MÖSSBAUER EFFECT STUDY OF $N_2H_5[Fe(N_2H_3COO)_3]H_2O$ IN THE SOLID AND FROZEN SOLUTION STATE

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ABSTRACT

Mössbauer spectra of piezoelectric $N_2H_5[Fe(hyc)_3]H_2O$ in an external magnetic field (H_{ex} = 45 kG) at 4.2 K showed, that the sign of the principal component of the electric field gradient, V_{zz}, is negative, and that the iron magnetic moments are oriented perpendicular to V_{zz}.

The Mössbauer spectra of frozen aqueous solutions of $N_2H_5Fe(hyc)_3.H_2O$ at a concentration of 0.08 M/l were measured at various temperatures. After quick cooling from RT to 77 K, the samples were warmed up to 235 K. The effects of cooling rate on the Mössbauer spectra were estimated to be negligible. The centre shift parameters in solution are similar to those of the corresponding solid compound. The microstructure of the Fe^{2+} ion in 0.08 M frozen solution may be that of $Fe(N_2H_3COO)_3^-$.

INTRODUCTION

The Mössbauer spectroscopy method has recently been applied[1,2] in our laboratory to the study of the piezoelectric chelate compounds $N_2H_5[Fe(hyc)_3]H_2O$ and $K[Fe(hyc)_3]$, where hyc = N_2H_3COO. Mössbauer spectra typical of the quadrupole interaction between the nuclear quadrupole moment of the first excited state of ^{57}Fe and the electric field gradient were obtained between 20 K and 450 K. Temperature dependences of the isomer shift parameters and recoilless factors of powdered samples were interpreted regarding the Debye model for lattice vibrations of molecular crystals while the temperature dependence of the quadrupole splitting parameters were interpreted in terms of the varying population of the ferrous $^5T_{2g}$ levels. The sign of maximal component of EFG tensor, V_{zz}, was determined for $N_2H_5[Fe(hyc)_3]H_2O$ from the Mössbauer spectra of the single crystal specimen. In the analysis of the data, the polarization effects were taken into account.

In this report Mössbauer effect measurements are given for:

a) the powdered compound $N_2H_5[Fe(hyc)_3] \cdot H_2O$ in an external magnetic field (45 kG) at 4.2 K and

b) frozen solutions of $N_2H_5[Fe(hyc)_3] \cdot H_2O$ at concentration of 0.08 M/l at different temperatures.

EXPERIMENTAL

The piezoelectric compound $N_2H_5[Fe(hyc)_3] \cdot H_2O$ was prepared according to the method proposed by Braibanti et al[4]. This compound is one of the isomorphous series with the formula $N_2H_5[Me(hyc)_3] \cdot H_2O$, where Me = Co, Fe, Ni, Zn. The unit cell is monoclinic with the space group C_c. The metal ion is surrounded by three O and three N atoms belonging to the chelate group N_2H_3COO forming a trigonally distorted octahedron. The sample is sensitive to oxidation and care has to be taken in order to prevent its transformation into a ferric form under the influence of air.

Mössbauer experiments in transmission geometry were made using a conventional spectrometer operated in the time mode. The source was ^{57}Co in a Rh matrix at room temperature.

Fine powdered samples with about 20 mg/cm^2 of iron were used as the absorbers for measurements at 4.2 K in an external magnetic field of 45 kG perpendicular to the γ-rays. These measurements were carried out at the Universität des Saarlandes. Velocity scale was calibrated with metallic iron and it was also used as a reference for the C.S. parameter.

Solutions were prepared by disolving the powdered sample $N_2H_5[Fe(hyc)_3] \cdot H_2O$ in water. Some pieces of filter paper were then soaked with the solution and as such quenched in liquid nitrogen. Six of them were then closed in a holder between two mylar foils and immediately put into the cryostat as absorbers for measurements of Mössbauer spectra at different temperatures. The rate at which the solution was frozen was about 700 deg/sec. Frozen solutions with concentrations of 0.08 Mol per liter were measured at different temperatures from 77 K to 240 K in an Elscint cryofurnace.

RESULTS

External magnetic field experiment with powdered $N_2H_5[Fe(hyc)_3]H_2O$

At 4.2 K and $H_{ext} = 0$ the Mössbauer spectrum of powdered $N_2H_5[Fe(hyc)_3]H_2O$ consists of the quadrupole doublet (Fig. 1) arising from high spin $^5T_2$ iron (II).

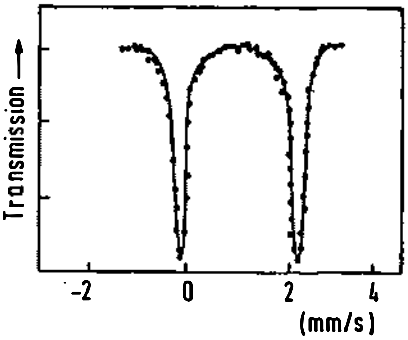

Fig. 1: Mössbauer spectrum of powdered $N_2H_5[Fe(hyc)_3]H_2O$ at 4.2 K taken with the source of ^{57}Co in Rh at room temperature.

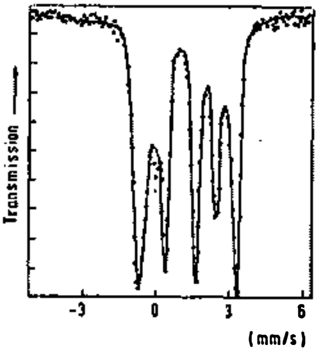

Fig. 2: Mössbauer spectrum of powdered $N_2H_5[Fe(hyc)_3]H_2O$ at 4.2 K submitted to an external magnetic field perpendicular to γ-rays, $H_{ex} = 45$ kG

The shape of the spectrum taken with the external magnetic field at the same temperature changed significantly (Fig. 2). It was suggested already by Ruby and Flinn$^{5)}$, and theoretically and experimentally demonstrated by Collins and Travis$^{6)}$, that the sign of the EFG could be determined from such magnetically perturbed spectra. Thus, the spectra of ^{57}Fe in $N_2H_5[Fe(hyc)_3]H_2O$ for a powdered sample at 4.2 K in an external magnetic field give evidence that the sign of e^2qQ is negative ($V_{zz} < 0$) and that the parameter of assymetry η is low. These results are in good agreement with previously reported ones obtained from RT single crystal analysis$^{3)}$.

On the basis of the known sign of the maximal component of the EFG tensor, V_{zz}, and the symmetry of the crystal field potential, it is possible to indicate the nature of the orbital ground state of the Fe^{2+} ion in $N_2H_5[Fe(hyc)_3]H_2O$ at low temperature. It is a singlet with wave function

$t_{2g} = z^2$, assuming that the crystal field potential at Fe^{2+} ion is mainly trigonally distorted, similar to that of the isomorphous $N_2H_5[Ni(hyc)_3]\cdot H_2O$ 4).

Further, it is necessary to note that the magnetically perturbed Mössbauer spectrum in Fig. 2 can give information about the value of the internal magnetic field and the direction of the magnetic moment relative to V_{zz}. Using the deviation 7) from unity of the ratio of the splitting for the "triplet" and "doublet" pattern in Fig. 2, it follows that the angle ϵ between V_{zz} and the internal field is nearly 90° in $N_2H_5[Fe(hyc)_3]\cdot H_2O$. Thus the internal field induced by the external magnetic field at the iron site is perpendicular to V_{zz}.

The approximate value of the internal field, as calculated from the "triplet" splitting, is 75 kG for $N_2H_5[Fe(hyc)_3]\cdot H_2O$ at 4.2 K. This is only a crude approximation since the internal magnetic field in paramagnet at low temperature can be different in magnitude and also in direction relative to the external magnetic field. Nevertheless, the augmentation of the internal field is not unreasonable since at low temperature the susceptibility for paramagnetic $N_2H_5[Fe(hyc)_3]\cdot H_2O$ is not negligible.

Frozen solutions

Frozen solutions of Fe (II) salts 8) have been widely investigated by Mössbauer effect and other methods. They usually showed typical behaviour i.e. solutions rapidly quenced from room temperature to liquid nitrogen exhibit properties of the amorphous state, they undergo the glass transition at about 170 K, and then transform to a supercooled phase and finally recrystallize.

The spectra of ^{57}Fe in frozen solution are quadrupole split patterns. The relatively narrow ($\Gamma = 0.35$ mm/s) and temperature independent widths of the absorption peaks indicate that all iron ions are equivalent. The variation of Mössbauer spectra parameters of 0.08 M/l frozen solutions of $N_2H_5[Fe(hyc)_3]\cdot H_2O$ are smooth curves, without discontinuities at expected phase transitions. The temperature dependence of quadrupole splitting parameter ΔE_Q, and centre shift, CS which are given in Fig. 3 resemble very much those of the corresponding solid compound 2). These results show that the microstructure of the Fe^{2+} ion in aqueous solutions are the thermodynamically stable anions $Fe(hyc)_3^-$. Also the rates at which the solutions were frozen have essentially no effect on the Mössbauer spectra of $N_2H_5[Fe(hyc)_3]\cdot H_2O$ dissolved in water or in a mixture of water and glycerol.

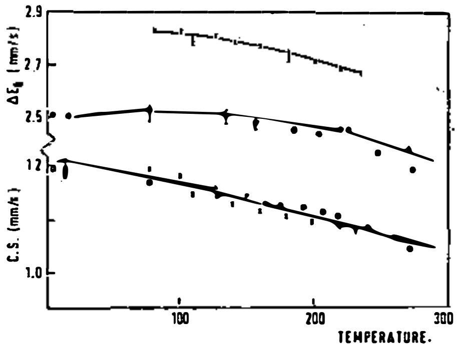

Fig. 3: Temperature dependences of ΔE_Q and CS for 0.08 M frozen solution (x) and powdered $N_2H_5Fe(hyc)_3 \cdot H_2O$ (·)

The slight difference in ΔE_Q (of about 0.3 mm/s) for the two states-solid solutions with the corresponding solid compound (Fig.3). can be understood on the basis of the lattice contribution to the total EFG. The valence contributions present the major part of the quadrupole splitting in ferro solutions and are a Boltzmann average over all the energy states of the Fe^{2+} ion. The magnitude and temperature dependence of ΔE_Q(val) depends upon the order and separation of the various orbital levels. By making use of the results of magnetic perturbed spectra the temperature dependence of ΔE_Q(val) of 0.08 M frozen solution might be explained by considering the crystal field potential at the iron site in the $Fe(hyc)_3^-$ anion to be octahedral with a small trigonal component. The latter splits the T_{2g} state into higher doublet and lower singlet. Following the least squares fitting procedure given in ref.2, we estimate that the splitting δ is around 900 cm^{-1} for 0.08 M frozen solution.

ACKNOWLEDGMENTS - One of the authors (Darko Hanžel) is very grateful to Professor U. Gonser, Universität des Saarlandes, for his kind hospitality, and to Dr. H.G. Wagner for multifold help during the measurements of magnetic perturbed spectra and to other members of the Mössbauer group at that University for their kindness. Financial support from the Res.Community of Slovenia is also acknowledged.

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