

## Local electronic and charge state of iron in FeTe<sub>2</sub>

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**Abstract** From <sup>57</sup>Fe Mössbauer spectrum of FeTe<sub>2</sub> taken in high external magnetic field ( $B = 4.6$  T), the sign of electric field gradient was determined as negative, with an asymmetry parameter of 0.2. A comparison of these data with results of calculation of the electric field gradient within point charge model suggests the lattice character of electric field gradient with some contribution from covalency effects. The effective magnetic field acting on <sup>57</sup>Fe is less than the applied, which points out the diamagnetic Fe<sup>+2</sup> state of iron. This “electronic state” is in a contradiction to Fe<sup>+3</sup> “charge state” concluded from <sup>125</sup>Te experiments on 3*d* transition metal ditellurides as well as from <sup>57</sup>Fe quadrupole splitting and isomer shift.

**Key words** Mössbauer • chemical bonding • charge state • tellurides

### Introduction

A theoretical and experimental study of the relations between crystal structures and local electronic states of their elemental constituents is a key for understanding many basic problems of solid state physics. Although present numerical methods are able to reproduce, in some cases, the electronic properties of broad classes of compounds with known structure, the experiments which are sensitive to local electronic states are necessary for testifying assumptions applied in the calculation.

The present work is a continuation of the study of an interesting group of materials, 3*d* transition metal ditellurides, which exhibit gradual changes in crystal structure from pyrite type, through marcasite to CdI<sub>2</sub>-type with increasing number of 3*d* electrons of cations. Previous Mössbauer experiments on <sup>125</sup>Te [1, 5] supplied the data on charge states of Te which determine as well the charge states of metals. This charge state of metal may be directly checked only in case of FeTe<sub>2</sub>. However, by substitutional doping <sup>57</sup>Fe into other ditellurides it appears feasible to observe how the crystal structure forces the charge and electronic states of this probe [4].

In this paper we concentrate on valence and charge states of iron in FeTe<sub>2</sub>. The problem is not trivial. The magnetic measurements clearly show the diamagnetic state of iron, with formal low spin 3*d*<sup>6</sup> configuration ( $S = 0$ ). This was, at first look, in a contradiction with the <sup>125</sup>Te Mössbauer investigations as described in Discussion.

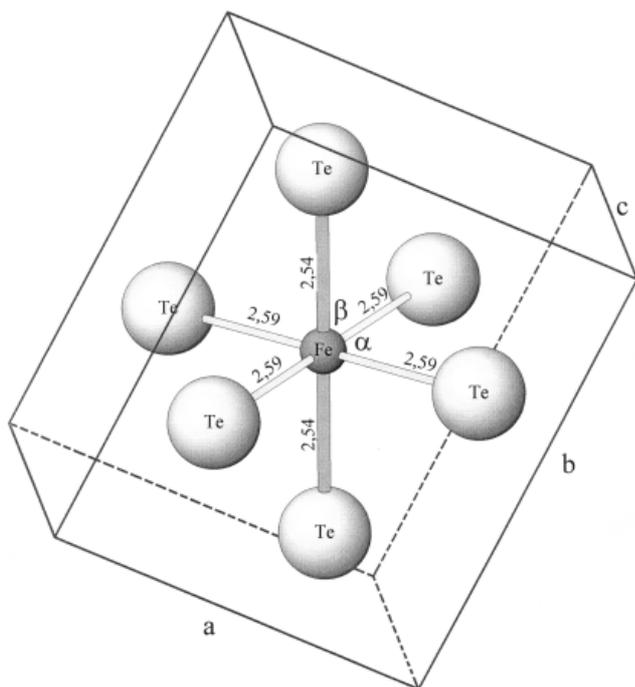
### Experimental and results

The crystal structure of FeTe<sub>2</sub> is orthorhombic marcasite type (Pnmm). Each tellurium atom has one Te atom as the nearest neighbour at a distance of 0.293 nm, iron is octa-

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Received: 28 June 2004, Accepted: 20 September 2004



**Fig. 1.** The octahedral coordination of Fe in  $\text{FeTe}_2$  unit cell. Iron has two linear nearest and four planar next-nearest tellurium neighbours. The distances are in Å. The octahedron is distorted: the marked angles are:  $\alpha = 88.1^\circ$ ,  $\beta = 96.0^\circ$ .

hedrally coordinated by Te atoms. The distorted  $\text{Te}_6$  octahedron is compressed, which leads to quasi-linear coordination of Fe. The details of the local surrounding of Fe are shown in Fig. 1. In general, the structure of  $\text{FeTe}_2$  may be described as formed of Fe cations and weakly bounded  $\text{Te}_2$  molecular anions.

Sample of  $\text{FeTe}_2$  was synthesised from high purity elements employing dry evacuated silica tube technique. The specimen was heated, quenched, reground and annealed at  $400^\circ\text{C}$  several times until complete, single phase equilibrium, tested by X-ray diffraction, was obtained. The details of the preparation are given in [1]. The  $^{57}\text{Fe}$  Mössbauer spectra were recorded at a temperature between 293 K and 4.2 K. In addition, at 4.2 K the spectrum was recorded in an external magnetic field of 4.6 T, parallel to gamma radiation.

The spectra taken without magnetic field are symmetric quadrupole doublets with quadrupole splitting,  $\Delta = 0.52$  mm/s, practically invariant between room temperature and 4.2 K and isomer shift,  $\delta = 0.47$  mm/s at room temperature, see Fig. 2. The spectrum taken in external field, shown as well in Fig. 2, was numerically evaluated using the Gabriel-Ruby procedure. The fit gives negative sign of the electric field gradient tensor,  $V_{zz} < 0$ , which is obvious from visual inspection of the spectrum, and asymmetry parameter  $\eta = 0.2(1)$ . Moreover, the fitted effective magnetic field was less by 2% than the applied one.

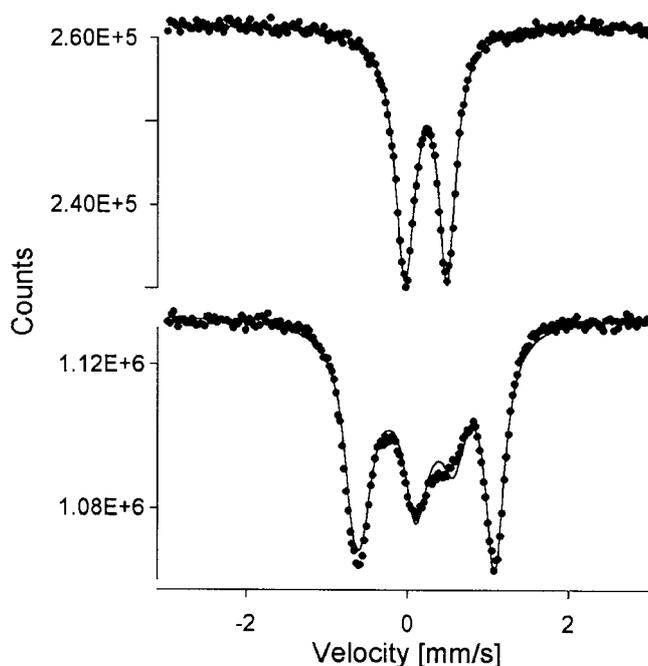
## Discussion

From the previous  $^{125}\text{Te}$  experiments on  $\text{MeTe}_2$  series, (Me = Mn, Cr, Fe, Co, Ni) a linear correlation between  $\Delta$  and  $\delta$  was found. The isomer shift may be expressed by deficit  $a$

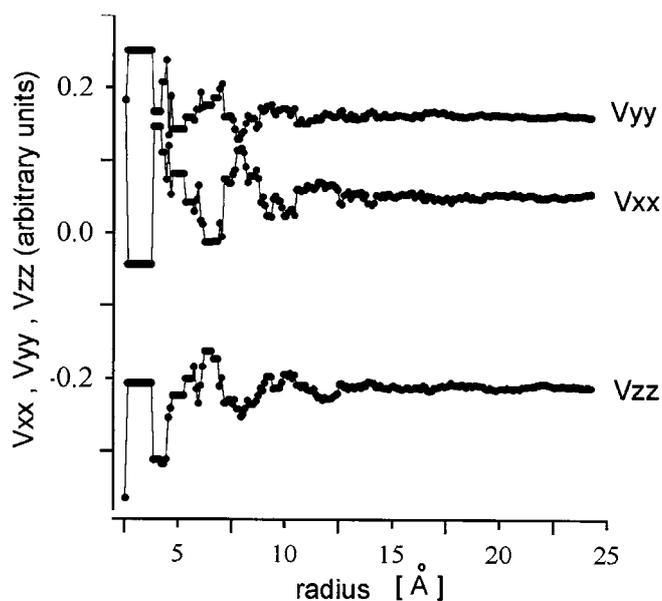
and  $b$  in  $5s$  and  $5p$  orbitals, respectively, as:  $\delta = \delta_0 - 2.4a + 0.4b$  [2] where  $\delta_0 = 1.66$  mm/s is the isomer shift in the hypothetical  $\text{Te}^{-2}$  anion with  $5s^25p^6$  configuration. In addition, the quadrupole splitting is:  $\Delta = b\Delta_0$ , where  $\Delta_0 = 12$  mm/s is the quadrupole splitting produced by one electron hole in the  $5p_z$  orbital [3]. These relations allowed the determination of electron configuration of Te in form of  $5s^{2-a}5p^{6-b}$  in this group of materials and lead to the effective charges of Te:  $-0.98, -1.12, -1.50, -1.61$  and  $-1.96$  for  $\text{MnTe}_2, \text{CrTe}_2, \text{FeTe}_2, \text{CoTe}_2$  and  $\text{NiTe}_2$ , respectively. Consequently, the charge states of cations were determined as well. In particular, the Fe charge state of +3 was predicted for  $\text{FeTe}_2$ .

Indeed, the  $\Delta$  and  $\delta$  values of  $^{57}\text{Fe}$  in  $\text{FeTe}_2$  are typical for high spin  $\text{Fe}^{+3}$  state. Moreover, for such iron state the electric field gradient (efg) has only lattice origin, being weakly temperature dependent, which is confirmed by experiment. To study this problem more accurately, the lattice efg was calculated in the point charge model. Certainly, such approach is a significant approximation and cannot give reliable values of quadrupole splitting but, at least, the sign and asymmetry parameter of efg are reliable. The calculations were carried out considering the sphere surrounding Fe atom with the radius up to 2 nm; it turned out that the values of efg are determined by charges placed up to 1.5 nm from Fe atom, see Fig. 3.

The results of calculations are interesting. The sign of  $V_{zz}$  is negative, as expected from the quasi linear coordination of Fe. However, the difference in distances between linear and planar tellurium neighbours is small (0.005 nm) and the efg coming from  $\text{Te}_6$  non axially distorted octahedron is positive. The next neighbours of the Te atoms in this structure change the sign of efg again to the negative one. The final asymmetry parameter is  $\eta = 0.5$ , significantly higher than the experimental one,  $\eta = 0.2(1)$ . This difference points out some covalency effects: the covalent bonding of



**Fig. 2.**  $^{57}\text{Fe}$  Mössbauer spectra of  $\text{FeTe}_2$  taken at 297 K (above) and at 4.2 K in external magnetic field  $B = 4.6$  T (below). Solid line is the fit.



**Fig. 3.** Components of electric field gradient tensor ( $V_{xx}$ ,  $V_{yy}$ ,  $V_{zz}$ ) in principal axes system calculated in point charge approximation vs. radius of the sphere surrounding Fe included for calculations.

Fe with two nearest Te ligands increases axial electron density and reduces the asymmetry of the lattice efg.

Summarising, the  $^{125}\text{Te}$  and  $^{57}\text{Fe}$  measurements give a consistent picture of the charge transfer from Fe to Te in FeTe<sub>2</sub>. The crystal is built from  $(\text{Te}_2)^{-3}$  molecules and  $\text{Fe}^{+3}$  ions with some residual Te-Fe-Te covalent bonds. However, from the text books of inorganic chemistry it is well known that Fe in FeTe<sub>2</sub> is diamagnetic, which leads to  $\text{Fe}^{+2}$  (low spin,  $S = 0$ ) state. Indeed, the spectrum taken in external magnetic field shows that the effective field at  $^{57}\text{Fe}$  nuclei is reduced in comparison with the applied field that confirms the  $S = 0$  state of iron.

In fact, this is only an apparent discrepancy of linguistic character. Three lowest electronic levels of Fe are occupied

by paired electrons which give the spin  $S = 0$ . However, these levels are only partly filled, there is a significant charge transfer from iron to tellurium. In consequence, the localised charge is such as in typical  $\text{Fe}^{+3}$  state.

### Summary

This simple minded work points out that the terms “electronic state”, “charge state” and “valence state” should not be used equivalently. In the case studied, iron in FeTe<sub>2</sub> has low spin “electronic state” with nominal  $3d^6$  configuration. Such configuration means only that electronic levels are populated by paired electrons. However, if the charge localised on Fe is considered, due to the significant electron flow from Fe to Te, directly measured by  $^{125}\text{Te}$  resonance the “charge state” of Fe should be described as  $\text{Fe}^{+3}$  which is in agreement with the observed isomer shift of  $^{57}\text{Fe}$ . In other words, in FeTe<sub>2</sub> the low spin  $\text{Fe}^{+2}$  orbitals are used to form +3 charge state of iron; its electronic configuration may be written as  $3(d^6)^x$ ,  $x = 5/6$ .

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