MÖSSBAUER EFFECT IN Fe-DOPED KMgF_3

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Résumé. — Un monocristal de KMgF_3 dopé avec du fer a été étudié par effet Mössbauer. Les deux états de valence Fe^{2+} et Fe^{3+} sont observés. En dessous de 12 °K un doublet quadrupolaire apparaît pour l'état Fe^{2+} . Utilisant le modèle de contraintes proposé par Ham, on déduit que le premier état excité dû à l'interaction spin-orbite se trouve à $\sim 120 \text{ cm}^{-1}$ au-dessus du niveau fondamental Γ_{5g} .

Abstract. — An iron-doped KMgF_3 single crystal has been studied with the Mössbauer technique. The two charge states, Fe^{2+} and Fe^{3+} , are observed. Below 12 °K an Fe^{2+} quadrupole doublet appears. Using Ham strain model we calculate that the first excited spin-orbit level lies $\sim 120 \text{ cm}^{-1}$ above the Γ_{5g} ground state.

In order to explain the appearance of a quadrupole doublet in the Mössbauer spectrum of the system $\text{MgO} : \text{Fe}^{2+}$ at temperatures below 14 °K [1, 2]. Ham developed a model [3] including random strains in the crystal. These strains can lift the threefold degeneracy of the Γ_{5g} spin-orbit triplet (effective $J = 1$) and a quadrupole doublet with a splitting ΔE is to be expected at temperatures sufficiently low that the relaxation time τ_1 for electronic transitions among the three states is long compared to $\tau_2 = \hbar/\Delta E$ (Fig. 1).

FIG. 1. — On the left is shown the energy-level scheme of the $\text{Fe}^{2+} 5D$ term, on the right the partial energy level scheme of the ^{57}Fe nucleus. The nuclear excited state is split by the electric field gradient due to the random strain splitting of the electronic ground state.

Ham showed that the rapid temperature dependence of the quadrupole splitting could be explained if the transitions between the states went via an Orbach process involving the first excited spin-orbit level and calculated that this level must lie at $2\lambda = 95 \text{ cm}^{-1}$

above the Γ_{5g} ground state, in contrast to the free ion value of 200 cm^{-1} . This has been confirmed by far infra-red measurements [4]. Ham et al. concluded that this reduction in 2λ is too large to be attributed to covalency and is predominantly the result of the Jahn-Teller (J. T.) coupling [5].

We present here the preliminary results of the Mössbauer study of Fe-doped KMgF_3 . This system is of interest because of its similarity to Fe-doped MgO . However the strain coupling coefficients for Fe^{2+} in KMgF_3 , $G_{11} = 1340 \text{ cm}^{-1}$ and $G_{44} = 1000 \text{ cm}^{-1}$ [6] are nearly twice as large as the $\text{MgO} : \text{Fe}^{2+}$ values. Since the J. T. energy is proportional to the square of the coupling coefficients, one expects that $\text{KMgF}_3 : \text{Fe}^{2+}$ may show larger J. T. effects than $\text{MgO} : \text{Fe}^{2+}$ [5]. Covalency effects can also be important, but fortunately the isomer shift (I. S.) of the Mössbauer spectrum provides a measure of the covalent character and thus allows a comparison of the covalency and J. T. effects.

Single crystals of KMgF_3 doped with 0.05 at % of ^{57}Fe were grown by the Czochralski method [7]. The room temperature Mössbauer spectrum of a 0.8 mm slice [100] is shown in (Fig. 2). It can be interpreted as resulting from two valence states, Fe^{3+} and Fe^{2+} , having I. S. of 0.77 mm/s and 1.42 mm/s respectively (relative to sodium ferrocyanide). These I. S. values are interesting in regard to the problem of the I. S. calibration. In the Walker et al. scale [8], the purely ionic Fe^{3+} configuration was assumed to correspond to an I. S. of 0.55 mm/s (relative to stainless steel). On the basis of molecular orbital calculations, Danon [9] proposed a free ion I. S. of 1.0 mm/s. Our experimental value for $\text{KMgF}_3 : \text{Fe}^{3+}$ indicates that KMgF_3 is almost purely ionic and corresponds to a configuration $3d^5 4s^{0.17}$ on Danon's scale. The Fe^{2+} I. S. indicates a negligible amount of covalency ($\sim 3 d^6 4s^0$).

When the temperature of the sample is decreased, the Fe^{2+} line undergoes a transition at $\sim 12 \text{ °K}$ to a quadrupole doublet with a splitting $\Delta E = 0.44 \text{ mm/s}$ (Fig. 2). This splitting corresponds to

$$\tau_2 = \hbar/\Delta E = 3 \times 10^{-8} \text{ s.}$$

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FIG. 2. — Experimental Mössbauer spectra of Fe-doped KMgF_3 at 300 °K and 4.2 °K showing the onset of an Fe^{2+} quadrupole doublet at a low temperature. The source is ^{57}Co in a chromium matrix.

At 12 °K then we have $\tau_1 = \tau_2$. Assuming an Orbach type relaxation process, the temperature dependence of τ_1 is [3] :

$$\frac{1}{\tau_1} = \frac{6 G_{44}^2 \Delta^3}{\pi \rho \hbar^4 V_T^5} \left| 1 + \frac{2}{3} \left(\frac{V_T}{V_L} \right)^5 \right| \exp \left(- \frac{\Delta}{kT} \right), \quad (1)$$

where $\Delta = 2 |\lambda|$, ρ ($= 3.15 \text{ g/cm}^3$) is the density of KMgF_3 and V_T and V_L are the velocities of propagation of transverse and longitudinal acoustic waves. Using $V_L = 6.47 \times 10^5 \text{ cm/s}$ and $V_T = 3.94 \times 10^5 \text{ cm/s}$ [10] and $G_{44} = 1000 \text{ cm}^{-1}/\text{unit strain}$ [6], we derive from eq. 1 that $\Delta \simeq 120 \text{ cm}^{-1}$. This value is somewhat higher than the value (95 cm^{-1}) found for $\text{MgO} : \text{Fe}^{2+}$, but still represents a strong reduction from the free ion value (200 cm^{-1}). Such a reduction can have two origins : covalency or dynamic J. T. [11]. From the I. S. value, one can rule out any significant covalency effect. Therefore the reduction can be attributed to a J. T. coupling, similar in strength to that existing in $\text{MgO} : \text{Fe}^{2+}$. Although we expected a larger J. T. coupling in $\text{KMgF}_3 : \text{Fe}^{2+}$ from the strain coupling coefficients [5, 6], the similarity between the two systems is indicated by the reduced orbital contribution to the g-factors of 3.37 for $\text{KMgF}_3 : \text{Fe}^{2+}$ [12] and 3.428 for $\text{MgO} : \text{Fe}^{2+}$ [13] compared to the crystal field theoretical value of 3.5.

Further information can be obtained from the magnetic hyperfine interaction induced by application of an external magnetic field at low temperature. The same effect of covalency and J. T. that reduces the orbital contribution to the g-factor should also reduce the orbital contribution to the magnetic hyperfine field. Experiments are underway to check this point.

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