INTERPRETATION OF MÖSSBAUER MEASUREMENTS OF DIFFUSIVITY

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PROBLEMS RELATED TO DIFFUSION

INTERPRETATION OF MÖSSBAUER MEASUREMENTS OF DIFFUSIVITY (*)

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Résumé. — Il a été prétendu que l'élargissement de raie, $\Delta\Gamma_m$, mesuré directement dans les spectres Mössbauer à haute température était proportionnel à la diffusivité. Une correction $\Delta\Gamma_{th}$, tenant compte de la diminution de la largeur de raie avec la température, a été introduite. On a montré que ceci rapproche les résultats expérimentaux des valeurs prédites par le modèle de diffusion par saut ($2\,\hbar/\tau$).

On montre que l'élargissement de raie dû à la diffusion peut être détecté à une température plus basse en tenant compte de la correction $\Delta\Gamma_{th}$.

Abstract. — The line broadening, $\Delta\Gamma_m$, measured directly from high temperature Mössbauer spectra has been claimed to be proportional to the diffusivity. A correction, $\Delta\Gamma_{th}$, accounting for the decrease in the line width with temperature, was introduced. It was shown that this brings experimental results closer to the values predicted by the diffusion-jump model $2\,\hbar/\tau$.

It is shown that diffusive line broadening can be detected at a lower temperature than if the correction $\Delta\Gamma_{th}$ is ignored.

Singwi and Sjölander have predicted that zero-phonon Mössbauer resonance should broaden in proportion to the diffusivity [1]. Mössbauer results have been discussed in terms of the continuous-diffusion and sudden-jump models [2] in view of a number of experimental studies. Experimentally, the line broadening, $\Delta\Gamma_m$, measured directly from high temperature spectra, was claimed to be proportional to the diffusivity. The effect of change in the effective thickness of the measured sample has been ignored, in spite of the fact that samples of considerable thickness have been used in order to overcome the drastic decrease of the f-factor at high temperatures$_s$

The measured width Γ_m of a Mössbauer resonance line in a high temperature absorber experiment, can be considered as consisting of three contributions :

$$\Gamma_m = \Gamma_s + \Gamma_a + \Gamma_{th} ,$$

where :

Γ_s, is the line width of the source,

Γ_a, the line width extrapolated to zero thickness of the absorber,

Γ_{th}, the broadening due to the finite effective thickness of the absorber.

The broadening, Γ_{th} can be calculated if $f(t)$, the temperature dependence of the f-factor is known.

The second term Γ_a, is the intrinsic line width of the absorber and is influenced by processes affecting the lifetime of the nuclear transition ; e. g. diffusion. Therefore, Γ_a is the term which will reflect changes in atomic motion with changing temperature.

Consider a line width measured at a low temperature T_0, for which $f(T)$ reaches practically its highest value, then :

$$\Gamma_m(T_0) = \Gamma_s + \Gamma_a^0 + \Gamma_{th}(T_0)$$

at a higher temperature $T > T_0$

$$\Gamma_m(T) = \Gamma_s + \Gamma_a + \Gamma_{th}(T) \quad \text{holds} .$$

Hence the measured difference in the line width is :

$$\Gamma_m = (\Gamma_a - \Gamma_a^0) + [\Gamma_{th}(T) - \Gamma_{th}(T_0)]$$

with

$$[\Gamma_{th}(T) - \Gamma_{th}(T_0)] < 0$$

hence

$$[\Gamma(T_0) - \Gamma_{th}(T)] = \Delta\Gamma_{th} > 0$$

and

$$\Delta\Gamma_m + \Delta\Gamma_{th} = \Gamma_a - \Gamma_a^0 .$$

The difference $\Gamma_a - \Gamma_0^a = \Gamma_D$ is the net intrinsic broadening caused by a change in atomic motion ; i. e. by diffusion. It is significant to point out that, if $\Delta\Gamma_m$ is measured and $\Delta\Gamma_{th}$ is calculated using an appropriate procedure [4], both then being plotted as a function of temperature, then at the temperature at which Γ_D starts to deviate from zero, diffusion begins to affect the line width significantly. An accurate estimate of the temperature at which diffusion begins to influence the line width may enable one to lower the temperature at which diffusion is measurable.

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Curves for Γ_m^*, Γ_{th} and Γ_D vs. $1/T$ were calculated using values taken from data of Kuaner and Mullen [3] for the diffusivity of iron in copper and are shown in figure 1. Γ_m^* is the experimentally measured line width from which $\Gamma_s + \Gamma_a$ were subtracted :

$$\Gamma_m^* = \Gamma_m - (\Gamma_s + \Gamma_a) .$$

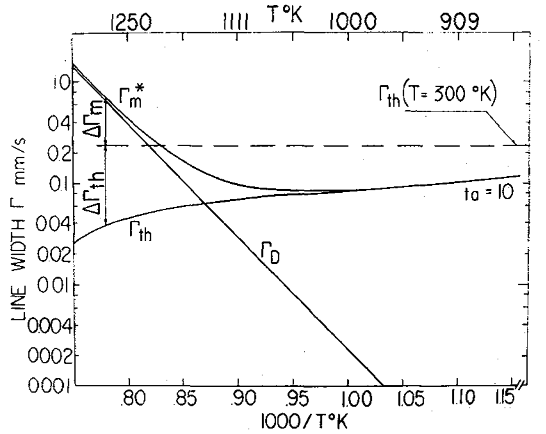

FIG. 1. — Γ_m^*, Γ_{th} and Γ_D, contributions to the line width, calculated for t_a (300 K) = 10 using data of reference [3], vs. 1 000/T K.

The sum $\Gamma_s + \Gamma_a$ was assumed to be equal to $\sim$ 0.20 mm/s.

Γ_{th}, the contribution to the line width, due to the finite effective thickness, t_a, was calculated on the basis of a linear approximation [4] :

$$\Gamma_{th} = 0.27\, \Gamma_0\, t_a \quad \text{where} \quad t_a = n\sigma_0 f(T)$$

here :

- n, is the number of Fe^{57} nuclei per cm^2,
- σ_0, the resonant cross section,
- $f(T)$, the Mössbauer f-factor for Fe in copper matrix, the temperature dependence of which is known [5].
- t_a, the effective thickness was estimated to be about 10 at room temperature.

The diffusion broadening Γ_D was calculated from data obtained by tracer diffusion experiments of iron in copper [6], using a Barden-Herring correlation factor of 0.8 and the same formula as used by Knauer and Mullen [3].

Under the conditions represented in figure 1 and with an accuracy of 0.003 mm/s the diffusive broadening can be detected at $\sim$ 730 °C. On the contrary, if the correction $\Delta\Gamma_{th}$, is ignored the broadening can be measured, firstly, at about 900 °C. The correction $\Delta\Gamma_{th}$ is seen to increase with temperature.

Finally, the change of t_a with temperature follows the fractional change in the f-factor, therefore for an effective thickness greater than $t_a = 10$, the curve Γ_{th} ($t_a > 10$) will lie parallel to Γ_{th} ($t_a = 10$) and the corresponding values of $\Delta\Gamma_{th}$ will also be higher.

The results of Mössbauer diffusivity measurements as given in table I of [3] were corrected for $\Delta\Gamma_{th}$ and shown in figure 2.

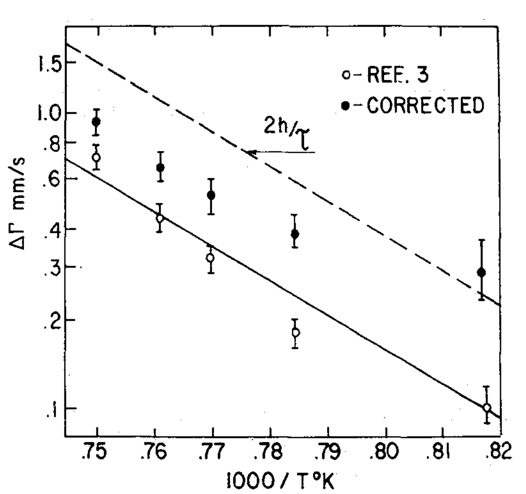

FIG. 2. — Line broadening vs. 1 000/T K. ○, values given by reference [3]. ●, corrected values.

The corrected values are closer to the value of $2\,\hbar/\tau$ which was predicted by the diffusive jump model and measured by tracer-sectioning technique. The remaining discrepancy may be related to the non-random state of a 1 % FeCu alloy [7] and other reasons discussed elsewhere [2].

In previous and recent years a number of Mössbauer diffusivity determinations have been published without correcting for $\Delta\Gamma_{th}$ [8].

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