MÖSSBAUER EFFECT STUDY OF IRON ACETYLACETONATE

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Abstract: From the measured Mössbauer spectra of iron in ferric acetylacetonate, values for quadrupole splitting and for isomer shift at room and liquid nitrogen temperature were determined. The obtained values indicate the electronic contribution of the ligands of the central iron ion.

1. Introduction

The Mössbauer spectrum of iron in ferric acetylacetonate, first obtained by Epstein[1] and Wertheim[2] as a single broad line was not observed in later investigations by Takashima[3]. Due to this uncertainty it was of interest to reexamine the resonance absorption in this molecular crystal in order to find additional information on the nature of iron oxygen bonding.

Iron acetylacetonate $Fe(C_5H_7O_2)_3$ has orthorhombic structure with the space group Pbca and eight molecules per unit cell[4]. Each molecule has a D_3 type symmetry, while single ligands are planar with C_{2v} symmetry. The molecule has the chelate structure in which three $C_5H_7O_2$ ligands on the iron ion form a nearly octahedral arrangement of six neighbouring oxygen atoms. Discrete molecules are linked together in layers by Van der Waals forces.

The Mössbauer spectrum obtained by Epstein contained a broad structureless peak approximately Lorentzian in shape with the width of 2.00 ± 0.05 mm/s. The isomer shift with respect to stainless steel ranged from 0.57 to 0.77 mm/s at liquid nitrogen temperature which indicates a normal ferric ion with little covalency. The Mössbauer spectrum obtained by Wertheim et al. had a resonance peak with the width of 1.83 ± 0.09 mm/s which is large compared with the width expected for the ^{57}Fe resonance line. The quadrupole splitting was not evident from the shape of the bottom of the resonance

peak and would amount to the value of 4.0 Mc s^{-1} to the most. The isomer shift of the center of the spectrum corresponds to an effective 4 s electron contribution of about 5%.

2. *Experimental procedure and results*

The present Mössbauer measurements were performed on the powdered iron acetylacetonate samples using the absorber layers with 20 mg/cm^2 of natural iron at room and liquid nitrogen temperatures. Two different ^{57}Co sources were used, one with the initial activity of 1 mC in the chromium matrix and one with the initial activity of 5 mC in the palladium matrix. Source was moved sinusoidally and the spectra obtained by use of a 256 multichannel analyzer operated in pulse height mode were corrected in the usual way[6]. The velocity scale was calibrated on the base of the spectra of enriched metallic iron[5].

Samples were prepared by the method for the two valent[7] as well as by the method for the direct three valent transition metal complex[4, 8]. In both cases the same Mössbauer spectra, typical for three valent compounds, were obtained. The existence of the ferric acetylacetonate complex has been confirmed additionally by the independent spectroscopic analysis of the sample which indicated that the ferroacetylacetonate complex is unstable in presence of oxygen.
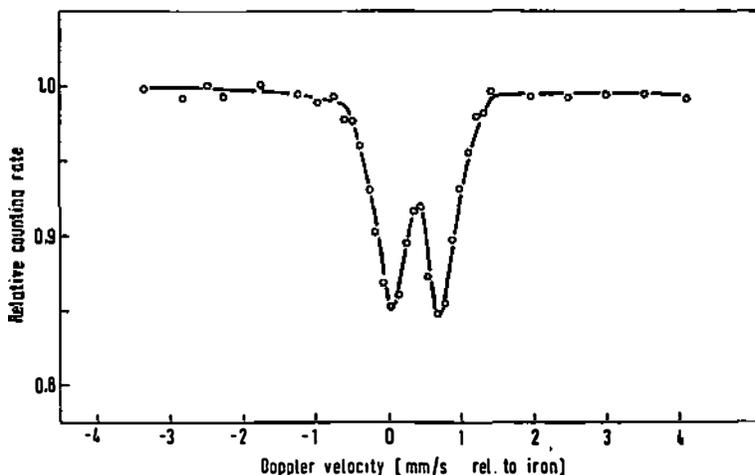
Fig. 1. The Mössbauer spectrum of Fe(C$_5$H$_7$O$_2$)$_3$ at room temperature taken with a source of ^{57}Co in the *Pd* matrix.

The Mössbauer spectra of ^{57}Fe in Fe(C$_5$H$_7$O$_2$)$_3$ at room and at liquid nitrogen temperature are nearly the same, both showing two dips in contrast to the measurements of Epstein[1] and Wertheim[2]. In Fig. 1 a typical spectrum of Fe(C$_5$H$_7$O$_2$)$_3$ at room temperature is given. The quadrupole splitting ΔE was

determined from the separation of the absorption peaks. The relation between the splitting ΔE and the electrical field gradient V_{zz} is derived from the Hamiltonian[9]

$$H = \frac{eQV_{zz}}{4I(2I-1)}\left[3I_z^2 - I(I+1) + \frac{\eta}{2}(I_+^2 + I_-^2)\right],$$

where e is the electronic charge, Q the nuclear quadrupole moment, I the nuclear spin, and $\eta = \dfrac{V_{xx} - V_{yy}}{V_{zz}}$ the asymmetry parameter. Taking into perature. The isomer shift δ connected to the electronic charge density is given by the relation[10]

$$\Delta E = \frac{eV_{zz}Q}{2}.$$

Values obtained from the measured spectra are $\Delta E = 0.665 \pm 0.036$ mm/s at room temperature and $\Delta E = 0.691 \pm 0.036$ mm/s at liquid nitrogen temperature. The isomer shift δ connected to the electronic charge density is given by the relation[10]

$$\delta = \text{const } R^2 \left(\frac{\Delta R}{R}\right) \Delta |\psi(0)|^2,$$

where R is the radius of the nucleus, ΔR the difference of the radius in the excited and the ground state and $\Delta |\psi(0)|^2$ the difference of s electron density at the nucleus in the absorber and the source. The isomer shift relative to metallic iron amounts to $\delta = 0.304 \pm 0.06$ mm/s at room temperature and to $\delta = 0.353 \pm 0.06$ mm/s at liquid nitrogen temperature. From the isomer shift systematics of Walker[11] it can be concluded that the ionic iron oxygen bonds are predominantly present.

The value of the magnetic susceptibility of $\mu_{ef} = 5.7$ Bohr magnetons[12] is pointing to a high spin compound. In a pure ionic compound the state $^6S_{1/2}$ does not produce any electronic contributions to the quadrupole splitting. The observed value of the quadrupole splitting could be assigned as a contribution of the ligands. A fine structure tensor component $D = 0.14$ cm^{-1} [13] determined by the electron paramagnetic resonance measurements could indicate that axial perturbations of the cubic potential are present at the iron nuclei.

This idea is also supported by the study[14] of the optical characteristics of the electron system of this compound, where local excitations are admixing to charge transfer and the ligand electrons are exchanging with the central iron ion. If the admixing of the ferrous structure is considered in the principal electric field gradient calculations from the electronic structure, the

observed splitting might be easily understood. The temperature insensitivity of the splitting corresponds to the above model since the thermal excitations are small compared to the energies of the charge transfer. The induced transition due to the scattered radiation could contribute to a slight change of the observed dynamic structure which is studied separately. The information derived from the isomer shift are much less selective as the quadrupole splitting data since the mentioned process is bond to the π electrons and the isomer shift will be hardly influenced by the electron transfer.

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ŠTUDIJ ŽELEZOVEGA ACETILACETONATA Z MÖSSBAUERJEVO SPEKTROSKOPIJO

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Vsebina

Iz merjenih Mössbauerjevih spektrov ^{57}Fe v železovem acetilacetonatu so bile določene vrednosti za kvadrupolno cepitev in izomerni premik pri sobni temperaturi in pri temperaturi tekočega dušika. Dobljene vrednosti lahko razložimo z upoštevanjem vpliva ligandov središčnega železovega iona.