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A HIGH PRESSURE INVESTIGATION OF THE CONDUCTION IN ILMENITE

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Résumé. — On a étudié l'effet de la pression sur la conductibilité et les spectres Mössbauer du semiconducteur FeTiO_3 . Les spectres sont interprétés en termes de deux doublets. Le doublet, le plus intense est causé par les ions de fer dans les couches $\langle 111 \rangle$ de fer ; le deuxième est causé par les ions de fer dans les couches $\langle 111 \rangle$ de titane dans la structure corundum. Nous comparons les changements, induits par la pression dans FeTiO_3 aux changements dans Fe_2O_3 , un isolateur, qui a la même structure. Nous expliquons l'augmentation de la conductibilité et la décroissance du déplacement isomérique des ions de fer dans les couches de fer par une délocalisation des électrons 3d dans ces couches de FeTiO_3 .

Abstract. — The effect of pressure on the conductivity and the hyperfine interactions at the ^{57}Fe nuclei of semiconducting FeTiO_3 has been studied. The Mössbauer spectra of ilmenite are interpreted in terms of two doublets. The most intense one is due to Fe^{2+} -ions in the Fe- $\langle 111 \rangle$ layers ; the second one is due to Fe^{2+} -ions in the Ti- $\langle 111 \rangle$ layers in the corundum structure. A comparison is made with the pressure induced changes in insulating $\alpha\text{-Fe}_2\text{O}_3$ which has the same structure. The increase of conductivity and the decrease of the isomer shift of the Fe^{2+} -ions in the Fe-layers of FeTiO_3 is explained by means of a delocalization of 3d electrons in these layers of ilmenite.

1. Introduction. — At high pressures the conductivity of semiconductors like ilmenite (FeTiO_3) may considerably change, due to the reduction of the lattice parameters and the related changes in the energy-band structure. Ilmenite, an antiferromagnet ($T_N = 57 \text{ K}$) has semiconducting properties, which can be described with a localized electron model [1, 2]. Due to the *extra* 3d electron of the Fe^{2+} ions, ilmenite is a semiconductor, instead of an insulator like haematite ($\alpha\text{-Fe}_2\text{O}_3$), showing the same corundum structure and which is also an antiferromagnet ($T_N = 956 \text{ K}$). Because of increasing overlap and transfer effects with increasing pressure, one may expect an increasing conductivity or even a nonmetal-metal transition in FeTiO_3 under externally applied pressure. In view of these expectations, we have studied the effects of pressure on the conductivity and the hyperfine interactions at the ^{57}Fe nuclei in FeTiO_3 . In particular we have compared the pressure induced changes in the hyperfine interactions FeTiO_3 and Fe_2O_3 , because the Fe ions have nearly the same surroundings in both oxides and in this way we may have information about the behaviour of the *extra* 3d electron in FeTiO_3 with pressure.

2. Structure. — Ilmenite has an ordered corundum structure [3] in which the Fe^{2+} and Ti^{4+} ions occupy alternating $\langle 111 \rangle$ layers. The cations are located in a slightly distorted octahedron of oxygen ions. In figure 1 the cation sublattice of FeTiO_3 is shown. No complete ordering of the Fe and Ti ions exists. A neutron diffraction study [4] revealed that about 5 % of the Fe ions are located in the Ti- $\langle 111 \rangle$ layers. The cationic puckering around the $\langle 111 \rangle$ basal planes, induced by the Fe^{2+} - Ti^{4+} electrostatic repulsion is relatively large compared to the puckering in other compounds with corundum structure.

3. Experimental. — The high pressure apparatus which is used in the Mössbauer and conductivity measurements, is based upon the Bridgeman-anvil technique. The apparatus is similar in design as the high pressure system, described by P. Debrunner *et al.* [5, 6]. Mössbauer experiments are performed with the absorber in the pressure cell. The sample mixed with boron, is placed in a hole (0.5 mm $\varnothing$) of a boron-epoxy disk (2 mm $\varnothing$, 0.35 mm thick). This disk, acting as a pressure vessel is pressurized between tungsten carbide anvils producing quasi hydrostatic

FIG. 1. — The cation sublattice of FeTiO_3 , showing the hexagonal unit cell.

pressure at the center of the disk. Before use the disk is prepressed in order to minimize the plastic deformation under pressure and to remove possible airbubbles in the boron-epoxy disk. By means of a manostat pressure regulator in conjunction with a pressure balance the pressure in the system could be kept constant for weeks, showing maximum deviations of about 2 kbar. Using a HP 3490A multimeter we measure the resistance of the pressure cell, including the anvils and the sample gasket. The known standard resistance discontinuities for bismuth at 25.4 kbar and 76 kbar were used to calibrate the pressure apparatus.

Mössbauer spectra were recorded using a spectrometer in conjunction with an Intertechnique Didac 4000 multichannel analyser. A commercial pointsource of 45 mC in a Rh matrix with an active area of about 2 mm² was used. The Mössbauer spectrometer was calibrated using absorbers of natural iron and powdered $\alpha\text{-Fe}_2\text{O}_3$ at room pressure. In order to maximize the Mössbauer absorption in the small samples in the pressure cell, we used enriched ^{57}Fe -samples and most

of the stray radiation was cut off by lead. Starting materials for the sample preparation were enriched or unenriched Fe_2O_3 , Fe and TiO_2 . After being mixed in stoichiometric proportions, a pellet was made. The pellets were fixed at 1 000 °C for more than ten hours under vacuum in a quartz tube. The pellets were quenched to room temperature. The X-ray diffraction patterns of the unenriched samples showed only lines corresponding to the ilmenite structure. Spectra of the enriched and unenriched samples with about 5 mg/cm² ^{57}Fe showed the same Mössbauer pattern.

4. Results. — We show in figure 2 the resistance of FeTiO_3 as a function of quasihydrostatic pressure. The pressure scale is based upon calibration curves with Bi. The curves are the best fits through the data points from several independent runs. As can be seen, up to about 20 kbar FeTiO_3 shows a strongly decreasing resistance. At higher pressures the resistance is still decreasing but not as strong as in the first region of 20 kbar.

FIG. 2. — The resistance of FeTiO_3 as a function of pressure at room temperature, together with the Bi calibration curve.

As has been mentioned before, some of the Fe ions in ilmenite are located in the $\text{Ti-}\langle 111 \rangle$ layers. We interpret the spectra of FeTiO_3 in terms of two doublets. The most intense doublet is due to Fe^{2+} ions in the $\langle 111 \rangle$ -Fe layers; the other one is due to Fe^{2+} ions in the $\langle 111 \rangle$ layers of Ti^{4+} ions. In figure 3 the room temperature spectrum of a thin absorber of FeTiO_3 is shown, together with our interpretation. In Table I the results of the analysis of room temperature spectra of FeTiO_3 at 1 bar are given.

If one defines an ordering parameter s as follows: let f be the fraction of Fe ions at the $\text{Fe-}\langle 111 \rangle$

FIG. 3. — Mössbauer spectrum of FeTiO_3 recorded at room pressure and room temperature.

layers, then we define $s \equiv 2f - 1$. s ranges from 1 for complete order and 0 for complete disorder. We find from our Mössbauer results (Table I) $s = 0.88 \pm 0.01$ which is in good agreement with the result obtained by Shirane *et al.*: $s = 0.90$ by means of a neutron diffraction study [4].

TABLE I

Doublet notation	I	0
IS rel to Fe (mm/s)	1.08	1.01
$ 2\epsilon $ (mm/s)	0.69	1.78
Relative intensity	16.2	1

In figure 4 a Mössbauer spectrum of FeTiO_3 is shown recorded at 14 kbar, together with our interpretation. The linewidth is of the order of 1 mm/s, due to the rather thick absorber in the pressure cell. If we

FIG. 4. — Mössbauer spectrum of FeTiO_3 recorded at 14 kbar and at room temperature.

interpret the high pressure Mössbauer spectra in terms of one doublet, we obtain reasonable agreement with Vaughan and Drickamer [7]. A better analysis is

found in terms of two doublets as has been shown before. In figure 5 the hyperfine parameters IS and ϵ are given for these two doublets (I and 0) as a function of pressure. It can be seen that the isomer shift of the doublet (I) due to the Fe-ions in the Fe-layers decreases with about 0.06 mm/s per 10 kbar while the isomer

FIG. 5. — The isomer shift (rel to Fe) and the absolute value of the quadrupole shift of the two doublets (I and 0) of FeTiO_3 as a function of pressure obtained from spectra recorded at room temperature.

shift of doublet (0) due to the Fe ions in the Ti-layers remains constant within the experimental error. It is interesting to compare this behaviour with the pressure induced changes in the hyperfine parameters of $\alpha\text{-Fe}_2\text{O}_3$, where the Fe-ion has nearly the same surroundings. We have obtained Mössbauer spectra of $\alpha\text{-Fe}_2\text{O}_3$ up to 40 kbar. It is important to note that in this pressure range the isomer shift is constant within the experimental error

$$(IS \text{ rel to Fe} = 0.38 \text{ mm/s} \pm 0.01).$$

In figure 6 the quadrupole shift (ϵ) is given as a function of pressure. At about 25 kbar there is a change in sign of the quadrupole shift.

FIG. 6. — The quadrupole shift of Fe_2O_3 as a function of pressure obtained from spectra recorded at room temperature. Values obtained by Vaughan and Drickamer ([7], (O)) and our results ((●), (Δ thin absorber)) are presented.

5. Discussion. — The hyperfine interaction parameters like the isomer shift and the quadrupole interaction and their behaviour as a function of pressure, provide information concerning the electronic structure in semiconducting FeTiO₃.

The quadrupole interaction, depending on the site-symmetry and geometry, structural properties of the iron sites, has two contributions: one ionic and one lattice contribution [8]. For the Fe³⁺ ions in the ⁶S_{5/2} state, which is the case for α-Fe₂O₃, the ionic contribution is zero; the observed quadrupole splitting results from the lattice. The measured change in sign of the quadrupole splitting is associated with the Morin-transition in α-Fe₂O₃ [7, 9].

Concerning the Fe²⁺ ions in FeTiO₃, the extra 3d electron will give rise to an ionic contribution to the quadrupole interaction, which is usually much larger than the lattice contribution. The electric field gradient at the ⁵⁷Fe nuclei caused by the extra electron reflects the deviation from cubic symmetry. The increase of the quadrupole splitting with pressure of the Fe²⁺ ions in the Fe and Ti layers in FeTiO₃ indicate an increase of the site distortion, assuming no radial expansion of the 3d orbitals with pressure [10]. A more detailed discussion can be given if the groundstates of the two different Fe²⁺ ions in the < 111 >-layers are better known.

Pressure induced changes in the isomer shift may have different causes. The isomer shift depends upon the s electron charge at the ⁵⁷Fe nucleus. A change in the charge of 3d character will effect the s electrons of the iron ions via Coulomb and exchange interactions [11]. The isomer shift is also related to covalency parameters such as overlap and transfer integrals, which depend upon the interionic distances [12]. Apart from a change in isomer shift also a pressure induced change in the second order Doppler shift is possible. A reasonable estimate of the change in shift of Fe₂O₃ due to a change in second order shift [7] and in

covalency parameters [10] with pressure is about – 0.005 mm/s per 10 kbar. This explains well the constancy of the isomer shift of the Fe³⁺ ions in Fe₂O₃, because no change in charge of 3d character with pressure can be expected. Concerning the behaviour of the isomer shift of the Fe-ions in the Fe-layers with pressure, we think that the decrease of 0.06 mm/s per 10 kbar is mostly due to an increase of the s electron density at the ⁵⁷Fe nuclei. Assuming that the extra 3d electron of the Fe²⁺-ion in the Fe-layer becomes delocalized with increasing pressure, we can say that the s electrons are less screened from the nucleus, causing an increase of s electron density at the ⁵⁷Fe nucleus. In this way it is easy to see why the isomer shift of the Fe-ions in the Ti-layers is constant with pressure: the extra 3d electrons are well localized in the Ti⁴⁺-layers in comparison with those in the Fe²⁺-layers. This delocalization process in the Fe-layers will also explain the increase of conductivity of ilmenite with pressure.

6. Conclusion. — Up to about 20 kbar, FeTiO₃ shows a strongly increasing conductivity. This fact and the high pressure Mössbauer spectra of semiconducting FeTiO₃ can be interpreted in terms of a charge delocalization process of the Fe²⁺-ions in the Fe-< 111 > layers. This interpretation results from a comparison of the high pressure Mössbauer data of insulating Fe₂O₃.

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