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DISTRIBUTION OF STRAINS AT Fe_A^{2+} SITE IN THE THIOSPINEL FeSc_2S_4

L. BROSSARD, H. OUDET, P. GIBART

Laboratoire de Magnétisme, C. N. R. S., 92190 Meudon-Bellevue, France

Résumé. — Le thiospinelle FeSc_2S_4 a été étudié par effet Mössbauer jusqu'à 1,5 K. Les spectres paramagnétiques ont été analysés par une distribution de doublets dont le nombre, l'intensité et la scission quadrupolaire ε varient avec T .

— Une première interprétation considère l'influence sur les niveaux nucléaires du ^{57}Fe d'un effet tunnel cohérent entre 3 puits de potentiel correspondant à 3 distorsions Jahn Teller équivalentes (généralisation du modèle de Hartmann Boutron). L'effet des contraintes et du couplage spin orbite sur le doublet fondamental $^5\text{E}_g$ du Fe^{2+} en site A sont négligés. Les calculs ont été conduit dans le cas d'un effet Jahn Teller linéaire fort et comportent un terme d'anisotropie. Un système de 3 doublets est obtenu à basse T dans l'hypothèse de relaxation lente : les intensités et les positions des pics varient avec le rapport $3\Gamma/\varepsilon$ où 3Γ est l'énergie tunnel entre le doublet vibronique fondamental et le premier singulet excité. Mais les résultats expérimentaux ne correspondent pas à ceux du modèle.

— Une seconde interprétation est proposée et qui tient compte de l'effet sur le doublet vibronique fondamental du couplage spin-orbite au 2^e ordre et d'une distribution aléatoire de contraintes : ces dernières peuvent causer des levées de dégénérescence de l'ordre du cm^{-1} sur les niveaux d'énergie des ions présentant une dégénérescence orbitale. Le calcul conduit à un gradient de champ électrique axial à toute température : la variation avec T de la composante principale $V_{zz} (< 0)$ de ce gradient est obtenue pour différentes valeurs de contraintes. Un accord qualitatif avec les résultats expérimentaux est observé pour des scissions énergétiques dues aux contraintes comprises entre 1 et 10 cm^{-1} .

Abstract. — The paramagnetic thiospinel FeSc_2S_4 was studied by Mössbauer effect down to 1.5 K. Spectra have been analyzed by a distribution of doublets whose number, intensity and hyperfine quadrupole splitting ε vary with temperature.

— A first tentative interpretation used a generalised Hartmann Boutron's model : the influence on the ^{57}Fe nuclear levels of the coherent tunneling between three equivalent potential wells (corresponding to three Jahn Teller distortions) is considered. Strains and spin orbit coupling are not taken into account on the $^5\text{E}_g$ ground state of A site Fe^{2+} . Calculation were done in the case of strong linear Jahn Teller coupling and include warping terms. At low temperatures in the case of slow relaxation, a system of three doublets is obtain : the intensities and peak's positions of them vary with the ratio $3\Gamma/\varepsilon$, where 3Γ is the tunneling energy between the vibronic doublet ground state and the first excited singlet. But experimental data cannot be fitted by such a model.

— A second interpretation is proposed, taking into account the effect on the vibronic doublet ground state of second order spin-orbit coupling and of random strains, which are known to induce splitting of the order of 1 cm^{-1} in the orbitally degenerate state of ions. The variation with temperature of the principal component $V_{zz} (< 0)$ of the electric field gradient — which is axially symmetric — is obtained for different values of strains. Strains splitting of 1 to 10 cm^{-1} is deduced in qualitative agreement with experimental results.

1. Introduction. — Low temperature Mössbauer data on the ferrimagnetic thiospinel FeCr_2S_4 have been interpreted assuming either dynamic Jahn Teller effect [1] or antidistorsive transition below 10 K [2]. In this compound Fe^{2+} ions are in A site. A dynamic or static Jahn Teller effect on this ^{57}Fe ion is expected. However such an effect, if any, in FeCr_2S_4 might be complicated by the effect of exchange.

The present study reports the ^{57}Fe Mössbauer data on insulating thiospinel FeSc_2S_4 ⁽¹⁾ which remains paramagnetic down to 4.2 K.

2. Experimental. — Powder sample (10 mg Fe/cm^2) does not contain any glue, to prevent any induced external strain.

Mössbauer spectra were done down to 1.5 K ⁽²⁾. At 300 K, the absorption peak seems to be a singlet, but with a linewidth rather large ($\Gamma_{\text{exp}} = 0.40\text{ mm/s}$ instead of $\Gamma_{\text{exp}} = 0.27\text{ mm/s}$ for FeCr_2S_4). At lowest temperatures, Γ_{exp} increases and for $T \sim 50\text{ K}$, some symmetric peaks appear on both sides of the singlet ; for $T \sim 30\text{ K}$, this one begins to be splitted and the external lines become asymmetric (Fig. 1).

⁽¹⁾ The sample of FeSc_2S_4 was provided by the *laboratoire de Chimie minérale* (Pr Flahaut) Faculté de Pharmacie, Paris.

⁽²⁾ The experiment at $T = 1.5\text{ K}$ was done at Saclay, in Dr Imbert's group.

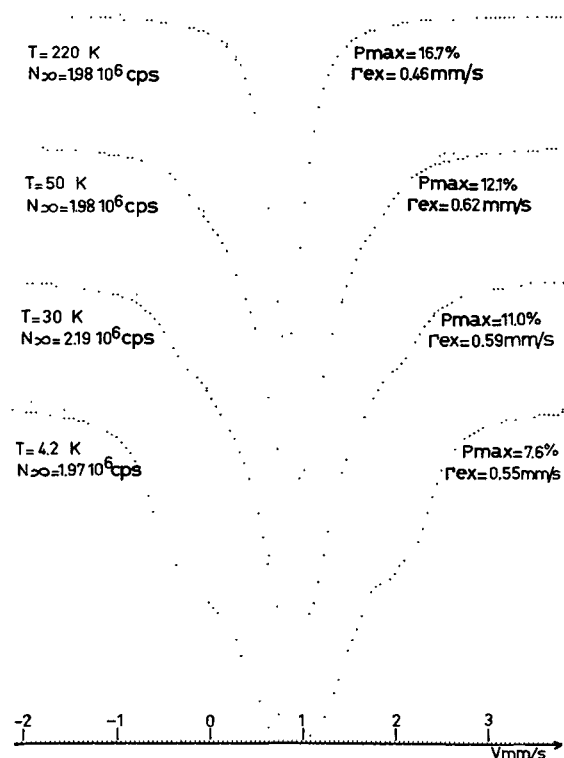


FIG. 1. — Experimental and calculated Mössbauer Spectra of FeSc_2S_4 at different temperatures.

The unusual shape of low T spectra cannot be understood on the basis of classical crystal field theory where quadrupole splitting can be ascribed to the action of spin-spin and spin orbit interaction on the 5E_g electronic ground state.

Spectra were analysed from least squares refinement of convolution of lorentzian peaks; they can be solved in many doublets whose number, intensity and hyperfine characteristic of each, vary with T . For a given temperature, the number of these doublets has been chosen to be minimum and to be compatible with a *good* reproduction (minimum of the mean quadratic error and coherent variation of hyperfine characteristics of doublets with T).

Figure 2 shows the temperature dependence of the quadrupole interaction ε of each site with its respective normalised intensity. At room temperature the isomer shift was found to be 0.72 mm/s towards iron metal (instead of 0.58 mm/s in semiconducting FeCr_2S_4). Such a value, suggests the d electrons of iron to be localized and FeSc_2S_4 to be insulator.

It should be also noticed the high counting spectra obtained ($\sim 2 \times 10^6$ counts per channel near infinite velocity) in order to detect the eventual presence of iron in B site and correlatively the existence of a Fe(A)-Fe(B) pair effect. Such an effect is absent from the spectra.

Specific heat measurements were also carried out in the range 15-250 K (Fig. 3): no anomaly appears — Moreover X rays measurements down to 4.2 K

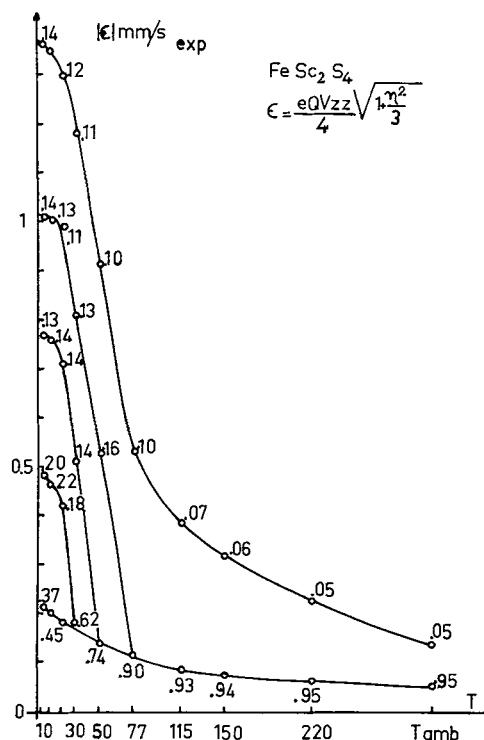


FIG. 2. — Temperature dependance of the quadrupole splitting ε of the different sites with their respective normalized intensity.

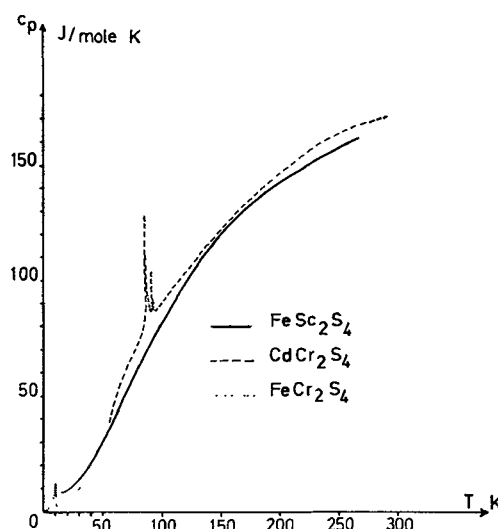


FIG. 3. — Specific heat vs T for FeSc_2S_4 (data were taken by Chaussy at the CRTBT Grenoble) and FeCr_2S_4 from ref. [2], and CdCr_2S_4 from ref. [7].

show that the compound keeps its spinel structure.

In other words, no cristallographic or magnetic transition seems to occur in FeSc_2S_4 in the temperature range studied.

Fe^{2+} in A site of FeCr_2S_4 has been characterized by a Mössbauer singlet in the paramagnetic phase and by an exchange induced quadrupole interaction under T_N . The unexpected shape of Mössbauer spectra of A site Fe^{2+} of FeSc_2S_4 at low temperatures could be

related either to a dynamical Jahn-Teller effect or to the influence of random local strains.

3. Discussion. — To explain these features, two models of Jahn-Teller coupling will be examined: dynamical Jahn-Teller coupling with coherent tunneling between three potential wells, and random strains with weak vibronic coupling. In particular the shape of the spectrum at 4.2 K seems to be typical of a three potential model.

3.1 COHERENT TUNNELING BETWEEN THREE POTENTIAL WELLS. — In this first step an attempt has been made to interpret the low temperature spectra ($T < 10$ K) in a slow relaxation hypothesis. The model used in this derivation starts from Hartmann-Boutron's calculations [3] but consider three potential wells instead of two. Spin-orbit interaction and strains are not taken into account. The static part of the Hamiltonian is the following (J is the unit matrix)

$$\mathcal{H} = V(Q_\theta U_\theta + Q_\varepsilon U_\varepsilon) + M \frac{\omega^2}{2} \times (Q_\theta^2 + Q_\varepsilon^2) J + A_3 \rho^3 \cos 3\theta J \quad (1)$$

where $Q_\theta = \rho \cos \theta$, $Q_\varepsilon = \rho \sin \theta$ are the normal coordinates of the tetrahedra. The last term, introduced by O'Brien [5] is called the warping term and lead to three potential wells, the first two terms of (1) being the usual hamiltonian in the linear Jahn-Teller coupling as defined by Ham [4].

Let $\psi = \psi_e(\theta) \psi_N(\rho, \theta)$ be the vibronic eigenfunction of (1) where

$$\psi_e(\theta) = \cos \frac{\theta}{2} \begin{vmatrix} 0 > \\ - \sin \frac{\theta}{2} \end{vmatrix} \begin{pmatrix} |2 > + | - 2 > \\ \sqrt{2} \end{pmatrix}$$

is the electronic wave function and ψ_N the wave function of the cluster. The full vibronic Hamiltonian is obtained by adding the kinetic terms:

$$\frac{1}{2M} (P_\theta^2 + P_\varepsilon^2) J. \quad (2)$$

The solutions give a ground vibronic doublet, $\psi_e(\theta) \psi_E(\rho, \theta)$ and $\psi_e(\theta) \psi_E(\rho, \theta)$ and a first excited singlet $\psi_e(\theta) \psi_A(\rho, \theta)$ separated by 3Γ [4, 5]. According to O'Brien derivation [5], this splitting 3Γ get smaller the larger the warping terms. When 3Γ is very small ($\sim 10^{-3} \text{ cm}^{-1}$) the quadrupole Hamiltonian couples the states of the excited nucleus with the vibronic states through the electrons.

Let $\psi_e \psi_N \psi_{I,z}$ be the wave function of the vibronic cluster-nucleus system, where ψ_N , ψ_e have already been defined and $\psi_{I,z}$ is the wave function of the nucleus.

Let

$$\mathcal{H}_q = \frac{\varepsilon}{6} \left[U_\theta (3 I_z^2 - I(I+1)) + \frac{\sqrt{3}}{2} U_\varepsilon (I_+^2 + I_-^2) \right] \quad (3)$$

be the quadrupole hamiltonian where

$$\varepsilon = \frac{2}{7} e^2 Q \langle r^{-3} \rangle_{3d}.$$

We put

$$C_2 = - \langle \psi_e \psi_E | U_\theta | \psi_e \psi_E \rangle$$

$$C_1 = - \langle \psi_e \psi_A | U_\theta | \psi_e \psi_A \rangle.$$

In Ham's formalism, $C_2 = q$, $C_1 = -r$ and $\psi_e \psi_E = \psi_{g0}$.

The diagonalization of $\mathcal{H}_{JT} + \mathcal{H}_q$ gives two doublets and two singlets for the excited state $I = \frac{3}{2}$ of the nucleus, with energies

$$E_{1/2} = \frac{\Gamma}{2} \pm \frac{3\Gamma}{2} \sqrt{1 + \chi^2},$$

for the doublets, and

$$E_{3/4} = -\Gamma \mp \varepsilon C_2$$

for the singlets, with

$$\chi^2 = 2 \left(\frac{\varepsilon C_1}{3\Gamma} \right)^2.$$

The eigenfunctions of the singlets E_3, E_4 are made only with E and E' vibronic states but no A, so that six transitions only are possible to the nuclear vibronic states with $I = \frac{1}{2}$ (Fig. 4).

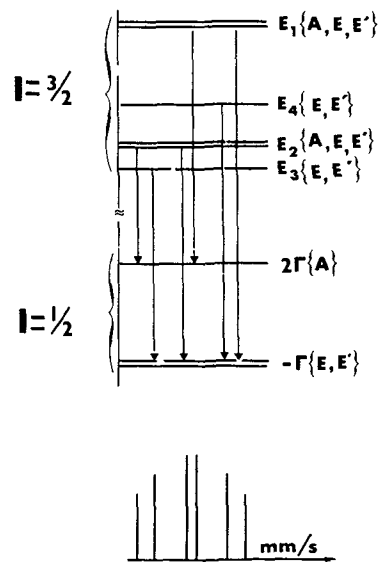


FIG. 4. — a) Nuclear levels in case of Jahn Teller coupling with three potentials wells, b) theoretical absorption spectrum.

Moreover, these transitions form three doublets, the quadrupole splittings of which are:

$$3\Gamma \{ \sqrt{1 + \chi^2} + 1 \}, 2\varepsilon C_2, 3\Gamma \{ \sqrt{1 + \chi^2} - 1 \}$$

with the same isomer shift.

The doublets are symmetric and the intensities of each peak, assuming an equal population of the states, are the following

$$\frac{1-x^2}{3}, \frac{1}{6}, \frac{x^2}{3}, \frac{x^2}{3}, \frac{1}{6}, \frac{1-x^2}{3}$$

with

$$x^2 = \frac{\chi^2}{\chi^2 + (\sqrt{1 + \chi^2} - 1)^2} > \frac{1}{2}.$$

Let look at two limit cases :

— When $\Gamma \gg \varepsilon$, $\chi \rightarrow 0$ and $x^2 \rightarrow 1$. We get a central line and one doublet εC_2 the intensities being in the ratio 1 : 4 : 1.

— When $\Gamma \ll \varepsilon$, $\chi \rightarrow \infty$ and $x^2 \rightarrow \frac{1}{2}$. We get only one doublet (ε) as in a static Jahn-Teller distortion.

It can be seen that the intensities deduced from the model cannot reproduce correctly the spectra at low temperature. It is also known that dynamical A site Jahn-Teller effect is not so large it has been supposed in this approach.

3.2 RANDOM STRAINS ON A WEAK VIBRONIC COUPLING.

— Following the Ham's derivation of a 5E state, the second order spin orbit coupling will be written

$$\mathcal{H}_{so} = -\frac{1}{6}K \{ (3 S_z^2 - S(S+1)) U_\theta + \sqrt{3}(S_x^2 - S_y^2) U_\varepsilon \} \quad (4)$$

with

$$K = 6 \left(\frac{\lambda^2}{A} + \rho \right).$$

The effect of the $J-T$ coupling on the spin-orbit is to replace the effective interaction coefficient K by $K' = qK$, where q is the Ham's reduction factor. Now on the vibronic doublet the hamiltonian (4) becomes

$$\mathcal{H}_{so} = -\frac{1}{6}K' \{ (3 S_z^2 - S(S+1)) U_{g\theta} + \sqrt{3}(S_x^2 - S_y^2) U_{g\varepsilon} \}. \quad (5)$$

The $U_{g\theta}$ and $U_{g\varepsilon}$ matrices were introduced and discussed by Ham [4].

At the same time, the strain in the crystal, described by

$$\begin{cases} e_\theta = e_{zz} - \frac{1}{2}(e_{xx} + e_{yy}) \\ e_\varepsilon = \frac{\sqrt{3}}{2}(e_{xx} - e_{yy}) \end{cases}$$

gives a term

$$\mathcal{H}_{st} = V_2(e_\theta U_\theta + e_\varepsilon U_\varepsilon) \quad (6)$$

and on the vibronic doublet, (6) leads to

$$\mathcal{H}_{st} = qV_2(e_\theta U_{g\theta} + e_\varepsilon U_{g\varepsilon}). \quad (7)$$

Putting $e_\theta = e \cos \theta$, $e_\varepsilon = e \sin \theta$ and $\delta = qeV_2$, the total hamiltonian (5) + (7) is :

$$\begin{aligned} \mathcal{H}_{so} + \mathcal{H}_{st} = & U_{g\theta} \left[\delta \cos \theta J_s - \frac{K'}{6} (3 S_z^2 - S(S+1)) \right] + \\ & + U_{g\varepsilon} \left[\delta \sin \theta J_s - \frac{K'}{6} \sqrt{3}(S_x^2 - S_y^2) \right] \end{aligned} \quad (8)$$

where J_s is the unit matrix acting on the spin part of the wave function.

In order to diagonalize this hamiltonian (8), we use as a basis the eigenstates of H_{so} only which belong to the well-known representations :

$$A_1, T_1, E, T_2, A_2.$$

The strain mixes A_1 , A_2 and E representations and the hamiltonian (8) between these states give the 4×4 matrix :

	A_2	E_θ	E_ε	A_1
A_2	$2K'$	$\delta \sin \theta$	$-\delta \cos \theta$	0
E_θ	$\delta \sin \theta$	0	0	$\delta \cos \theta$
E_ε	$-\delta \cos \theta$	0	0	$\delta \sin \theta$
A_1	0	$\delta \cos \theta$	$\delta \sin \theta$	$-2K'$

On the other hand strains mixes T_1 and T_2 representations. This gives a 6×6 matrix which reduces in three 2×2 matrices. Let T_{11} , T_{12} , T_{13} be the states of the T_1 representation transforming as x , y , z except that they do not change sign under inversion and T_{21} , T_{22} , T_{23} be the states of the T_2 representation transforming as x , y , z . Strain mixes T_{1j} and T_{2j} and (8) leads to the matrices

	T_{11}	T_{21}
T_{11}	$-K - \frac{1}{2}\delta \cos \theta + \frac{\sqrt{3}}{2}\delta \sin \theta$	$-\frac{\sqrt{3}}{2}\delta \cos \theta - \frac{1}{2}\delta \sin \theta$
T_{21}	$-\frac{\sqrt{3}}{2}\delta \cos \theta - \frac{1}{2}\delta \sin \theta$	$K + \frac{1}{2}\delta \cos \theta - \frac{\sqrt{3}}{2}\delta \sin \theta$

$T_{12} = -K - \frac{1}{2}\delta \cos \theta - \frac{\sqrt{3}}{2}\delta \sin \theta$ $T_{22} = \frac{\sqrt{3}}{2}\delta \cos \theta - \frac{1}{2}\delta \sin \theta$ $T_{13} = -K + \delta \cos \theta$ $T_{23} = \delta \sin \theta$	$T_{22} = \frac{\sqrt{3}}{2}\delta \cos \theta - \frac{1}{2}\delta \sin \theta$ $K + \frac{1}{2}\delta \cos \theta + \frac{\sqrt{3}}{2}\delta \sin \theta$ $T_{23} = \delta \sin \theta$ $K - \delta \cos \theta$
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At this stage, in order to make simple calculations of the eigenstates and of the derived electric field gradient, we may fix a value to the angle θ of the strain and choose for example $\theta = 0$. Otherwise we would have to make the calculations for any value of θ and take the average over the values of θ from 0 to 2π (Fig. 5). We believe that this simplification does not change drastically the main features of the model.

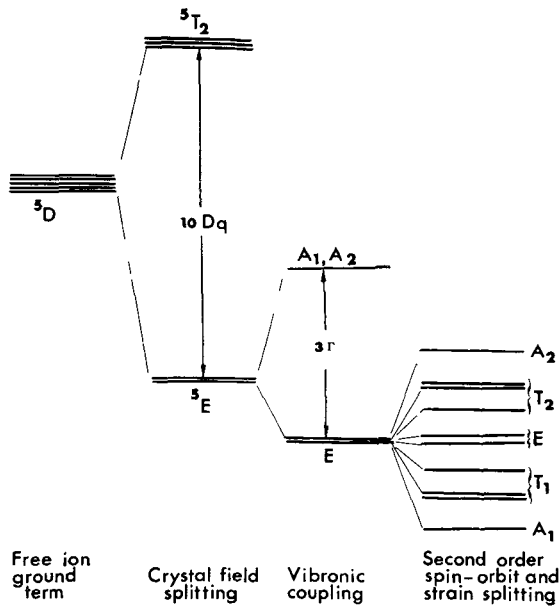


FIG. 5. — Schematic representation of the effects of cubic crystal field, vibronic coupling, strain and second order spin orbit coupling on a $5D$ electronic state.

Starting from the ten eigenstates calculated as described before, we calculated the V_{xx} , V_{yy} , V_{zz} produced by each state (for states arising from an orbital doublet E the only non vanishing components of the EFG tensor are V_{xx} , V_{yy} , V_{zz}). Then, using the calculated eigenvalues of the energy, the thermal average of V_{xx} , V_{yy} , V_{zz} has been computed. At sufficient low temperatures, the only state to be considered is the singlet ground state A_1 . At higher temperatures, the rapid relaxation of the spin justify the thermal average procedure. The results are the

following : $\langle V_{zz} \rangle$ is the largest component of the EFG tensor, with $\langle V_{zz} \rangle < 0$ and

$$\langle V_{xx} \rangle = \langle V_{yy} \rangle (\eta = 0)$$

at any temperature. The EFG induced by the states from the triplet T_1 is larger than the EFG induced by the ground singlet A_1 . So we may expect a maximum of $\varepsilon(T)$, ($\varepsilon = eQ/4 \langle V_{zz} \rangle$) when the states from the singlet begin to be populated. The $\varepsilon(T)$ curves computed using $K = 13 \text{ cm}^{-1}$, $\delta = 1, 4, 10 \text{ cm}^{-1}$ are given on figure 6.

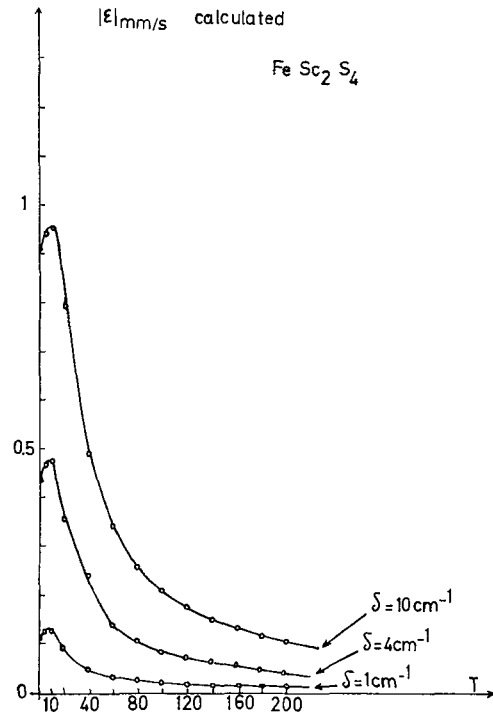


FIG. 6. — Theoretical ε vs T due to random strain with $1/7 e^2 Q \langle r^{-3} \rangle_{3d} = 1.5 \text{ mm/s}$ (from ref. [6]). $K = 13 \text{ cm}^{-1}$; $\delta = 1, 4$ and 10 cm^{-1} ; q (HAM factor) = 1.

In conclusion the as derived random strain model is in fair agreement with experimental results, but the values of strain δ needed to fit the $\varepsilon(T)$ curves seems

to be large. It appears necessary to do with susceptibility measurements at low temperatures in order to discuss the effect of dipole-dipole interactions in such a compound [8] : In the same way, Mössbauer studies on ZnSc_2S_4 : ^{57}Fe with different concentrations of iron are on progress in order to observe the influence on the shape of the spectra of pairs $\text{Fe(A)}\text{-Fe(A)}$ and to do

an usefull comparison with the present experimental results.

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