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DEBYE WALLER FACTOR FOR ^{57}Fe IN $K(Fe(N_2H_3COO)_3)$, DETERMINED BY MöSSBAUER EFFECT

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Abstract

Debye Waller factor of ^{57}Fe in $K(Fe(N_2H_3COO)_3)$ was determined from the saturation corrected areas of the Mössbauer spectra. Temperature dependence of - lnf is well reproduced by the Debye model with effective Debye temperature Θ_D = 158 K. The average mean square displacement $\langle x^2 \rangle$ of the iron ion in the direction of the incident γ-ray is 3.10^{-2} Å^2 at 300 K.

Introduction

A important quantity obtained from Mössbauer spectra is the fraction of nuclear radiation that occurs without recoil. This fraction is Debye Waller factor, and its temperature dependence is related with the detailed properties of the lattice such as the phonon spectrum, the damping of anomalous modes and anharmonic effects. Many experimental results indicate anomaly in temperature dependence of f near phase transition, see for example references(1-4).

For a lattice in which all nuclei occupy equivalent lattice sites Debye Waller factor can be given as:

$$f = \exp\left(-\langle x^2 \rangle_T / \bar{\lambda}^2\right) \qquad (1)$$

where $\bar{\lambda}^2$ is reduced wave lengh of the γ-ray ($\bar{\lambda}^2$ = 0,0188 Å^2 for 14,4 keV γ-ray of ^{57}Fe); $\langle x^2 \rangle_T$ is the mean square vibration amplitude of the Mössbauer atom in the direction of γ-ray at temperature T averaged over the lifetime of the nuclear excited state ($\tau = 0{,}97 \cdot 10^{-7}$s for ^{57}Fe). From Eq. 1 follows that the condition for the Mössbauer effect is fulfilled, when: $\langle x^2 \rangle_T \ll \lambda\!\!\!^{-}{}^2$. Since in liquids is $\langle x^2 \rangle_T$ normaly compared to $\lambda\!\!\!^{-}{}^2$ and Mössbauer effect experiments are therefore impossible.

Expanding $\langle x^2 \rangle_T$ in normal coordinates and using the Debye approximation for the phonon spectrum, Eq. 1 becomes as:

$$f = \exp\left[-\frac{3R}{2k\theta_D}\left(1 + 4\left(\frac{T}{\theta_D}\right)^2 \int_0^{T/\theta_D} \frac{x\,dx}{e^x - 1}\right]\right. \qquad (2)$$

where R is the free nucleus recoil energy ($R = \frac{E_\gamma^2}{2Mc^2} = 2{,}10^{-2}$ eV for ^{57}Fe), k is Boltzman constant and θ_D Debye temperature.

Several features of the Mössbauer spectra can be used to determine the Debye Waller factor of an absorber such as thickness dependence of the width of Mössbauer lines(5) the maximum intensity(6) of the Mössbauer absorption peaks and the integrated intensity (areas) of Mössbauer spectra(7). The last method was used for analysing the spectra of ^{57}Fe in $K(Fe(N_2H_3COO)_3)$.

Experiment and results

The piezoelectric compound $K(Fe(N_2H_3COO)_3)$ was grown from an aqueus solution as described in ref. 8. The identity of the compound was confirmed by chemical analysis and X-ray patterns from which unit cell parameters very close to those reported(8) were obtained. The crystals were dried in vacuo at 380 K and finely powdered samples having about 0,2 mg/cm^2 of ^{57}Fe were used as absorbers for Mössbauer measurements in transmission geometry. The ^{57}Co in Pd source was kept at room temperature and spectra of the absorber were measured in the region from 77 K to 450 K with a 512 channel analyzer operated in the time mode, using Elron's constant acceleration equipment. The velocity scale was calibrated with iron and it was also used as reference for the center shift parameter. The spectra were analysed by a nonlinear least squares program assuming Lorentzian line shapes.

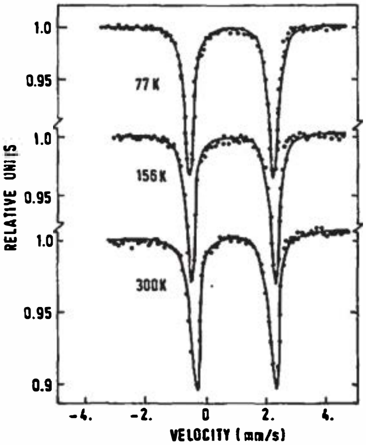

Fig. 1: Mössbauer spectra of ^{57}Fe in K(Fe($N_2H_3COO)_3$) at different temperatures taken with the source of ^{57}Co in Pd.

In Fig. 1 there are plotted some typical spectra of ^{57}Fe in K(Fe($N_2H_3COO)_3$). They remain of the similar form until 470 K with two resolved lines and were analysed in order to obtain hyperfine parameters of ^{57}Fe nucleus (Table I).

The temperature dependence of Debye Waller factor for ^{57}Fe in K(Fe($N_2H_3COO)_3$) (Fig. 2a) was obtained from the total areas (A_{tot}) of Mössbauer spectra which were corrected due to non-resonant radiation and finite thickness of the sample, by using the following expression$^{(7)}$:

$$A_{tot} = S \pi f_s \Gamma_o t \, e^{-t/2} \left[I_o(t) + I_1(t) \right] \qquad (3)$$

where f_s is the Debye Waller factor of the source (for ^{57}Co in Pd $f_s = 0{,}66$), $I_o(t)$ and $I_1(t)$ are the zeroth and the first order Bessel functions and t is the effective cross section thickness of the absorber which can be given as:

$$t = \frac{1}{2} \, n \, \sigma_o' \, f \, \Gamma_o / \Gamma_a \qquad (4)$$

Table I: Hyperfine parameters of ^{57}Fe in $K(Fe(N_2H_3COO)_3)$ (ΔE_Q - quadrupole splitting parameter, δ - isomer shift relative to metallic iron, A(T)/A(77) normalised areas).

T(K) ±0.5	ΔE_Q(mm/s) ±0.03 mm/s	δ_{IS}(Fe)(mm/s) ±0.03 mm/s	A(T)/A(77)
77	2,90	1,10	1,00 ± 0,04
125	2,91	1,09	0,90
152	2,92	1,09	0,89
195	2,87	1,07	0,82
229	2,86	1,06	0,77
249	2,86	1,06	0,74
300	2,81	1,05	0,66
328	2,80	1,04	0,63
398	2,67	0,98	0,54

where f is the Debye Waller factor of the absorber, Γ_0 is the natural width of the γ-ray ($\Gamma_0 \approx 0,097$ mm/s for ^{57}Fe) Γ_a is the width of Mössbauer peak(8), σ_0 is the resonance cross section for ^{57}Fe ($\sigma_0 = 2,56 \cdot 10^{-18}$ cm^2) and n is the number of atoms of ^{57}Fe per cm^2.

The correction of experimental data due to nonresonant radiation was taken into account with the factor S in Eq. 3. It was estimated by the filter technique ($S = 0,86$) and by the measurements of Mössbauer spectra of absorbers with known Debye Waller factor such as metallic iron and $Na[Fe(CN)_5NO] \cdot H_2O$ ($S \approx 0,81$).

Temperature dependence of the mean square displacement $\langle x^2 \rangle$ (Fig. 2b) is the straight line. This indicates that the high temperature approximation for Debye Waller factor of ^{57}Fe in

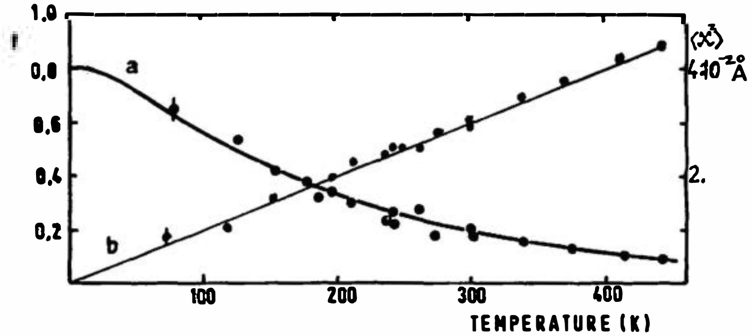

Fig. 2: a) temperature dependence of Debye Waller factor of ^{57}Fe in $K(Fe(N_2H_3COO)_3)$,
b) temperature dependence of the mean square displacement ($\langle x^2 \rangle = - \bar{\lambda}^2 \ln f$). The solid curves represent the best fit to Eq. (2) with $\Theta_D = 157 \pm 5$ K.

and $K(Fe(N_2H_3COO)_3)$ can be used which gave for the Debye temperature:

$$\Theta_D = 157 \pm 5 \text{ K}$$

This value is quite larger than one obtained in ref. 10 where a molecular crystal like treatment of the iron ion vibrations were considered.

Above 470 K the spectrum of ^{57}Fe in $K(Fe(N_2H_3COO)_3)$ changes from one doublet of equal intensity into four lines indicating phase transition of the sample.For this temperature region the effective absorber thickness for a single line decreases. Detailed analysis of the Debye Waller factor which is in progress will take into account the fact that the vibration amplitudes of iron ions are anisotropic.

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