Influence of the Jahn-Teller effect on the linewidth of the Mössbauer spectra of natural spinels

2000 J. Phys.: Condens. Matter 12 1451

(http://iopscience.iop.org/0953-8984/12/7/326)

J. Phys.: Condens. Matter **12** (2000) 1451–1460. Printed in the UK PII: S0953-8984(00)05618-6

Influence of the Jahn–Teller effect on the linewidth of the Mössbauer spectra of natural spinels

V Kuncser†, U Russo‡, R Graziani‡, A Della Giusta§ and G Filoti†

† National Institute for Physics of Materials, PO Box MG 7, 76900, Bucharest, Romania
‡ Dipartamento di Chimica Inorganica, Metallorganica e Analitica, Università di Padova, Via Loredan 4, I-35131 Padova, Italy
§ Dipartamento di Mineralogia e Petrologia, Università di Padova, Corso Garibaldi 37, I-35122 Padova, Italy

Received 30 June 1999, in final form 9 November 1999

Abstract. The temperature dependence of the Mössbauer doublet linewidth of tetrahedrally coordinated Fe^{2+} ions, distorted by the Jahn–Teller effect, was analysed by means of a new mathematical approach. The idea was that the linewidth depends on a distribution of quadrupole splittings that are in turn dependent on temperature. The variation of the quadrupole splitting was supposed to be connected with the temperature dependent population of the ground state E_g orbitals, split by the local Jahn–Teller effect. The model was applied to three sets of experimental data. The barrier splitting Δ between the two E_g electronic states as well as their widths, $\delta\Delta$, were obtained.

1. Introduction

In many spinels containing Fe^{2+} ions in tetrahedral coordination and presenting non-cooperative Jahn–Teller distortion, unusual behaviours of the Mössbauer doublet linewidths have been reported [1, 2]. Two cases, one with a sharp and the other with a flat maximum in the linewidth–temperature curve, are known. Both trends for the doublet linewidth are out of the normal behaviour especially at higher temperatures when an increasing linewidth is expected due to the strong activation of the vibrating modes.

This paper presents a mathematical approach in order to explain such an unusual behaviour of the linewidths of the Mössbauer spectra for the peculiar case of a tetrahedral Fe^{2+} ion subject to the Jahn–Teller effect. The basic ideas can be also extended to other cases presenting a temperature dependence of the quadrupole splitting. The proposed model is applied over three sets of experimental data, previously reported in the literature [1, 2].

2. The basis of the model. Physical considerations

As a general observation, the Mössbauer spectrum of tetrahedrally coordinated Fe^{2+} spinels consists of broad doublets with quadrupole splitting strongly dependent on temperature. The broadness of the Mössbauer doublets suggests a rather large distribution of the local configurations with the same symmetry. Such a possibility seems to be realistic in the natural spinels due to both crystal imperfections and impurities in the Fe^{2+} second coordination sphere (SCS).

0953-8984/00/071451+10$30.00

In a previous paper dealing with ferrous ions in natural spinels [2], we explained the quadrupole splitting behaviour via a local Jahn–Teller effect that reduces the tetrahedral symmetry at the iron site. Applying the Ingalls theory [3] in the case of an Fe^{2+} ($3d^6$) ion in a distorted cubic (T_d) symmetry, the quadrupole splitting dependence on temperature was expressed as [2]:

$$\mathrm{QS}(T) = C_1 + \mathrm{QS}^0_{val} F(\Delta, T) \tag{1}$$

with

$$F(\Delta, T) = \frac{1 - \mathrm{e}^{-\Delta/kT}}{1 + \mathrm{e}^{-\Delta/kT}} = \tanh\left(\frac{\Delta}{2kT}\right)$$

where:

- C_1 represents the quadrupole splitting contribution derived from the lattice distortion and assumed to be independent of the temperature (T)
- QS^0 represents the sixth 3d electron contribution to the quadrupole splitting extrapolated at 0 K, estimated as 3.1 mm s^{-1} [2]
- Δ is the splitting energy between the two lowest orbitals d_{z^2} and $d_{x^2-y^2}$, induced by the non-cooperative Jahn–Teller distortion.

The magnitude of the splitting barrier Δ could depend on the deviation of the four oxygens surrounding the central iron from the original positions giving the T_d cubic symmetry as well as on the partial charge transferred from the oxygen anions toward the cations in the SCS. It was pointed out in [2] that the last mechanism is related to the electronegativity of these cations. In natural spinels there are usually many different cations in the second coordination sphere [4, 5] and consequently a wide spread of Δ splitting is expected.

The proposed model relates the broadness of the Mössbauer doublets and its evolution against temperature with a distribution of quadrupole splitting, each one presenting a specific dependence of T, in agreement with (1).

3. The mathematical approach

Let us define a symmetrical distribution $P(\Delta)$ centred on the average $\boldsymbol{\Delta}$ and characterized by a width (at half height) of $2\,\delta\Delta$ (figure 1). By using relation (1) a similar function can express the temperature dependent distribution of the quadrupole splitting, $P(QS)$, centred on the average **QS** and with the width $2\,\delta\mathrm{QS}$ (as in figure 1, but for QS instead of Δ). An infinitesimal variation of QS is expressed as:

$$\mathrm{dQS}(T) = \frac{\mathrm{dQS}}{\mathrm{d}\Delta}\mathrm{d}\Delta. \tag{2}$$

Differentiating (1) with respect to Δ one obtains:

$$\frac{\mathrm{dQS}}{\mathrm{d}\Delta} = (2\mathrm{QS}^0/kT)\frac{\exp(-\Delta/kT)}{(1 + \exp(-\Delta/kT))^2}. \tag{3}$$

Equation (3) is then introduced into equation (2) and the integration of the thus obtained equation is carried out, the left side over $\mathbf{QS} - \delta\mathrm{QS}$ to $\mathbf{QS} + \delta\mathrm{QS}$, and the right side over $\boldsymbol{\Delta} - \delta\Delta$ to $\boldsymbol{\Delta} + \delta\Delta$. The resulting width $2\,\delta\mathrm{QS}$ can be written as:

$$2\,\delta\mathrm{QS} = 2\mathrm{QS}^0\frac{\sinh(\delta\Delta/kT)}{\cosh(\Delta/kT) + \cosh(\delta\Delta/kT)}. \tag{4}$$

Figure 2 shows the variation of the width $2\,\delta\mathrm{QS}$ with temperature for different values of the splitting energy Δ and halfwidth $\delta\Delta$. Depending on the values of Δ and $\delta\Delta$, various shapes,

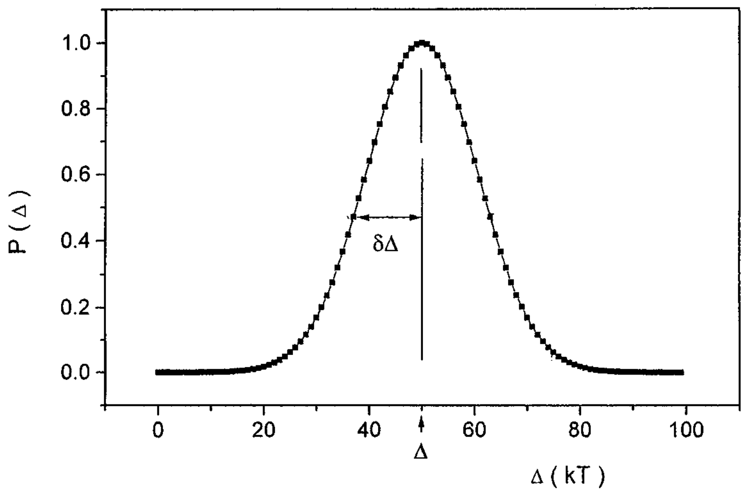

Figure 1. Symmetrical distribution $P(\Delta)$ centred on Δ and characterized by a width at half height $2\,\delta\Delta$. The same type of distribution can be considered for QS.

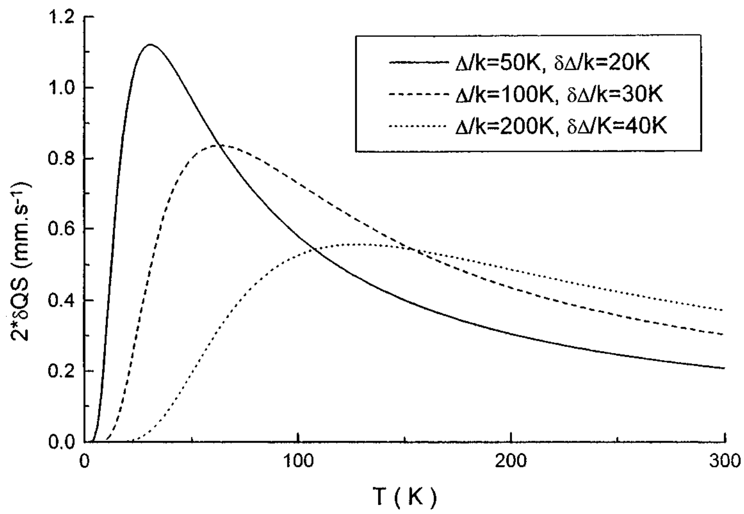

Figure 2. Dependences of the width $2\,\delta$QS on temperature for different values of the energy splitting Δ and halfwidth $\delta\Delta$.

with a more or less pronounced maximum, are evidenced. A deeper analysis of these curves can be performed starting from relation (4). It is worth noticing that $2\,\delta\mathrm{QS} \to 0$ for both $T \to 0$ and $T \to \infty$. The maximum value for $2\,\delta$QS is provided by the usual procedure of deriving the expression (4) and then setting the resulting expression to zero. Finally the following relation is obtained:

$$\frac{\delta\Delta}{\Delta} = \frac{\sinh(\Delta/kT)\sinh(\delta\Delta/kT)}{1 + \cosh(\Delta/kT)\cosh(\delta\Delta/kT)}. \tag{5}$$

All the detailed calculations concerning equations (3) to (5) are presented in the appendix. The graphical solution of equation (5) is obtained by the intersection of the functions $f(T) = \delta\Delta/\Delta = b$ (constant) and $g(T)$ given by the right side of (5). The solutions obtained

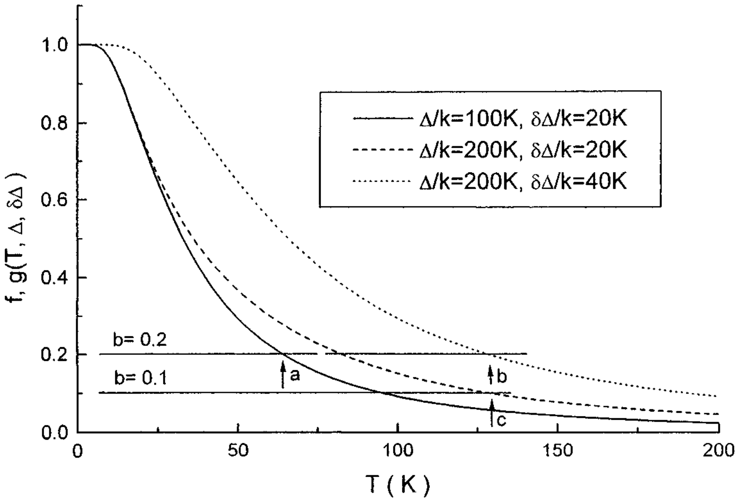

Figure 3. Graphical solutions of equation (5): for the same b the solutions are strongly dependent on Δ (arrows a and b) and for the same Δ the solutions are almost independent of b (arrows b and c).

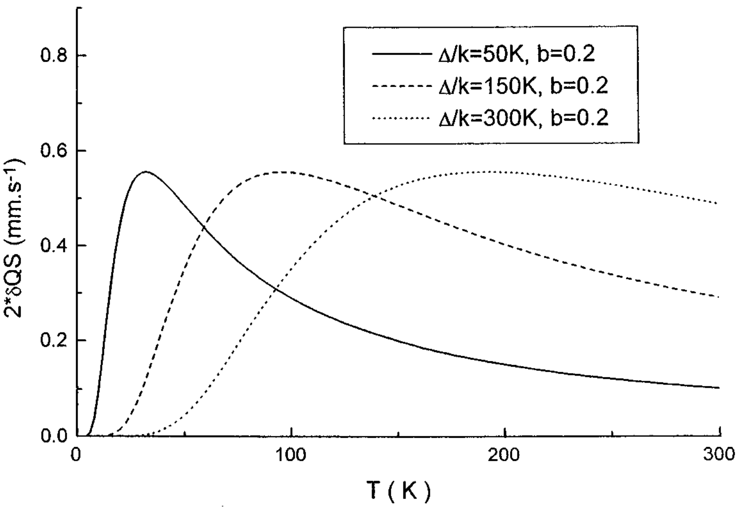

Figure 4. Dependences of the widths $2\,\delta$QS on T for different Δ and the same b.

for different values of Δ and $\delta\Delta$ are shown by arrows in figure 3. There are two observations: (i) there is a unique solution for equation (5) and (ii) the solution is scarcely dependent on the mean splitting Δ, but almost independent of the ratio $\delta\Delta/\Delta$. Consequently the function $2\,\delta$QS will show a trend with only one maximum. Its position depends strongly on Δ, but not on $\delta\Delta/\Delta$. In figures 4 and 5 the functions $2\,\delta$QS against T are shown for different values of Δ, but for the same ratio $b = \delta\Delta/\Delta$ and respectively for different halfwidths $\delta\Delta$ but for the same mean splitting Δ. The temperatures where the maximum values of the curves are reached increase almost linearly with Δ (figure 4), while the values themselves increase with b (figure 5).

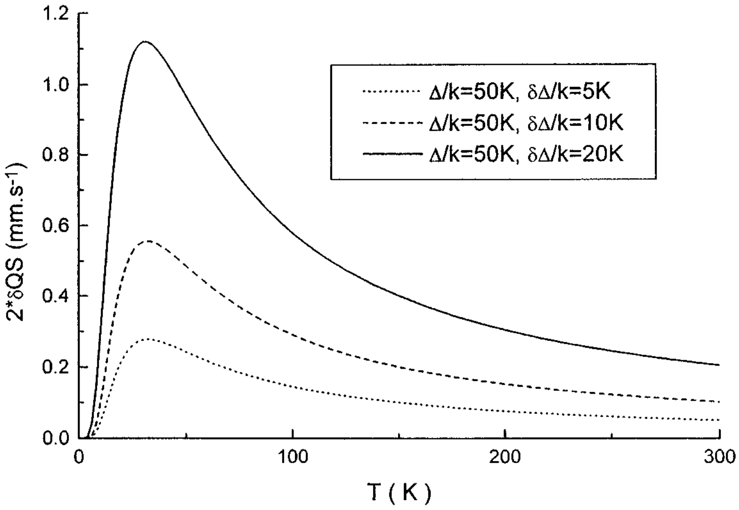

Figure 5. Dependences of the widths $2\,\delta$QS on T for different b and the same Δ.

In the case of a distribution of quadrupole splitting, the Mössbauer line shape is expressed by the convolution of the typical Lorentzian line shape with the distribution probability $P(\mathrm{QS})$:

$$f(v) = \int_0^\infty P(\mathrm{QS})\{1 + [(v - v_i)/\,\Gamma_0^{\mathrm{exp}}]^2\}^{-1}\mathrm{dQS} \qquad \text{with} \qquad v_i = h(\mathrm{IS}, \mathrm{QS}) \tag{6}$$

where v is the relative velocity, v_i is the resonance velocity, h is a linear function of IS and QS, while Γ_0^{exp} is the minimum experimental Mössbauer linewidth. This linewidth corresponds to a unique value of QS, e.g. for $\mathrm{QS} = \mathrm{QS}^*$, as obtained for $P(\mathrm{QS})$ equal to the Dirac distribution, $\delta(\mathrm{QS} - \mathrm{QS}^*)$. Relation (6) could describe the evolution of the Mössbauer line shape with T only if the temperature evolution of $P(\mathrm{QS})$ is known. The analytical solution for $\Gamma(T)$ leads to important mathematical difficulties. Therefore, we propose as a first approximation for the total linewidth, taking into account the temperature dependent quadrupole distribution, the following simplified expression:

$$\Gamma = \Gamma_0^{\mathrm{exp}} + 2\,\delta\mathrm{QS}. \tag{7}$$

The most usual expression for $P(\mathrm{QS})$ is the Gaussian one with $\mathrm{QS}(T)$ given by (1). The temperature effect can be transformed into a T-dependence of its width $2\,\delta$QS.

For $T \to 0$, $2\,\delta\mathrm{QS} \to 0$ in accordance with (4) and $P(\mathrm{QS}) = \delta(\mathrm{QS} - \mathrm{QS}^0)$ for all possible splittings Δ. Also for $T \to \infty$, $P(\mathrm{QS}) = \delta(\mathrm{QS} - C_1)$ due to the same effect. Taking into account relation (6), in these two limiting situations it seems to be reasonable to consider the linewidth of the Mössbauer spectrum as the minimum experimental value Γ_0^{exp} that can be obtained with a particular set-up. On the other hand, in the intermediate range of temperature where the contribution of the width $2\,\delta$QS may considerably surpass the contribution of Γ_0^{exp}, the first term in (7) will introduce only minor errors in the value of Γ.

In order to have a complete estimation of the errors introduced by the use of relation (7) compared with a real Mössbauer linewidth, we proceeded to the numerical evaluation of the Mössbauer lineshape as described by (6) in the condition of a normal distribution $P(\mathrm{QS}) \sim \exp\{(\mathrm{QS} - \mathbf{QS})/\delta\mathrm{QS}\}^2$. The simulations were performed for various widths δQS (the width at the half maximum), with a discretization of 20 steps over a range of 3 mm s^{-1} for QS and considering $\mathbf{QS} = 1.5$ mm s^{-1} and $\Gamma_0^{\mathrm{exp}} = 0.25$ mm s^{-1}. The main data concerning

Table 1. Mössbauer linewidths obtained starting from both the approximation (7) and relationship (6) and the absolute and relative errors in the Mössbauer linewidths as they are introduced by using the proposed approximation (7).

$2\,\delta$QS (mm s^{-1})	$\Gamma = \Gamma_0^{exp} + 2\,\delta$QS (mm s^{-1})	Γ_{sim}, according to (6) (mm s^{-1})	$\Delta\Gamma = \Gamma_{sim} - \Gamma$ (mm s^{-1})	$\varepsilon = \Delta\Gamma/\Gamma_{sim}$ (%)	$r = 2\,\delta$QS$/\Gamma_{sim}$ (%)
0.06	0.31	0.39	0.08	20	15
0.16	0.41	0.42	0.01	2	38
0.55	0.80	0.84	0.04	5	65
1.10	1.35	1.43	0.08	6	77
1.39	1.64	1.82	0.18	10	76

the Mössbauer linewidths obtained starting from both the approximation (7) and relationship (6) are presented in table 1.

As can be observed in table 1, relation (7) described pretty well the Mössbauer linewidth in the range 0.4–1.2 mm s^{-1} where the absolute errors are below 0.1 mm s^{-1} and the relative ones below 6%. Larger deviations are expected for very narrow (δQS/QS < 0.05) or very large (δQS/QS > 0.3) distributions, namely at very low and very high temperatures. The relative contribution of the QS distribution to the total linewidth increases with the distribution width and the real linewidth surpasses generally the value obtained by (7).

Three sets of experimental data will be evaluated under the assumption of the simplified relation (7).

4. Applications

4.1. The VASA spinel

In a previous paper reporting data on natural spinels [2], we analysed two natural compounds labelled VASA and CR5. For the VASA spinel, Fe^{2+} ions were located in two different tetrahedral configurations, characterized by different ions in the SCS as follows: a non-homogeneous NNN sphere with 11 Al + 1Mg was assigned to the configuration T1 giving rise to the lower Δ_1 splitting value, while a homogeneous one with 12Al surrounding atoms to the configuration T2 showing a higher splitting Δ_2. This behaviour was proved to be connected with the electronegativity of the cations in the SCS. Values of 35 K for Δ_1/k and 240 K for Δ_2/k were obtained from the QS(T) dependences. The experimental linewidths of the Mössbauer doublets and their fitting curves based on $\Gamma_0^{exp} = 0.26$ mm s^{-1} are shown in figure 6. Average splitting values of 50 K and 180 K were obtained for Δ_1/k and Δ_2/k respectively. A difference of about 25% between the values obtained by the two methods, the one using the QS(T) dependence [2] and the one using the $\Gamma(T)$ dependence, has to be mentioned. The localization of the $\Gamma(T)$ maximum should be more precise than the fit of the QS(T) curve, leading probably to more reliable values for the barrier Δ. The distributions $P(\Delta)$ are characterized by $\delta\Delta/k = 15$ K for T1 and 35 K for T2, showing a more pronounced influence of the SCS on the distribution of the local configurations in T1 ($\delta\Delta/\Delta = 30\%$) compared with T2 ($\delta\Delta/\Delta = 20\%$).

4.2. The CR5 spinel

Two configurations with tetrahedral symmetry were again evidenced for Fe^{2+} ($3d^6$) [2]. The first configuration, T1, presenting the lower splitting ($\Delta_1/k = 150$ K), was assigned to the Fe^{2+} ions with 11(Al+Cr)+1Fe in the SCS whereas the other one (T2), with the higher splitting

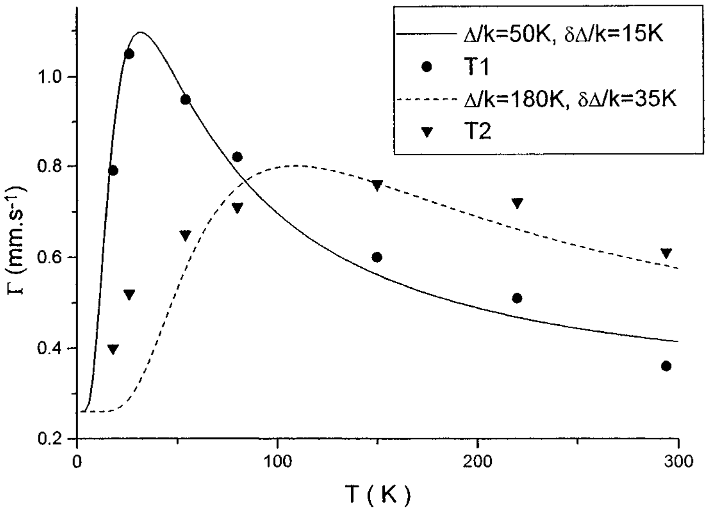

Figure 6. Dependences of the linewidth for the two iron configurations in the VASA spinel on T. The fitted curves according to equation (7) are presented as continuous and dotted lines respectively.

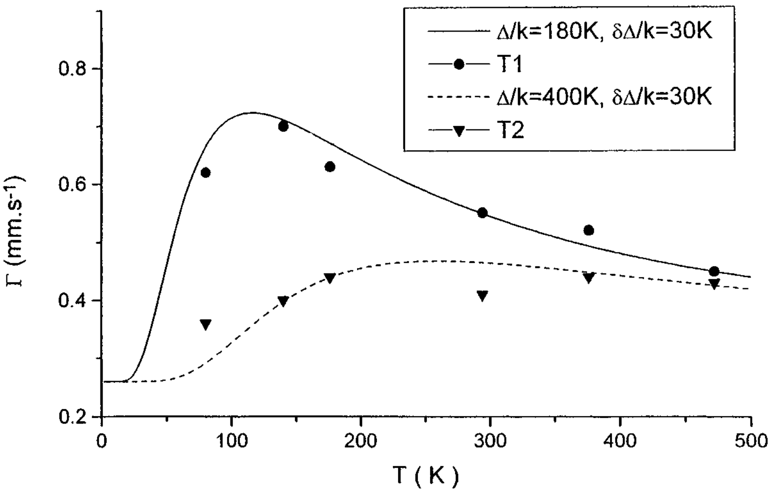

Figure 7. Dependences of the linewidth for the two iron configurations in the CR5 spinel on T. The fitted curves according to equation (7) are presented as continuous and dotted lines respectively.

energy ($\Delta_2/k = 410$ K), corresponds to an SCS with 10(Al + Cr) + 2Fe. Figure 7 presents the experimental linewidths of the Mössbauer doublets and their fittings according to relation (7). The resulting mean values $\Delta_1/k = 180$ K for T1 and $\Delta_2/k = 400$ K for T2 are in pretty good agreement with the above-mentioned ones, deduced from the QS(T) dependences. The two almost identical splittings for the configuration T2 in VASA and T1 in CR5, respectively, suggest for the last one no or one Fe ion in the SCS. For both positions the distribution $P(\Delta)$ is characterized by $\delta\Delta/k = 30$ K.

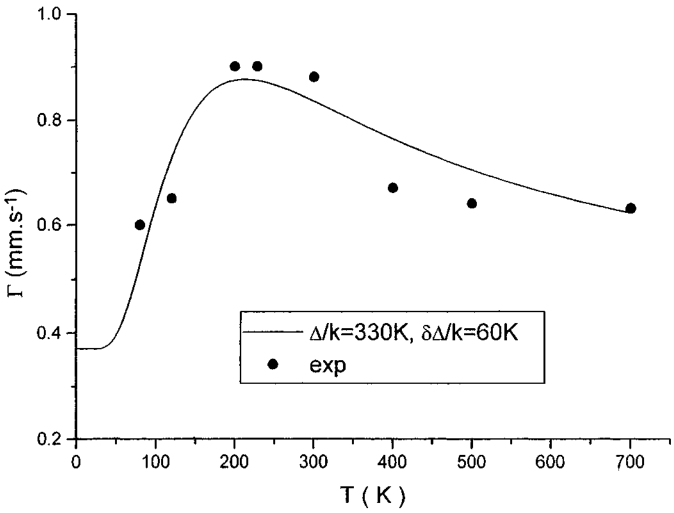

Figure 8. The dependence of the Mössbauer linewidths on T for the $FeAl_2O_4$ spinel. The fitted curve according to equation (7) is presented as a continuous line.

4.3. $FeAl_2O_4$

This is one of the first reported examples of spinels with Fe^{2+} ($3d^6$) ions in a tetrahedral distorted configuration analysed by Mössbauer spectroscopy [1]. Even if the quality of the spectra collected at that time were lower than today, this is not expected to affect the general trend of the Mössbauer parameters with the temperature. A splitting $\Delta/k = 300$ K derived from the QS(T) dependence was reported for that compound, together with a short qualitative analysis of the linewidth evolution that presents a maximum at intermediate temperatures. We have fitted their experimental linewidths by using relation (7) with $\Gamma_0^{exp} = 0.37$ mm s^{-1} and the results are presented in figure 8. A mean splitting energy $\Delta/k = 330$ K, in good agreement with the above mentioned datum, as well as a halfwidth of the splitting distribution $\delta\Delta/k = 60$ K were obtained.

4.4. Comments

The main differences among the various locations of Fe^{2+} in the studied samples derive from the relative number and the electronegativity of the different surrounding ions.

Comparing T2 (12Al in SCS) and T1 (11Al + 1Mg) in VASA the charge transferred from oxygens will be lower (electronegativity of Mg 1.2 compared with a 1.5 value for Al) in the T1 configuration. This fact gives rise to a smaller distortion of the initial tetrahedral symmetry and consequently to a smaller Δ split, as found from our calculations. By using the same reasoning for CR5 case, a higher Δ split is expected in the T2 configuration, again in agreement with experimental data.

Taking into consideration the T1 site in CR5 with 11(Al + Cr) + 1Fe in the SCS and the T2 site in VASA with only Al in the SCS, the larger Δ split observed in T1 of CR5 confirms the envisaged processes.

The width of the energy splitting distribution, $\delta\Delta$, is clearly related to the distribution of iron distorted positions and consequently to the disorder in the SCS. The larger distribution of the energy splitting in CR5 sample, compared with the VASA one, seems to be correlated with the atomic composition of the SCS. On the other hand, in the $FeAl_2O_4$ and in the T2 sites in VASA, where the SCS is formed only by Al ions, this distribution must be only due to distributed geometrical distortions. The present results stand for larger distributed geometrical distortions in the former compound.

5. Conclusions

The linewidths of the Mössbauer doublets assigned to the tetrahedral Fe^{2+} positions locally distorted by the Jahn–Teller effect were analysed as a function of the temperature. A new model describing the temperature effect on the Mössbauer linewidths was proposed starting from a temperature dependent distribution of the quadrupole splitting. The model was developed for the peculiar dependence $\mathrm{QS}(T) \sim \tanh(\Delta/2kT)$ where Δ is the splitting energy between the two orbitals d_{z^2} and $\mathrm{d}_{x^2-y^2}$.

Compared to other models based on the Jahn–Teller effect giving information only on the mean splitting energy, the above reported mathematical analysis of the $\Gamma(T)$ dependence is the only one supplying information on the distribution of the splitting energy characterized by mean splitting energy and distribution width. As a proof of the model validity, the splitting energies obtained from the $\Gamma(T)$ dependences are in agreement with the previous results obtained from the $\mathrm{QS}(T)$ ones for all three considered sets of experimental data.

Acknowledgments

The authors want to thank the National Agency for Science and Technology from Romania and the Ministry of Foreign Affairs from Italy for their financial support in the frame of the XIIIth Protocol for Scientific and Technologic Cooperation between Romania and Italy, positions 9 and 23.

Appendix

Differentiating expression (1):

$$\mathrm{QS}(T) = C_1 + \mathrm{QS}^0_{val} F(\Delta, T)$$

with

$$F(\Delta, T) = \frac{1 - \mathrm{e}^{-\Delta/kT}}{1 + \mathrm{e}^{-\Delta/kT}}$$

with respect to Δ, one obtains:

$$\frac{\mathrm{dQS}}{\mathrm{d}\Delta} = \mathrm{QS}^0 \frac{(1/kT)\,\mathrm{e}^{-\Delta/kT}(1 + \mathrm{e}^{-\Delta/kT}) + (1/kT)\,\mathrm{e}^{-\Delta/kT}(1 - \mathrm{e}^{-\Delta/kT})}{(1 + \mathrm{e}^{-\Delta/kT})^2}$$

$$= \frac{\mathrm{QS}^0}{kT}\mathrm{e}^{-\Delta/kT}\frac{1 + \mathrm{e}^{-\Delta/kT} + 1 - \mathrm{e}^{-\Delta/kT}}{(1 + \mathrm{e}^{-\Delta/kT})^2} = \frac{2\mathrm{QS}^0}{kT}\frac{\mathrm{e}^{-\Delta/kT}}{(1 + \mathrm{e}^{-\Delta/kT})^2}.$$

Consequently, the infinitesimal variation of QS will be expressed as:

$$\mathrm{dQS}(T) = \frac{2\mathrm{QS}^0}{kT}\frac{\mathrm{e}^{-\Delta/kT}}{(1 + \mathrm{e}^{-\Delta/kT})^2}\mathrm{d}\Delta.$$

The width of the $\mathrm{QS}(T)$ distribution at half maximum, $2\,\delta\mathrm{QS}$, is obtained by integrating the above equation over $\mathrm{QS} - \delta\mathrm{QS}$ to $\mathrm{QS} + \delta\mathrm{QS}$ on the left side and correspondingly over $\Delta - \delta\Delta$

to $\Delta + \delta\Delta$ on the right side, with QS and Δ mean values.

$$\int_{QS-\delta QS}^{QS+\delta QS} \mathrm{dQS} = \int_{\Delta-\delta\Delta}^{\Delta+\delta\Delta} \frac{2\mathrm{QS}^0}{kT} \frac{\mathrm{e}^{-\Delta/kT}}{(1+\mathrm{e}^{-\Delta/kT})^2}\,\mathrm{d}\Delta$$

$$2\delta\mathrm{QS} = \frac{2\mathrm{QS}^0}{kT}(-kT)\int_{\Delta-\delta\Delta}^{\Delta+\delta\Delta} \frac{\mathrm{d}(1+\mathrm{e}^{-\Delta/kT})}{(1+\mathrm{e}^{-\Delta/kT})^2}$$

$$2\delta\mathrm{QS} = 2\mathrm{QS}^0\left[\frac{1}{(1+\mathrm{e}^{-\Delta/kT})}\right]_{\Delta-\delta\Delta}^{\Delta+\delta\Delta} = 2\mathrm{QS}^0\left[\frac{1}{1+\mathrm{e}^{-(\Delta+\delta\Delta)/kT}} - \frac{1}{1+\mathrm{e}^{-(\Delta-\delta\Delta)/kT}}\right]$$

$$= 2\mathrm{QS}^0 \frac{1+\mathrm{e}^{-\Delta/kT}\mathrm{e}^{\delta\Delta/kT} - 1 - \mathrm{e}^{-\Delta/kT}\mathrm{e}^{-\delta\Delta/kT}}{1+\mathrm{e}^{-(\Delta+\delta\Delta)/kT} + \mathrm{e}^{-(\Delta-\delta\Delta)/kT} + \mathrm{e}^{-2\Delta/kT}}$$

$$= 2\mathrm{QS}^0 \frac{\mathrm{e}^{-\Delta/kT}\left(\mathrm{e}^{\delta\Delta/kT} - \mathrm{e}^{-\delta\Delta/kT}\right)}{\mathrm{e}^{-\Delta/kT}\left(\mathrm{e}^{\Delta/kT} + \mathrm{e}^{-\delta\Delta/kT} + \mathrm{e}^{\delta\Delta/kT} + \mathrm{e}^{-\Delta/kT}\right)}.$$

Introducing the hyperbolic functions, $\sinh x$ and $\cosh x$, ($\sinh x = (\mathrm{e}^x - \mathrm{e}^{-x})/2$, $\cosh x = (\mathrm{e}^x + \mathrm{e}^{-x})/2$), the linewidth of the QS(T) distribution can be finally expressed as:

$$2\delta\mathrm{QS} = 2\mathrm{QS}^0 \frac{\sinh(\delta\Delta/kT)}{\cosh(\Delta/kT) + \cosh(\delta\Delta/kT)}.$$

Differentiating 2δQS with respect to T, one obtains ($(\cosh x)' = \sinh x$ and $(\sinh x)' = \cosh x$):

$$\frac{\mathrm{d}}{\mathrm{d}T}\left(2\mathrm{QS}^0 \frac{\sinh(\delta\Delta/kT)}{\cosh(\Delta/kT) + \cosh(\delta\Delta/kT)}\right)$$
$$= 2\mathrm{QS}^0\{(-\delta\Delta/kT^2)\cosh(\delta\Delta/kT)[\cosh(\Delta/kT) + \cosh(\delta\Delta/kT)]$$
$$- \sinh(\delta\Delta/kT)[-(\Delta/kT^2)\sinh(\Delta/kT) - (\delta\Delta/kT^2)\sinh(\delta\Delta/kT)]\}$$
$$\times[\cosh(\Delta/kT) + \cosh(\delta\Delta/kT)]^{-2}.$$

Imposing $(\mathrm{d}/\mathrm{d}T)(2\delta\mathrm{QS}) = 0$:

$$-\frac{\delta\Delta}{kT^2}\left[-\sinh^2\left(\frac{\delta\Delta}{kT}\right) + \cosh^2\left(\frac{\delta\Delta}{kT}\right) + \cosh\left(\frac{\delta\Delta}{kT}\right)\cosh\left(\frac{\Delta}{kT}\right)\right]$$
$$+\frac{\Delta}{kT^2}\sinh\left(\frac{\delta\Delta}{kT}\right)\sinh\left(\frac{\Delta}{kT}\right) = 0$$

and considering $\cosh^2 x - \sinh^2 x = 1$:

$$\delta\Delta\left[1 + \cosh\frac{\delta\Delta}{kT}\cosh\frac{\Delta}{kT}\right] = \Delta\left[\sinh\frac{\delta\Delta}{kT}\sinh\frac{\bar{\Delta}}{kT}\right] \qquad \text{or}$$
$$\frac{\delta\Delta}{\Delta} = \frac{\sinh(\Delta/kT)\sinh(\delta\Delta/kT)}{1 + \cosh(\Delta/kT)\cosh(\delta\Delta/kT)}.$$

References

[1] Ono K, Ito A and Syono S 1966 Mössbauer study of Fe^{2+} in some natural spinels *Phys. Lett.* **19** 620–1

[2] Kuncser V, Russo U, Graziani R, DellaGiusta A, Palade P, Bulinski M and Filoti G 1999 Jahn–Teller configuration in natural spinels *Phys. Chem. Miner.* at press

[3] Ingalls R 1964 Electric-field gradient tensor in ferrous compounds *Phys. Rev.* A **133** 787–95

[4] Carbonin S, Russo U and DellaGiusta A 1996 Cation distribution in some natural spinels from x-ray diffraction and Mössbauer spectroscopy *Mineral. Mag.* **60** 355–67

[5] Lucchesi S, Russo U and DellaGiusta A 1997 Crystal chemistry and cation distribution in some Mn-rich natural and synthetic spinels *Eur. J. Mineral.* **9** 31–42