

The Electric Field Gradient of FePS₃ : a calculation.

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Electron density functional theory calculations, using the WIEN2k computer package, are carried out on the monoclinic symmetric FePS₃ structure. The aim is to support recent work carried out at Monash University on the elucidation of its anti-ferromagnetic structure and Mössbauer spectrum.

1. Introduction

FePS₃ is a layered structure material of considerable fundamental and technological importance, with its lithium intercalation properties of particular application in battery design [1]. It is a member of the metal phosphorous trisulphide family (MPS₃), and analogies can be made to members of the layered metal dichalcogenide family, such as molybdenum disulphide, by rewriting the formula unit as M_{2/3}(P₂)_{1/3}S₂. Recent work at Monash University has centred on the elucidation of the anti-ferromagnetic structure of this material by neutron diffraction [2]. As an extension to this work the Mössbauer spectrum has been determined [3]. By careful analysis, this allows the electron charge density close to the Fe atom to be determined [4]. The present work shows results from electron density functional theory calculations using the WIEN2k computer package [5].

2. Simple Understanding of the FePS₃ structure by close packing structures

The simplest way of understanding the FePS₃ structure is by considering the packing of the formula unit Fe_{2/3}(P₂)_{1/3}S₂. Initially the S anions are taken to be close packed and then 2/3 and 1/3 of the octahedrally co-ordinated sites are occupied by the Fe cations and P₂ dimers respectively [6].

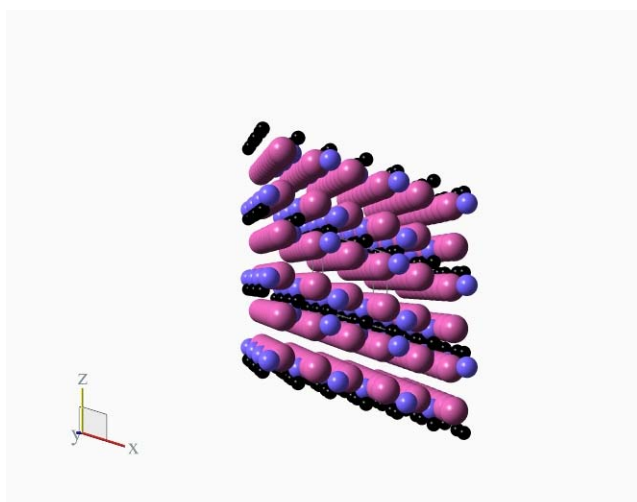


Fig.1 FePS₃ structure showing layered structure. Largest (purple) spheres S atoms, smallest (black) spheres Fe atoms, medium (blue) spheres P atoms, y axis is down into plane of paper, x y z are parallel to the original monoclinic a b c axes.

Examples of close packing structures are well known for single elements: cubic close packed (face centred cubic) and the hexagonal close packed structures. Similar layered structures can be described by anion stacking followed by alternate cation layer filling for cadmium iodide and cadmium chloride [7]. It is then possible to approximately describe the FePS_3 structure by analogy with cadmium chloride [8].

3. Choice of monoclinic crystal system

As FePS_3 adopts a face centred monoclinic structure, C 2/m (International Tables of Crystallography [10] Space Group No. 12), there is a choice as to the setting of the unique crystal axis (see discussion on pages 54 and 77 in [10]). In the EFG calculation the structural parameters of Klingen et al. [11] have been used, which are given by $a = 5.934 \text{ \AA}$, $b = 10.28 \text{ \AA}$, $c = 6.772 \text{ \AA}$ and $\beta = 107.2^\circ$ with Fe, P and S specified in 4g, 4i, 4i and 8j Wyckoff positions. This corresponds to unique axis b, cell choice 1 (page 160 in [10]). The cell is then face centred (C-centred) in the XY plane (page 77 in [10]). However WIEN2k requires such a monoclinic structure to be described by a cell face centred in the XZ plane and with orthogonal axes [5] (see page 77 in [10]). This corresponds to a B face centred cell with unique axis c. Accordingly structure parameters need to be input using the unique axis c cell choice (page 165 in [10]). Rather than just a simple exchange of b and c values the crystal lattice parameters become $c = 10.28 \text{ \AA}$ (original b), $b = 7.567 \text{ \AA}$ (short diagonal of original b c face), $a = 5.934 \text{ \AA}$ and $\gamma = 121.29^\circ$ with alterations in b and γ values because of the change of reduced mesh for the monoclinic structure (page 35 in [10]). This is, however, automatically determined by a program within the WIEN2k package [12].

4. The Electric Field Gradient

An energy splitting in the Mössbauer spectrum is created by the interaction of the nuclear electric quadrupole moment with the electric field gradient of the surrounding crystalline lattice. As this depends on the electric charge density it provides valuable information on the chemical bonding. It is simplest to write the electric field as the negative derivative of the electrostatic potential with respect to the Cartesian co-ordinates at the nuclear site. Then taking the derivative once more, the Electric Field Gradient (EFG) can be found. The EFG can be regarded as a second rank symmetric tensor, with careful definitions it has zero trace and thus in general only 5 components [4].

As the local point symmetry at the Fe (4g) site is monoclinic, the associated EFG as a second-rank tensor has only four independent terms. [9] Accordingly the traceless condition results in only three independent components to be determined for the EFG.

5. Principal Axis System of the EFG

Considering the EFG as a real symmetric matrix, it can be diagonalised by a transformation to the principal axis system (PAS). Owing to the traceless condition, this has only two independent components in the PAS. Conventionally, results are expressed by the EFG component with the largest magnitude Φ_{zz} and the asymmetry parameter η ($0 \leq \eta \leq 1$) defined by the magnitude of $(\Phi_{xx} - \Phi_{yy}) / \Phi_{zz}$ with $|\Phi_{zz}| > |\Phi_{yy}| > |\Phi_{xx}|$.

Accordingly for the case of FePS_3 , which has three independent components in the monoclinic crystalline system, there is a third parameter beyond Φ_{zz} and η . This can be taken as the rotation angle θ between the monoclinic crystal system and the principal axis system, with the unique monoclinic axis being required to also be a principal axis of the EFG.

6. Results of the EFG calculation

The calculated 3 x 3 matrix EFG, in units of 10^{21} V m^{-2} , that respects the monoclinic symmetry is:

$$\Phi_{ij} = \begin{bmatrix} -1.06604 & 1.36868 & 0. \\ 1.36868 & 1.97760 & 0. \\ 0. & 0. & -0.91155 \end{bmatrix}$$

On rotation into the PAS, this gives the largest value of the EFG, Φ_{zz} , equal to $2.50254 \times 10^{21} \text{ V m}^{-2}$, asymmetry parameter η as 0.27150 and rotation angle θ equal to 21.0°

Some care must be taken when interpreting these results as the original monoclinic crystal axes are not orthogonal. However, inside the WIEN2k program suite, the EFG is calculated from an expansion in spherical harmonics carried out in a Cartesian co-ordinate system. [13]. Taking into account the utilised gamma value of 121.29° followed by the 21° rotation, this means that the direction of the greatest EFG tensor component is at approximately 10° away from the normal of the almost hexagonal layers of Fe atoms towards the original a axis.

Acknowledgments

The graphical display was produced using the Balls & Sticks (BS) program, by Sung J. Kang & Tadashi C. Ozawa, which is available as freeware at tcozawa@yahoo.com.

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