

Optical far infrared properties of FeS₂

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In this paper are presented the far-infrared reflectivity spectra for a cleaved FeS₂ sample measured at room temperature and at 77 K.

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1. Introduction

Metal sulfides are widely spread minerals and a source for obtaining pure metals like Zn and Cu. FeS₂ (pyrite) is the most widely spread and is well known as a component of sediments [1]. It is also a waste material from mining processes which through dissolution could form sulphuric acid in lakes and rivers. Recently, quite a number of papers have focused again on various properties of pyrite using modern instruments [2-4]. Ab initio simulations of the fundamental vibrational frequencies of selected pyrite-type pnictides have also been studied recently [5]. Detailed infrared studies of lattice vibrations in iron pyrite were performed a long time ago [6]. Four infrared-active modes were observed. Infrared absorption bands of pyrite using a powdered sample were studied in [7] and there were some discrepancies between these results and the modes observed in [6].

Since pyrite can also be used as photovoltaic material in solar cells it is interesting, in our opinion, to see if the quality of natural mineral pyrite is good enough to be used for making modern devices.

We used a single crystal of the natural mineral pyrite (FeS₂) from the Novo Brdo mine – Serbia. The samples were cut from a natural single crystal cleaved parallel to the plane (210). In this work we present far-infrared reflectivity spectra for the cleaved FeS₂ sample measured at room temperature and at 77 K.

2. Experimental procedure

Single crystal samples of mineral FeS₂ were cleaved and examined with X-ray diffraction confirming that they were single crystals cleaved parallel to the c-axis. Far infrared reflectivity measurements were made at 77 K and room temperature using a Bruker IFS-113V spectrometer equipped with an Oxford Instruments cryostat.

Impurity atoms in FeS₂ samples were measured using mass spectroscopy (Spark Source Mass Spectrometer JEOL). We have found that an arsenic impurity was dominant and it was 0.002 wt. %.

3. Results

Measured far infrared reflection spectra at room temperature and 77 K of a FeS₂ single crystal sample are given in Fig. 1. These experimental reflectivity diagrams were numerically analyzed using a modified four parameter model for the dielectric function [8] which takes into account that there is an influence between the plasma mode of the free carriers and the longitudinal LO-modes of the lattice [9]. More details of this modified model are given in our previous work [10].

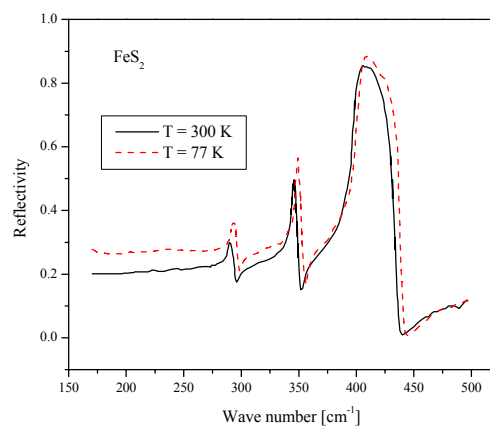


Fig. 1. Far infrared reflection spectra of FeS₂ at room temperature and 77 K.

Since the bonding properties of pyrite atoms can be investigated by vibrational spectroscopy the discussion of

our FIR reflectivity spectra will be started giving the unit cell of the pyrite structure in Fig. 2. FeS₂ crystallizes in a cubic structure with 12 atoms per primitive unit cell with a cube edge [11, 12] of $a_0 = 5.441 \text{ \AA}$. Four formula units per unit cell where Fe²⁺ occupy the sites of a face-centered cubic sublattice and the (S₂)²⁻ dimers are centered at the

midpoints of the cube edge and body center and their axes are oriented along the [111] directions. So each Fe atom is coordinated by six sulfur atoms in a slightly distorted octahedron and each S atom is bonded to three Fe atoms as it is shown in Fig. 2.

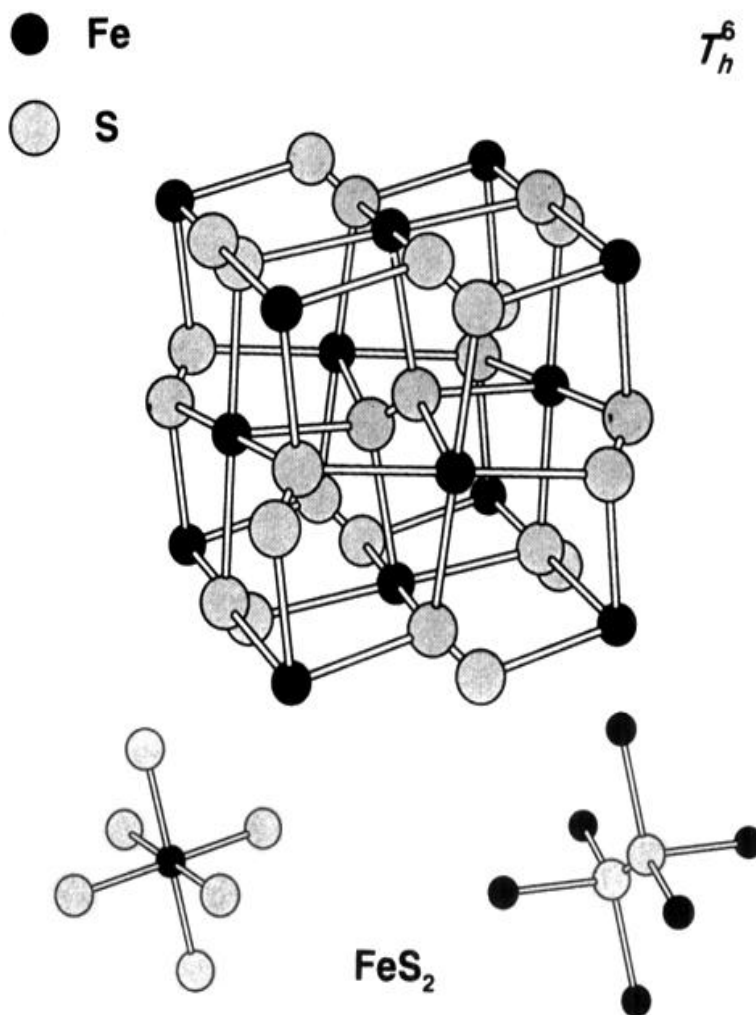


Fig. 2. Unit cell of the pyrite structure.

An electronic structure study of FeS₂ and its measured and calculated phonon frequencies was made in [4, 13] starting with 36 dimensional representations of the vibrational matrix for pyrite decomposed into the following irreducible representation:

$$\Gamma = A_g + E_g + 3T_g + 2A_u + 2E_u + 6T_u \quad (1)$$

where A_g , E_g and T_g represent Raman active modes; $2A_u + 2E_u$ are optically inactive. T_u characterizes five IR active and one acoustic mode.

In our measured data (Fig. 1) we observed three well exposed IR-active modes at room temperature while two weak modes were registered only at lower temperature (77

K). Plasma frequency was observed only at room temperature, at about 150 cm^{-1} , which obviously moved to a lower frequency when the temperature was decreased.

Calculated spectra obtained for FeS₂ are given, for room and liquid nitrogen temperature in Fig. 3 and Fig. 4, respectively, while the values of some calculated optical parameters are given in Table 1. The impurity local modes are marked as ω_{01} , ω_{02} , ω_{03} , ω_{04} and ω_{05} and their longitudinal optical modes are given with ω_{L1} , ω_{L2} , ω_{L3} , ω_{L4} and ω_{L5} , where γ_{01} to γ_{05} and γ_{L1} to γ_{L5} present their damping factors, respectively and ϵ_∞ is the high frequency dielectric permittivity.

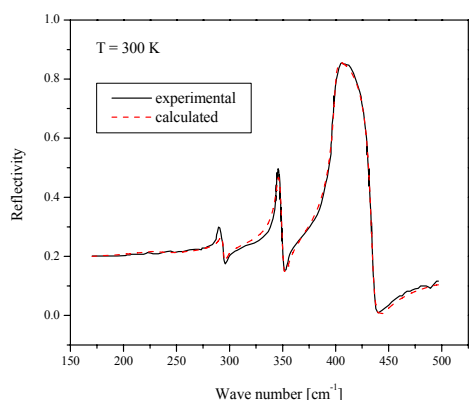


Fig. 3. Measured (solid line) and calculated (dash line) FIR spectra of FeS_2 at room temperature.

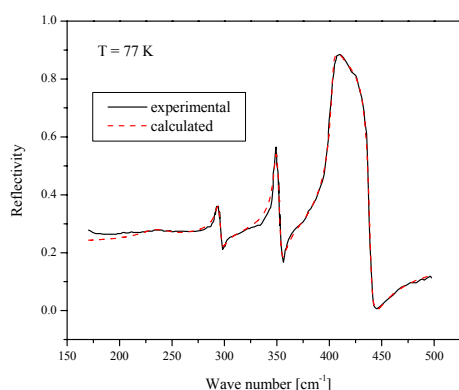


Fig. 4. Measured (solid line) and calculated (dash line) FIR spectra of FeS_2 at 77 K.

Table 1. Calculated optical parameters for FeS_2 at room temperature and 77 K, and literature data.

FeS_2	300 K	77 K	Ref. 6	Ref. 13	Ref. 4 cal.
ω_{01}	230.2	235.5		230	221
γ_{01}	53.8	31.0			
ω_{L1}	231.6	236.0		230	221
γ_{L1}	55.2	36.0			
ω_{02}	291.7	294.6	293	293	317
γ_{02}	4.40	4.43			
ω_{L2}	293.0	295.4	294	294	320
γ_{L2}	5.60	4.99			
ω_{03}	347.4	348.9	348	346	360
γ_{03}	3.5	3.7			
ω_{L3}	350.9	353.0	352	348	361
γ_{L3}	4.8	5.0			
ω_{04}	403.1	403.0	402	401	392
γ_{04}	13.40	2.29			
ω_{L4}	411.30	414.26	414	411	392
γ_{L4}	58.90	37.44			
ω_{05}	417.4	417.1	415	412	428
γ_{05}	39.7	38.0			
ω_{L5}	442.4	439.1	439	439	480
γ_{L5}	7.1	3.76			
ω_p	149.8				

4. Discussion

The experimental results obtained in this work can be compared with some old incomplete [6] and newer experimental [13] and calculated [4] phonon frequency data. All these phonon frequencies and our room temperature results are given in Table 1 enabling an easy comparison. Our room temperature infrared phonon frequencies are in good agreement with the room temperature experimental literature data [13]. This data was also confirmed by the performed IR reflectivity measurements at liquid nitrogen temperature. Furthermore, X-ray diffraction and mass spectroscopy measurements confirmed the high quality of mineral pyrite from the Novo Brdo mine so it can be used for making some useful modern devices starting with very cheap high quality minerals.

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