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MÖSSBAUER INVESTIGATION ON THE CRYSTAL FIELD SPLITTING ON Fe^{2+} ION IN ZINC FLUOSILICATE*

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ABSTRACT

The Mössbauer quadrupole interaction ΔE_Q of the Fe^{2+} ion has been measured with 2% at. ^{57}Fe in $ZnSiF_6,6H_2O$, between 1.3 - 20 K. The sign of ΔE_Q(<0) has been determined by using a single crystal absorber. These results are interpreted in terms of a trigonal crystal field potential that splits the Fe^{2+} orbitals into a ground state singlet and a first excited doublet whose distance is much smaller than that for $FeSiF_6,6H_2O$, in reasonable agreement with previous EPR measurements.

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value), and its determination with meaningful accuracy is possible since the absorption lines are not significantly broadened, even at low temperatures. The following differences are observed between this system and ferrous fluosilicate:

i) the ΔE_Q value extrapolated at 0^oK is much smaller;

ii) ΔE_Q versus T follows a trend which is markedly different from that of $FeSiF_6,6H_2O$ [1,3] and resembles that of $FeCl_2$ [4] for which it was concluded that $\delta \sim \lambda$.

In agreement with the EPR studies, these results indicate that δ is not much greater than λ for Fe^{2+} in $ZnSiF_6,6H_2O$.

The $\Delta E_Q(T)$ variation illustrated in Fig. 2 has been fitted by the method of Ingalls, by evaluating numerically the values of F in the equation:

$$\Delta E_Q(T) = \Delta E_{latt} + \Delta E_0 \times F(\lambda, \delta, T) . \qquad (1)$$

Satisfactory fits were found for a range of reasonable values of ΔE_{latt}, ΔE_0 and λ, giving as a consequence a range of values for δ. However, the ratio $|\frac{\delta}{\lambda}|$ kept essentially the same value and a confident result is $|\frac{\delta}{\lambda}| = 2.1 \pm 0.1$. The other parameters in Eq. (1) corresponding to the fitted $\Delta E_Q(T)$ in Fig. 2. (full line) have the following values: $\lambda = - 80\ cm^{-1}$, $\Delta E_{latt} = - 0.2$ mm/s, $\Delta E_0 = 3.9$ mm/s.

Our estimation $|\frac{\delta}{\lambda}|_5 = 2.1 \pm 0.1$ leads to a value of $g_{//} = 2.54 \pm 0.03$, from exact calculations in a D configuration by diagonalizing a 25 x 25 matrix (fortunately it factorizes into 8 x 8, 8 x 8 and 9 x 9 matrices [1]). This value is somewhat in disagreement with the value $g_{//} = 2.38 \pm 0.03$ measured by EPR, which would correspond, according to our calculations, to a ratio $\left|\frac{\delta}{\lambda}\right| = 2.6 \pm 0.1$. In order to vizualize the difference between these results, we have plotted in Fig. 2 ΔE_Q against T corresponding to $\left|\frac{\delta}{\lambda}\right| = 2.6$.

The experimental $\Delta E_Q(T)$ variation could be fitted with $\left|\frac{\delta}{\lambda}\right| \simeq 2.6$ if one would assume that the trigonal potential δ changes slightly with the temperature; a change of about 4% between 1.3 and 20 K would be sufficient.

In fact, preliminary measurements of ΔE_Q versus T above 20 K show a considerable deviation from an Ingalls plot, suggesting a dependence of δ on T; this has been proposed before from Mössbauer measurements on $FeSiF_6$, $6H_2O$ [1a] and from magnetic measurements on (Zn, Fe)SiF_6,$6H_2O$ [5].

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TABLE 1

T(K)	I.S(mm/s)	ΔE_Q(mm/s)	Γ(mm/s)
1.3	1.181	1.925	0.27
3	1.180	1.920	0.28
4.2	1.181	1.917	0.33
8	1.179	1.882	0.35
12	1.181	1.853	0.36
	1.180	1.830	0.35
20	1.181	1.820	0.37
standard deviation	± 0.002	± 0.002	± 0.01

Mossbauer parameters of $Fe^{57}_{0.02}$ $Zn_{0.98}$ $SiF_6,6H_2O$: isomer shift I.S. relative to a Co^{57}/Cu source, quadrupole splitting ΔE_Q and experimental line width Γ.

FIGURE CAPTIONS

Figure 1 - Room temperature Mössbauer spectrum of an oriented single-crystal absorber in which the rhombohedral crystal axis lies perpendicular to incident γ-ray.

Figure 2 - ΔE_Q versus T of $Fe^{57}_{0.02}Zn_{0.98}\ SiF_6,6H_2O$: best fit by Ingalls method with $\frac{\delta}{\lambda} = 2.1$ (full line); fit with $\frac{\delta}{\lambda} = 2.6$ from EPR data (dotted line).

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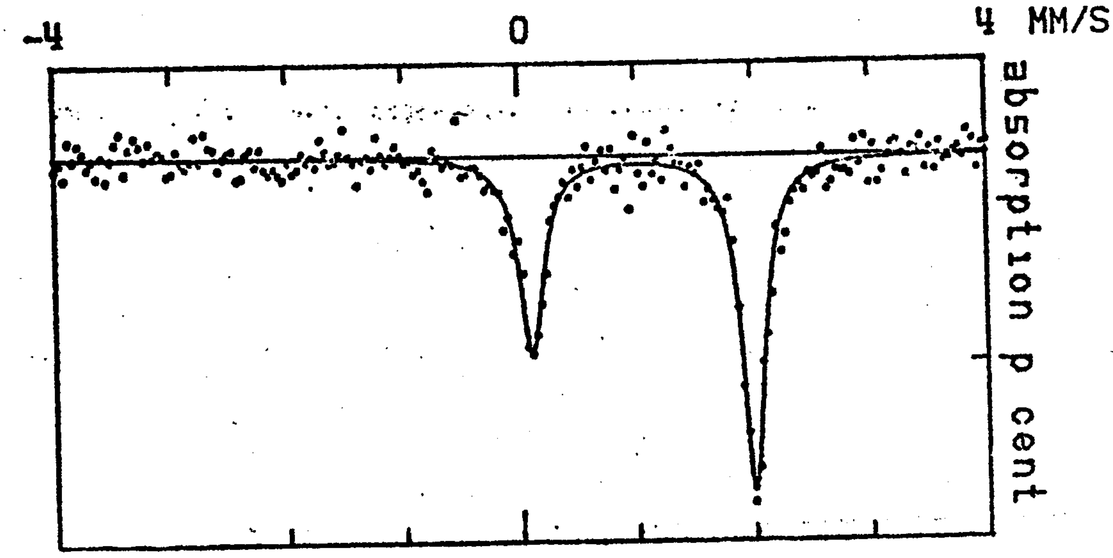

FIG. 1

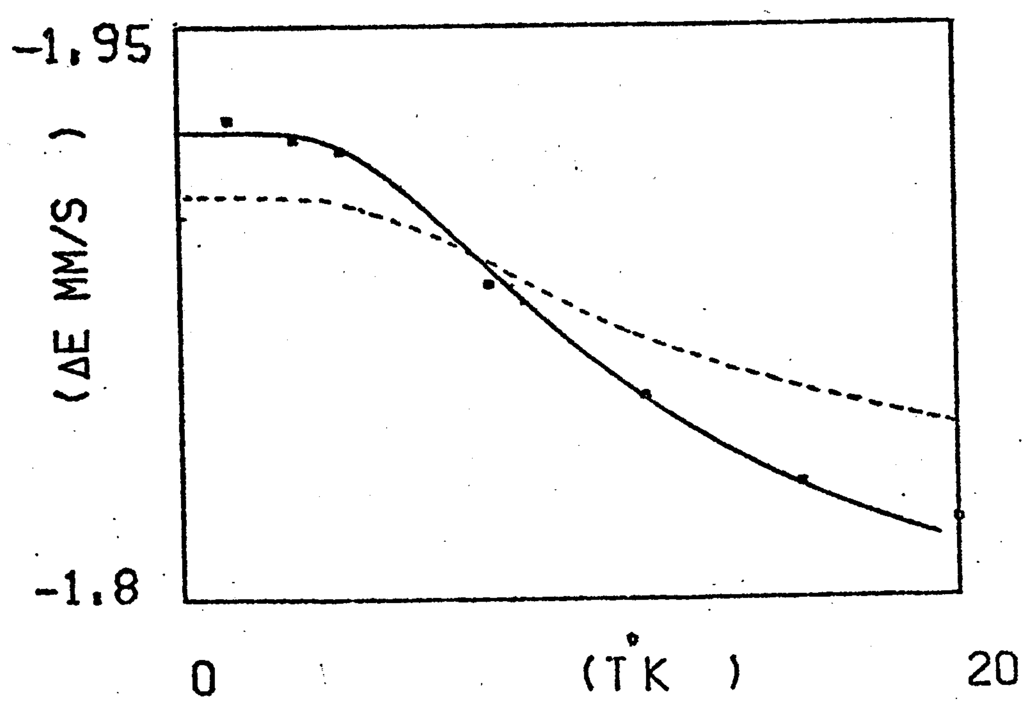

FIG. 2