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PRESSURE INDUCED ORBITAL GROUND STATE INVERSION IN Fe(H₂O)₆SiF₆

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1. Introduction

Over the past years much work has been done in investigations of pressure induced electronic changes in iron compounds by means of Mössbauer resonance measurements. Concerning only high spin ionic ferrous compounds, the effect of pressure to 200 kbar on the Mössbauer resonance in a series of compounds was studied [1,2]. In general only small effects were observed. The isomer shift slightly decreases with increasing pressure and usually the quadrupole splitting increases with pressure.

This work is a study of the effect of pressure on the Mössbauer resonance of ferrous fluosilicate hexahydrate. To the author’s knowledge a new type of pressure effect in ferrous ionic compounds is reported, which seems to be due to an orbital level reversion caused by a change of the crystal field.

2. Experimental and Results

The pressure cell used consists of a steel cylinder and a screw both with longitudinal holes for transmission of the γ-rays. The absorber samples, kept between two boron-carbide plates (B₄C), were embedded in talc powder, which has good homogeneity in transmitting pressure. The applied pressure can roughly be estimated by means of the torque to the screw with which the pressure is generated. Single crystals and powder samples were measured at room temperature.

The single crystal spectra obtained at room temperature are shown in fig.1. The γ-direction was chosen perpendicular to the three-fold crystal axis which nearly coincides with the principal axis $V_{zz}$ of the EFG. The two spectra in the middle part of fig.1 were recorded at a pressure of 7 kbar and 15 kbar, respectively. Each of the spectra consists of two well resolved doublets. The pressure induced inner doublet was nearly the same isomer shift as the outer doublet but a quadrupole splitting which is reduced by more than a factor of two in magnitude. The splittings and isomer shifts are mostly pressure independent, whereas the intensity ratio between the inner and outer doublet increases with pressure. After releasing pressure the spectrum consists again of only one doublet having the same isomer shift and quadrupole splitting as in the unpressed case. From comparison of

Fig.1: Spectra of a Fe(H₂O)₆SiF₆ single crystal without and with pressure (γ⊥V_{zz}; $T \approx 295 K$). From top to bottom: at atmospheric pressure (p=0) with pressure p=7 kbar; p=15 kbar; after releasing pressure (p=0).
the spectra on the top and bottom of fig.1 it can easily be seen that the intensity ratio before and after applying pressure has drastically changed in magnitude. The same effect is also observed for powder samples and is probably due to texture.

The Mössbauer parameters obtained from the least squares fits are summarized in table 1.

Table 1: Quadrupole splittings $\Delta EQ$ and isomer shifts $\delta$ (against metallic iron) in mm/sec of Fe($H_2O$)$_6^-$SiF$_6$ (Errors smaller than 0.005 mm/sec).

<table>
<thead>
<tr>
<th></th>
<th>normal phase</th>
<th>pressure phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta EQ$</td>
<td>before (p=0)</td>
<td>3.403</td>
</tr>
<tr>
<td></td>
<td>p=7kbar</td>
<td>3.458</td>
</tr>
<tr>
<td></td>
<td>p=15kbar</td>
<td>3.460</td>
</tr>
<tr>
<td>$\delta$</td>
<td>before (p=0)</td>
<td>1.271</td>
</tr>
<tr>
<td></td>
<td>p=7kbar</td>
<td>1.265</td>
</tr>
<tr>
<td></td>
<td>p=15kbar</td>
<td>1.271</td>
</tr>
</tbody>
</table>

Discussion
In the pressure induced new phase a drastic change of the crystal field must have occurred because of the strong reduction of the quadrupole splitting. The narrow lines and the pressure independence of the line positions are a hint to two well defined crystal field situations corresponding to the pressed and unpressed phase.

This pressure induced phase transition is very similar to the temperature dependent phase transition in the case of Fe($H_2O$)$_6^-$ClO$_4$, which was first observed by Dészti et al.\(^2\)/3/. For this compound the quadrupole splitting $\Delta EQ$ amounts to $3.4\text{mm/sec}$ below $223^\circ\text{K}$, whereas above $263^\circ\text{K}$ only a value of $1.4\text{mm/sec}$ was measured. Furthermore within a temperature range of about $30^\circ\text{K}$ both phases coexist.

The ligand field situations are quite similar in both compounds. The iron(II) ion is surrounded by a water octahedron, which is mainly distorted along its trigonal axis. In the case of Fe($H_2O$)$_6^-$ClO$_4$ this was verified by determining the signs of the main components of the EFGs of both phases /4/. From the signs of the EFG and the magnitudes of the quadrupole splittings it was deduced that at low temperatures the orbital ground-state is a singlet ($V_{z2} < 0$) whereas at high temperatures the low quadrupole splitting is due to an orbital doublet ground state ($V_{z2} > 0$).

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References