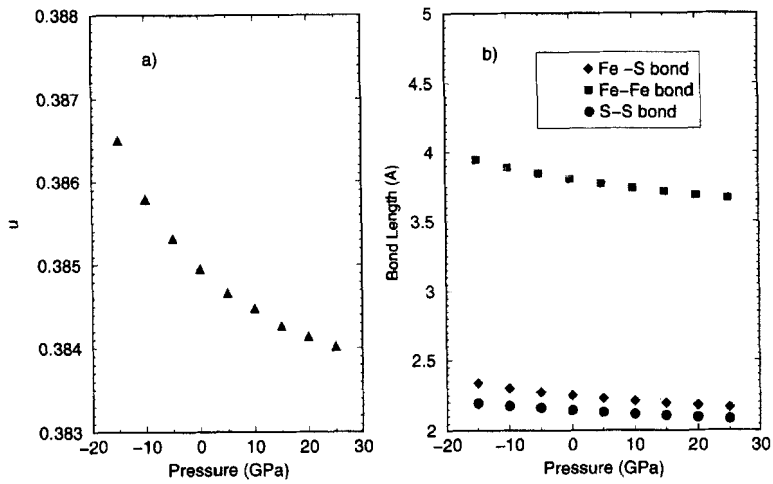

FIGURE 1 (a) Dependence of internal parameter u and (b) bond lengths in pyrite as a function of the applied hydrostatic pressure using CASTEP.

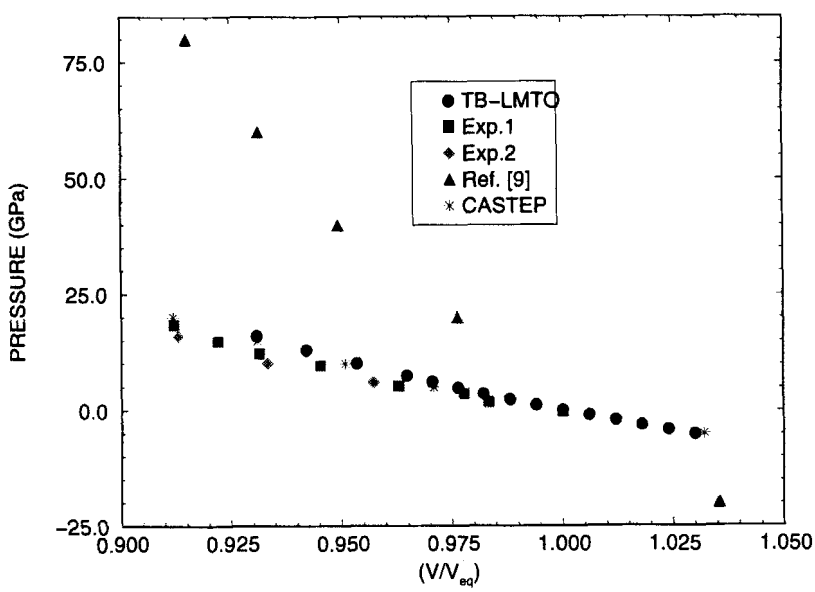

FIGURE 2 Pressure *vs.* renormalized equilibrium volume in pyrite. V_{eq} is the predicted equilibrium volume for the theoretical curves.

in which there is no relaxation of u. The volume has been normalized by the predicted equilibrium volume in both case. We also compare our results with the LMTO calculation of Temmerman *et al.* [9] where the P-V

dependence is poor due to an insufficient muffin-tin sphere treatment [2]. The CASTEP equilibrium volume $V_{eq} = 0.98\,V_{exp}$ is a slight improvement on our previous TB-LMTO result [2] which gave $V_{eq} = 0.97\,V_{exp}$. Our independent FP-LMTO optimisation gives $V_{eq} = 0.938\,V_{exp}$.

We see from the Figure 2 that the CASTEP EOS falls slightly closer to the experimental curves measured by Jephcoat [10]. This shows that simultaneous optimization of the volume and internal parameter can improve the prediction of the pressure-volume dependence of pyrite. The ratio of the equilibrium volumes of pyrite to marcasite (V_{pyr}/V_{mar}) is predicted to be 0.972 when the internal parameters are relaxed compared to the unrelaxed TB-LMTO prediction of 0.957 [2]. The relaxed prediction agrees well with the experimental value of 0.974.

C. Band Gaps

The total density of states (DOS) for both pyrite and marcasite were calculated at equilibrium optimized structure parameters using the TB-LMTO technique. The results are shown in Figure 3. The calculated DOS have similar features as discussed in previous paper [2] where we found that the $3d$(Fe)—$3s$(S) hybridization dominated the formation of the semiconductor gaps. The indirect gap of 0.72 eV for pyrite compares with of 0.91 eV for marcasite. The S—S bond length in marcasite is longer than in pyrite whereas the Fe—S bond length in marcasite is shorter. Hence, we emphasize again here that the energy gap in iron sulfide depends critically on the bonding properties of Fe—S rather than the conventional picture of the crystal-field splitting within transition metal d-band.

D. Elastic Constants of Pyrite

We have performed *ab initio* calculations of the elastic shear moduli of pyrite using the FP-LMTO technique. The calculations are made by finding the total energy as a function of a small strain, and extracting the second order terms numerically. In the case of C_{44} the strain is a stretch along the [111] direction. For the calculation of $C' = (C_{11} - C_{12})/2$ the principal axis are [001], [010] and [100] along which the strain are in the ratio $1:-0.5:-0.5$. One must be very careful to consider the symmetry dependence of shear strain under elastic constant calculations. The theoretical results are shown in Table I and are seen to agree well to within 7% with the experimental values [11]. The linearly extrapolated to 0K values from experimental dependences of the elastic constants as a function of temperature are also

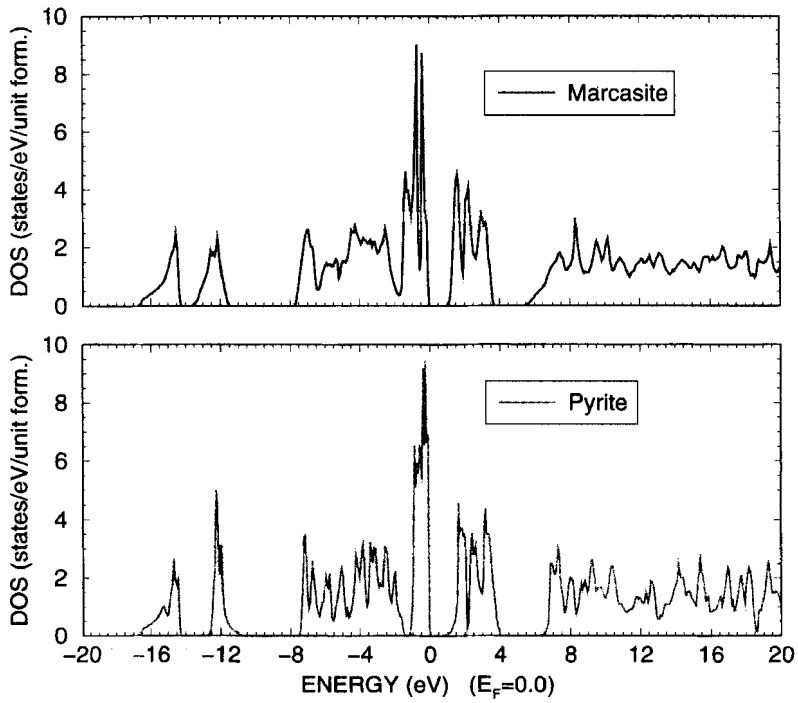

FIGURE 3 Self-consistent total density of states of FeS_2 in marcasite and pyrite structure types.

TABLE I Elastic properties of iron pyrite FeS_2 in GPa

Elastic moduli	*Exp. at 295 K*	*Exp. at 0 K*	*FP-LMTO*
C_{11}	366	385	401
C_{12}	49	44	47
C_{44}	103	107	109
$C' = (C_{11} - C_{12})/2$	159	171	176
$B = (C_{11} + 2C_{12})/3$	155	158	165

quoted in Table I. As far as we know, these are the first theoretical predictions in the literature. Note that the Cauchy pressure ($(C_{12} - C_{44})/2$) is strongly negative for pyrite, demonstrating that many-body interatomic potentials are very important for describing the bonding properties of FeS_2.

IV. CONCLUSIONS

We conclude that the internal electronic relaxation provides a better description of the equation of state of iron pyrite. A consistent account of

the semiconductor band gaps and bonding properties of both pyrite and marcasite types is related to the crucial role of the hybridization between Fe $3d$ and S $3p$ states. Despite the complex crystal structure of FeS_2 we are able to predict the elastic moduli in a very good agreement with experiment.

Acknowledgments

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