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SINGLE CRYSTAL STUDY OF $N_2H_5(Fe(N_2H_3COO)_3).H_2O$ BY MÖSSBAUER EFFECT

D.Hanžel and F.Sevšek

J. Stefan Institute, University of Ljubljana, Ljubljana, Yugoslavia

Abstract

An effective EFG tensor was determined in the piezoelectric chelate compound $N_2H_5(Fe(N_2H_3COO)_3).H_2O$ by taking into account polarisation effects in the analysis of the intensity of Mössbauer spectra of ^{57}Fe in single crystals. The major principal component (V_{zz}) was found to be negative, making an angle of 35^o with the crystallographic c axis. Parameter of asymmetry (η) was 0.15.

Introduction

The preparation procedure as well as structural data of the piezoelectric compound $N_2H_5(Fe(N_2H_3COO)_3).H_2O$ have been reported by Braibantti et al[1]. Recently, Mössbauer spectra[2] of powdered sample have been used to determine the hyperfine parameters of ^{57}Fe. From analysis of these data the crystal field parameters and the lattice dynamic properties of $N_2H_5(Fe(N_2H_3COO)_3).H_2O$ were deduced. In the previous report[3] Mössbauer absorption intensity measurements on single crystal sample have been used to determine the electric field gradient (EFG) tensor. Though these crystals were of finite thickness the polarisation dependence of the absorption cross section was neglected in analysing the experimental data. Therefore it was of interest to reexamine in this report the intensity absorption measurements by taking into account mentioned effect.

Results and interpretation

The characteristic Mössbauer spectra of ^{57}Fe in $N_2H_5(Fe(N_2H_3COO)_3).H_2O$ single crystals are given in Fig. 1. They consist of two resolved lines with different intensities and are typical of quadrupole interaction of the iron nucleus with the EFG tensor. The average values of the quadrupole splitting parameter ΔE_Q and isomer shift relative to metallic iron were determined at room temperature as:

$$\Delta E_Q = 2.39 \pm 0.04 \text{ mm/s}$$

$$\delta_{(Fe)} = 1.08 \pm 0.04 \text{ mm/s}$$

These values are in good agreement with the latest reported[2] measurements on powdered sample.

The ratio of the intensity of the two peaks in Mössbauer spectra (Fig. 1) varies in the complicated way with the crystal orientation relative to the incident γ-ray beam. In order to interpret the experimental data of $N_2H_5(Fe(N_2H_3COO)_3.H_2O$ relative to the principal axes of the effective electric field tensor at Fe sites it was necessary to consider absorption cross section and density matrix asthe effective values. The effect of dispersion on the intensity of Mössbauer peaks has been omitted for any direction of the γ-ray since all iron sites of $N_2H_5(Fe(N_2H_3COO)_3).H_2O$ are equivalent, although differing in spatial orientations of EFG tensor.

For analysing the spectra of ^{57}Fe in $N_2H_5(Fe(N_2H_3COO)_3.H_2O$ the intensity ratio of the two peaks corresponding to the $\pi(\pm 3/2 \longrightarrow \pm 1/2)$ and $\sigma(\pm 1/2 \longrightarrow \pm 1/2)$ transitions[4], were expressed as a function of crystal thickness, the polarization dependence of the nuclear cross section and the EFG tensor parameters in the following way[5,6,7]:

$$\frac{A_\pi}{A_\sigma} = \frac{K(\sigma'^{\pi}_{11}) + K(\sigma'^{\pi}_{22})}{K(\sigma'^{\sigma}_{11}) + K(\sigma'^{\sigma}_{22})} \qquad (1)$$

where $$\sigma'_{ii} = n.f\,\sigma_0\,\rho_{ii} \qquad \text{and} \qquad (2)$$

$$K(\delta) = \sigma\, e^{-\delta/2}\left[I_0(\delta/2) + I_1(\delta/2)\right] . \qquad (3)$$

The effective cross section matrix (σ) represents the average of the cross section matrices of the four equivalent iron sites in the unit cell of $N_2H_5(Fe(N_2H_3COO)_3).H_2O$. $I_0(\delta/2)$ and $I_1(\delta/2)$ are the zeroth and the first order Bessel functions, σ_0 the nuclear resonant cross section, n the number of absorbing nuclei of ^{57}Fe per cm^2, f the recoiless fraction for the absorber and ρ_{11}, ρ_{22} the eigen values of the effective density matrix[6]:

$$\rho'_{11} = \tfrac{1}{2} \pm \tfrac{1}{4}\sqrt{\frac{3}{3+\eta^2}}\,(1 + \eta\cos 2\varphi)$$

$$\rho'_{22} = \tfrac{1}{2} \mp \tfrac{1}{4}\sqrt{\frac{3}{3+\eta^2}}\,(1 - 3\sin^2\vartheta - \eta\cos^2\vartheta\cos 2\varphi) \qquad (4)$$

$$\rho'_{12} = \pm\frac{\eta}{4}\sqrt{\frac{3}{3+\eta^2}}\,\cos\vartheta\sin 2\varphi$$

The upper sign corresponds to the π and the lower to the σ transition, while ϑ and φ are polar and azimuthal angles of the γ-ray vector direction in the coordinate frame defined by the effective EFG tensor.

A least squares computer fit of the experimentally determined intensity ratios (Fig. 1) of the two peaks to Eq. 1 was made. For this purpose density matrices (Eq. 4) were first expressed by asimuthal and polar angles Θ, Φ of the γ-ray in the crystallographic coordinate system (bxc,b,c). The principal axis system of the EFG tensor was related by three Euler angles α, β, γ to the crystallographic coordinate frame. The recoilless fraction of $N_2H_5(Fe(N_2H_3COO)_3).H_2O$ was taken to be isotropic and

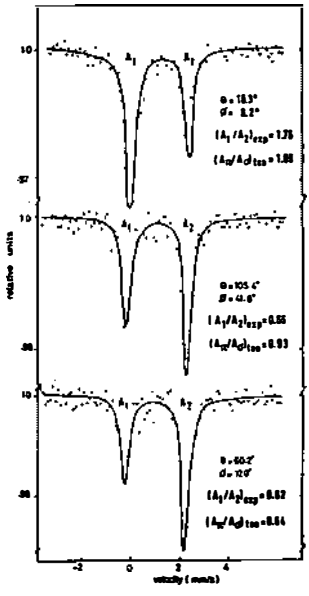

Fig.1: Mössbauer spectra of ^{57}Fe in monocrystalline samples $N_2H_5(Fe(N_2H_3COO)_3).H_2O$ at 300 K.

Θ,Ø - polar and asimuthal angles of γ-ray in the crystallographic system (a' = bxc,b,c);

$(A_1/A_2)_{exp}$ - relative intensity of two peaks;

$(A_\pi/A_\sigma)_{teo}$ - relative intensity calculated from Eq. 1

equal to 0.35 as determined from powder samples[2]. The effective EFG tensor, which represents the sum of the contributions from all the iron sites in the unit cell, must have one of its principal directions parallel to the crystallographic b-axis. Namely, the orientations of the EFG tensors of the four ferrous sites in the unit cell of $N_2H_5(Fe(N_2H_3COO)_3).H_2O$ are pairwise related by reflection through the crystallographic ac plane. Due to this symmetry restriction for any of the three possible orientations of the principal effective EFG axis system, only two fitting parameters were to be determined: one Euler angle and the asymmetry parameter (η). The parameters were varied to iteratively minimise the square of the differences between the experimentaly determined intensity ratios $(A_1/A_2)_{exp}$ (Fig. 1) and the calculated ratios of A_π/A_σ and A_σ/A_π (Eq. 1). The uniqueness of the solution was tested by repeating the procedure, each time with different randomly chosen starting values of the fitting parameters. The best fit was obtained with the values of $(A_\pi/A_\sigma)_{teo}$ given in Fig.1. The result of this analysis

is a unaxial effective EFG tensor with parameter of asymmetry $\eta = 0.15$ and negative V_{zz}. The largest axis of effective EFG tensor (V_{zz}) is angled at 35^{o} to the crystallographic c axis, while the smallest principal axis (V_{xx}) of the effective EFG tensor lies parallel to the crystallographic b axis, in disagreement with our previous results[3] using a thin absorber treatment[8] and the thickness corrected data for the areas of resonance lines. These results show that for a relatively thick absorber, the polarisation dependence of the resonant cross section must be taken into account in the analysis of area ratios of the quadrupole split peaks in the measured directions.

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