

MOSSBAUER STUDIES ON Fe^{2+} COMPOUNDS

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Mossbauer spectra of powdered samples of $\text{FeSO}_4 \times 7\text{H}_2\text{O}$ and $\text{Fe}(\text{SO}_4)(\text{NH}_4)_2 \times 6\text{H}_2\text{O}$ from liquid nitrogen temperature to room temperature were studied. For both compounds, strong temperature dependence was found in both centre shifts and quadrupole splittings, whose temperature-variation plots show discontinuities in slopes around roughly the same temperatures, indicating phase transitions at these temperatures.

1. INTRODUCTION

It has been pointed out by DeBenedetti et al [1] that typical Mossbauer spectra for Fe^{2+} and Fe^{3+} ionic compounds, relative to an unsplit room-temperature single line source, exhibit a shift δ of the centre of gravity from the zero-velocity position. This centre shift consists of two components $\delta_{i.s.}$ and δ_{sod} [2, 3], i.e.

$$\delta = \delta_{i.s.} + \delta_{sod} \quad (1)$$

or

$$\frac{\delta E}{E} = \frac{\delta E_{i.s.}}{E} + \frac{\delta E_{sod}}{E} \quad (1a),$$

where $\delta_{i.s.}$ is the isomer shift and δ_{sod} is the second order Doppler shift. The isomer shift $\delta_{i.s.}$ arises because of the interaction between nuclear charge and the *s*-electron density at the nucleus in the source and in the absorber, respectively. It can be written as [4]:

$$\delta_{i.s.} = \frac{2}{5} \pi Z e^2 (R_e^2 - R_g^2) [\psi(0)_{i,ab}^2 - |\psi(0)_{i,source}|^2] \quad (2)$$

where R_e and R_g are the nuclear radii of the excited and the ground state,

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respectively, and Z is the atomic number of the emitting nuclei. $|\psi(0)_{i,ab}|^2$ and $|\psi(0)_{i,source}|^2$ are the s -electron densities at the nucleus for absorber and source.

This isomer shift at temperature T K may be approximated as:

$$\delta_{i,s}(T) = \delta_{i,s}(0) + \alpha T \quad (3)$$

or

$$\frac{\delta E_{i,s}}{E} = \frac{\delta E_{i,s}(0)}{E} + \frac{\alpha T}{E} \quad (3a),$$

where the coefficient α can be estimated from the pressure dependence of the isomer shift, the coefficient of thermal expansion and the bulk modulus [5, 6].

The second order Doppler shift δ_{sod} arises from the difference between the mean square velocity of the Mossbauer probe in the absorber and in the source. It is a function of the source and the absorber temperature and the Debye temperature Θ_D of the host material if a Debye model is assumed.

The expression for the isomer shift was derived assuming a spherical nucleus and a uniform charge density. However, a nucleus with a spin quantum number $I > \frac{1}{2}$ can have a non-spherical charge distribution that contains a quadrupole

term in a multipole expansion. The electric quadrupole interaction involves the coupling of the nuclear quadrupole moment with the electric field gradient (EFG) due to the charge distribution of the lattice and the valence electrons. This electric quadrupole interaction splits the nuclear energy levels and gives rise to the quadrupole splitting of the Mossbauer spectrum. A number of investigators [1, 11, 15] has shown that the temperature dependence of the quadrupole splitting of ferrous compounds originates from the temperature dependence of the EFG, which has been attributed mainly to the valence electrons. In this work, we shall report the temperature dependence of the quadrupole splitting and the centre shift of the iron compounds $\text{Fe}(\text{SO}_4)_2(\text{NH}_4)_2 \times 6\text{H}_2\text{O}$ and $\text{FeSO}_4 \times 7\text{H}_2\text{O}$.

II. EXPERIMENTAL

In order to optimize the absorber thickness for improving the quality of the Mossbauer spectrum, the weight W of each of the samples was calculated by using the formula [7]

$$W = \frac{2}{\sum_i f_i \mu_{e,i}} \quad (7)$$

where f_i represents the mass fraction of the i th element in the absorber, $\mu_{e,i}$ is the electronic absorption coefficient of the i th element.

Each of the sample materials $\text{Fe}(\text{SO}_4)_2(\text{NH}_4)_2 \times 6\text{H}_2\text{O}$ and $\text{FeSO}_4 \times 7\text{H}_2\text{O}$ was ground into powder form and mixed well with an inert binder such as grease to ensure that the distribution of the material in the absorber was homogeneous. It was pressed into a small disc of uniform thickness. The sample was clamped onto the holder of the variable temperature insert and then lowered into the liquid nitrogen cryostat. The temperature of the absorber was varied by using an adjustable resistive heater controlled by a feedback system. Temperatures were measured with a copper-constantan thermo-couple. The temperature stability was better than ± 0.2 K but absolute sample temperature was not known to better than ± 0.5 K.

III. RESULTS AND DISCUSSION

Mossbauer measurements on the quadrupole splittings and centre shifts were made on two iron compounds $\text{Fe}(\text{SO}_4)_2(\text{NH}_4)_2 \times 6\text{H}_2\text{O}$ and $\text{FeSO}_4 \times 7\text{H}_2\text{O}$ from 77 K to room temperature. The results are presented in Figures 1—4. From the experimental results, δ for both ferrous compounds are large. This is expected since both absorbers are divalent salts. The $3d$ electrons in Fe^{2+} will increase the shielding of the $3s$ electrons from the nucleus, thereby reducing the charge density at the nucleus so that

$$|\psi(0)|_{i,2^+}^2 > |\psi(0)|_{i,2^+}^2 > |\psi(0)|_{i,2^{++}}^2$$

Since $R_2 > R_1$ for ^{57}Fe , equation (2) yields

$$\delta(\text{Fe}^{2+}) < \delta(\text{Fe}^{3+}) < \delta(\text{Fe}^{2++}).$$

From Fig. 1 and Fig. 2, the iron compound $\text{Fe}(\text{SO}_4)_2(\text{NH}_4)_2 \times 6\text{H}_2\text{O}$ appears to have discontinuities in the slopes of both graphs at 185 ± 5 K. In the case of the iron compound $\text{FeSO}_4 \times 7\text{H}_2\text{O}$ as shown in Fig. 3 and Fig. 4, the discontinuities at 175 ± 8 K in both graphs are in comparison very pronounced. These graphs show that both the quadrupole splitting and the isomer shift of $\text{FeSO}_4 \times 7\text{H}_2\text{O}$ exhibit a much stronger temperature dependence than those observed in $\text{Fe}(\text{SO}_4)_2(\text{NH}_4)_2 \times 6\text{H}_2\text{O}$. Phase transitions seem to take place at the discontinuities, probably due to stoichiometry variations or hysteresis phenomena. However, the temperatures at the discontinuities of both ferrous compounds are more or less the same, indicating the rather similar influence of the environment on the Mossbauer atom.

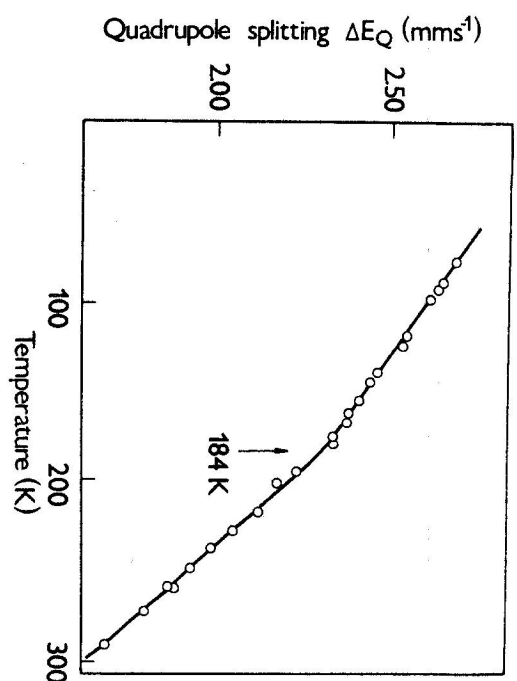


Fig. 1. Variation of quadrupole splitting with temperature for $\text{Fe}(\text{SO}_4)_2(\text{NH}_4)_2 \times 6\text{H}_2\text{O}$

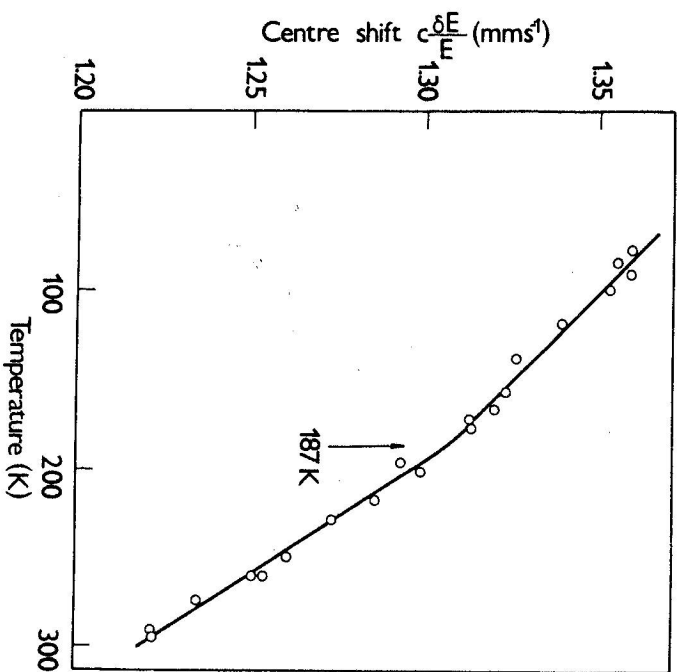


Fig. 2. Variation of centre shift with temperature for $\text{Fe}(\text{SO}_4)_2(\text{NH}_4)_2 \times 6\text{H}_2\text{O}$

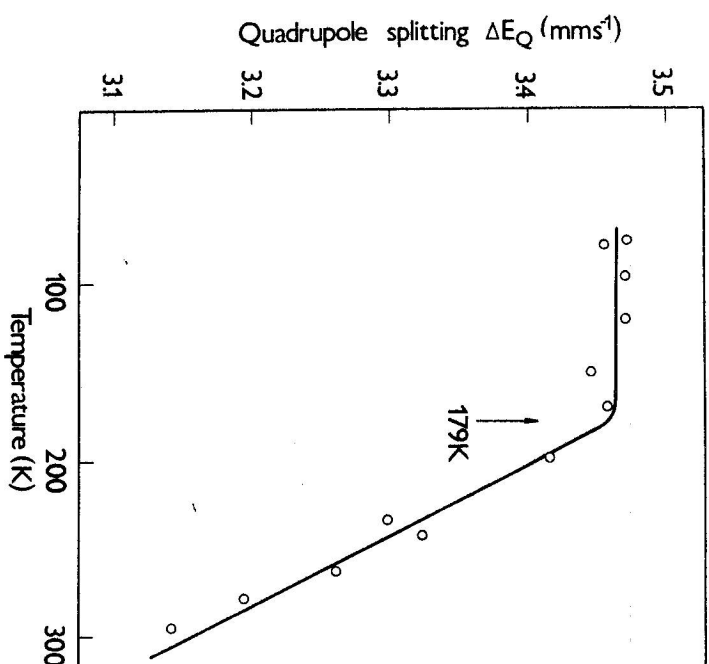


Fig. 3. Variation of quadrupole splitting with temperature for $\text{FeSO}_4 \times 7\text{H}_2\text{O}$

Table 1

Mossbauer parameters for $\text{FeSO}_4 \times 7\text{H}_2\text{O}$ and $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \times 6\text{H}_2\text{O}$			
Compound	Absorber Temperature	δ mms^{-1}	ΔE_Q mms^{-1}
$\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \times 6\text{H}_2\text{O}$	Room	1.22 ± 0.02	1.67 ± 0.03
	Liquid Nitrogen	1.36 ± 0.02	2.71 ± 0.03
$\text{FeSO}_4 \times 7\text{H}_2\text{O}$	Room	1.23 ± 0.02	3.14 ± 0.03
	Liquid Nitrogen	1.35 ± 0.02	3.47 ± 0.03

These values agree quite well the values quoted in literature [9—14].

The experimental values of the centre shift δ and the quadrupole splitting ΔE_Q at room and liquid nitrogen temperatures for both ferrous compounds are shown in Table 1.

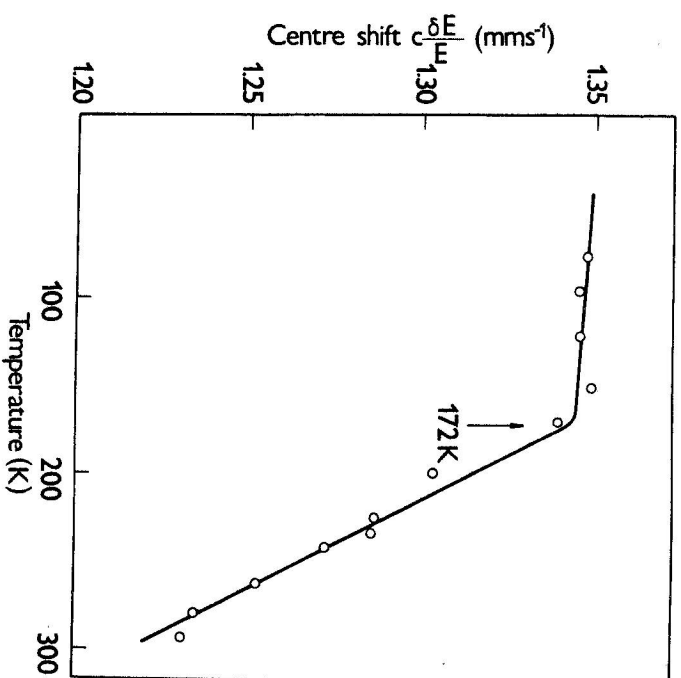


Fig. 4. Variation of centre shift with temperature for $\text{FeSO}_4 \times 7\text{H}_2\text{O}$

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ИССЛЕДОВАНИЕ СМЕСЕЙ Fe^{++} МЕТОДОМ МЕССБАУЭРА

Изучены спектры Мессбауэра, от комнатной температуры по температуру жидкого азота, образцов $\text{FeSO}_4 \times 7\text{H}_2\text{O}$ и $\text{Fe}(\text{SO}_4)_2(\text{NH}_4)_2 \times 6\text{H}_2\text{O}$. Найдена сильная температурная зависимость смещения центров и квадратичного расщепления спектров. Одновременно найдено нарушение непрерывности наклонных температурных зависимостей исследуемых образцов, что показывает на наличие фазовых переходов при примерно одинаковой температуре.