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Electronic properties of the Fe\(^{2+}\) ion in CaF\(_2\) from Mössbauer and far infrared spectroscopy

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Résumé. — Le système CaF\(_2\) : Fe\(^{2+}\) a été étudié par spectroscopie Mössbauer dans la zone de relaxation lente (4,2-14 K). Des expériences de spectroscopie infrarouge lointain ont été réalisées entre 1,5 et 35 K et en présence de champs magnétiques allant jusqu’à 8 T à 1,5 K. A partir de l’ensemble des résultats obtenus par spectroscopie Mössbauer et infrarouge lointain, on peut déduire que la distance moyenne entre les niveaux spin-orbite issus du doublet fondamental \(E_g\) est \(K = 17\) cm\(^{-1}\). Cette valeur située entre 10 et 20 cm\(^{-1}\) est en accord avec les prédictions de Ham. A partir de cette mesure de \(K\), on propose une estimation de la distance \(\Delta\) entre les états orbitaux \(E_g\) et \(T_{2g}\) : \(\Delta = 5\) 320 cm\(^{-1}\). La théorie du champ cristallin suffit à rendre compte des propriétés électroniques à l’intérieur du doublet orbital fondamental \(^3E_g\) et par conséquent l’effet Jahn-Teller dynamique peut être ici négligé en première approximation.

Abstract. — The system CaF\(_2\) : Fe\(^{2+}\) has been studied by Mössbauer spectroscopy in the slow relaxation regime (4.2-14 K). Far infrared experiments have been performed in the 1.5-35 K temperature range and at 1.5 K in an external magnetic field up to 8 T. From both Mössbauer and far infrared results, one can deduce that the average distance between the spin-orbit levels within the \(E_g\) state is \(K = 17\) cm\(^{-1}\). This value lies in the typical range 10-20 cm\(^{-1}\) predicted by Ham. From this measure of \(K\), we propose for the distance \(\Delta\) between the \(E_g\) and \(T_{2g}\) orbital states the calculated value \(\Delta = 5\) 320 cm\(^{-1}\). We conclude that crystal field theory alone can account for the electronic properties of the \(^3E_g\) ground state and consequently dynamical Jahn-Teller effects can be neglected.

1. Introduction. — Previous Mössbauer and far infrared (F.I.R.) studies of substitutional Fe\(^{2+}\) impurities in cubic diamagnetic matrices have shown the important role played by the covalency and the dynamical Jahn-Teller effects on the electronic properties of this ion [1]. In particular the consequences of the Mössbauer spectrum of the coupling between asymmetric vibrational modes and an electronic state having orbital degeneracy were examined [2]. Most of the ionic compound results concerned the Fe\(^{2+}\) in octahedral symmetry. A preliminary Mössbauer study of the CaF\(_2\) : Fe\(^{2+}\) system [3] having cubic symmetry (eightfold coordination) showed that (i) the substitution of Fe\(^{2+}\) on the cation site in CaF\(_2\) does not affect the cubic symmetry ; (ii) it is possible to observe the quadrupole interaction due to the slow relaxation contribution of the first excited triplet \(T_4\) of Fe\(^{2+}\) as predicted by Ham [2]. We report here detailed Mössbauer and F.I.R. studies of the CaF\(_2\) : Fe\(^{2+}\) system. For the Mössbauer part of this work, high statistics measurements have been developed in the slow relaxation regime in order to obtain a reliable evaluation of the energy distance \(K\) [2]. The F.I.R. experiments have been developed to obtain a direct measure of \(K\). In this study the magnetic field and temperature dependences of the F.I.R. transitions were examined. The CaF\(_2\) : Fe\(^{2+}\) system is of interest because (i) it is strongly ionic as indicated by the isomer shift value which is the largest value observed so far for the Fe\(^{2+}\) ion [4] ; (ii) it provides information on the importance of the Jahn-Teller effect in the case of an orbital doublet ; (iii) it gives the same electronic level scheme as the cubic systems with tetrahedral coordination. It is therefore interesting to compare the results with those obtained for ZnS : Fe\(^{2+}\), MgAl\(_2\)O\(_4\) : Fe\(^{2+}\), CdTe : Fe\(^{2+}\), etc...

In fact when Fe\(^{2+}\) is substitutionally introduced into CaF\(_2\), the \(^3D\) free ion ground state is split into
two orbital states $E_g$ and $T_{2g}$, the $E_g$ state being the
ground state (Fig. 1). Second order spin-orbit and
spin-spin interactions partially split the 10-fold dege-
eracy of the $E_g$ ground state into five equidistant
levels. These levels with their degeneracy are respec-
tively: $\Gamma_1(1), \Gamma_4(3), \Gamma_3(2), \Gamma_5(3), \Gamma_2(1)$. Ham has
shown that, to a good approximation, the five levels
remain equally spaced when the crystal field theory is
modified by a dynamic Jahn-Teller effect of weak or
moderate coupling strength [2], the common separa-
tion then given by

$$K = 6 q \left[ \frac{1}{2} + \rho \right],$$

where $\lambda$ and $\rho$ are the spin-orbit and spin-spin coupl-
ing parameters respectively, $A$ is the energy separation
between the $E_g$ and $T_{2g}$ orbital states and $q$ a reduction
parameter ($q < 1$) due to the Jahn-Teller coupling.
$K$ is found experimentally to be $15.0 \pm 0.1 \text{ cm}^{-1}$ for
$\text{Fe}^{2+}$ in ZnS [5]. As long as the local strains are small
compared to the separation $K$, neither the ground
singlet $\Gamma_1$, nor the first excited triplet $\Gamma_4$ in the fast
relaxation limit show any quadrupole splitting. But
Ham predicted that, in the slow relaxation limit [2],
this triplet should give a strain independent quadru-
pole splitting

$$\Delta E_Q = \frac{6}{7} q \langle r^{-3} \rangle \left[ \frac{e^2 Q}{I(2 I - 1)} \right].$$

To observe it, he suggested a careful study around
10 K, i.e. at a temperature high enough to populate
appreciably the triplet $\Gamma_4$, but avoiding fast relaxation.
The first experimental proof of Ham’s predictions was
reported in our previous work. The interesting point
in developing a Mössbauer study of $\text{Fe}^{2+}$ in CaF$_2$
was the possibility of calculating $K$ from the depen-
dence of the relative intensity of the quadrupole
doublet with temperature [3]. On the other hand the
-electronic transitions from the singlet ground state $\Gamma_1$
to the excited states within the $E_g$ electronic ground
state can be seen in the F.I.R. spectral region thus
giving a direct measure of $K$. The splitting of the
ground state manifold together with the magnetic
and electric dipole allowed transitions in the case of
cubic symmetry and tetrahedral symmetry (same level
scheme) are shown on figure 2.

Fig. 2. — Allowed transitions (arrows) among the spin-orbit levels
of the $E_g$ term of $\text{Fe}^{2+}$ ions for tetrahedral ($T_d$) and cubic ($O_h$)
coordinations allowed by the selection rules for electric and magne-
tic-dipole processes.
2.2 FAR INFRARED. — For the F.I.R. experiments, the crystal was grown in the same way except that the doping was done with natural FeF2. The chemical analysis indicated a Fe doping level of 0.27 at. %.

The absorption of Fe2+ in CaF2 due to electronic transitions was measured in the F.I.R. region with a Michelson interferometer RIIC 720. The spectra in the near infrared (N.I.R.) and visible regions were obtained with a Pye Unicam SP2000 and Cary spectrometer respectively. The main results are deduced from the F.I.R. measurements. Therefore we give some instrumental details on this last technique: low temperature measurements were performed with the crystal immersed in superfluid He at 1.5 K. The temperature variations could be obtained by heating the crystal, attached to a large copper block. Temperature accuracy within 0.5 K was determined with an Allen-Bradley resistor. Magnetic field dependence of the electronic transitions of Fe2+ could be followed up to 8 T.

3. Measurements. — 3.1 MöSSBAUER. — Figure 3 shows high statistics Mössbauer spectra of Fe2+ in CaF2 recorded at 4.2, 8, 10, 12 and 14 K. Previous measurements of this crystal have indicated that at room temperature the Mössbauer spectrum consists of a single line of width $2\Gamma_1 = 0.27$ mm/s and of isomer shift relative to iron metal $\delta_1 = 1.48$ mm/s. These results indicated that (i) we were in presence of one charge state Fe2+ substituting Ca2+ in CaF2 structure; (ii) the symmetry remained cubic around the Fe2+ impurity.

With the same crystal the 4.2 K spectrum consists of a single line of width $2\Gamma_1 = 0.31$ mm/s and of isomer shift 1.67 mm/s. However between 8 and 14 K some peculiar features appear in the Mössbauer spectra (Fig. 3): at 8 K a doublet with an isomer shift close to $\delta_1$ and a splitting $\Delta E_2 = 3.74$ mm/s is superimposed on the main line. The Mössbauer parameters concerning the single line and the quadrupolar doublet obtained by least square fits of the spectra are reported in table I.

In particular one can remark that the relative intensity $\frac{I_2}{I_1 + I_2}$ and the splitting of this doublet varies with the temperature. With a further increase of temperature the doublet broadens and disappears simultaneously with a considerable broadening of the single line. These features attributed to relaxation

Table 1. — Results of least-square fits of the Mössbauer spectra reported on figure 3. $\delta$ is the isomer shift relative to iron metal, $2\Gamma$ the linewidth, $\Delta E_2$ the quadrupolar interaction. The index 1 refers to the main line and the index 2 to the superimposed quadrupole doublet. $I_2/(I_1 + I_2)$ represents the relative intensity of the doublet.

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$\delta_1$ (mm/s)</th>
<th>$2\Gamma_1$ (mm/s)</th>
<th>$\frac{I_1}{I_1 + I_2}$ (%)</th>
<th>$\delta_2$ (mm/s)</th>
<th>$2\Gamma_2$ (mm/s)</th>
<th>$\Delta E_2$ (mm/s)</th>
<th>$\frac{I_2}{I_1 + I_2}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.2</td>
<td>1.67</td>
<td>0.31</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>1.67</td>
<td>0.34</td>
<td>86.3</td>
<td>1.67</td>
<td>0.42</td>
<td>3.74</td>
<td>13.7</td>
</tr>
<tr>
<td>10</td>
<td>1.66</td>
<td>0.34</td>
<td>81.2</td>
<td>1.71</td>
<td>0.52</td>
<td>3.67</td>
<td>18.7</td>
</tr>
<tr>
<td>12</td>
<td>1.65</td>
<td>0.36</td>
<td>77.2</td>
<td>1.69</td>
<td>0.68</td>
<td>3.58</td>
<td>22.8</td>
</tr>
<tr>
<td>14</td>
<td>1.66</td>
<td>0.46</td>
<td>70.5</td>
<td>1.71</td>
<td>1.18</td>
<td>3.12</td>
<td>29.5</td>
</tr>
</tbody>
</table>
phenomena are already significant on the 14 K Mössbauer spectrum. They will be discussed in detail elsewhere [6].

3.2 FAR INFRARED. — Figure 4 shows the F.I.R. absorption spectra of Fe$^{2+}$ at 1.5 K and 19 K obtained with a 27 mm thick crystal doped with 2 700 ppm Fe$^{2+}$. At 1.5 K there is one absorption line at

$$15.8 \pm 0.2 \text{ cm}^{-1}$$

with a half-width of 1.1 cm$^{-1}$ and an oscillator strength of about $10^{-9}$. At higher temperature an additional absorption was observed at $35.2 \pm 0.3 \text{ cm}^{-1}$ with approximately the same half-width 1.2 cm$^{-1}$. The temperature dependence of these F.I.R. absorptions due to the electronic transitions of Fe$^{2+}$ is illustrated in figure 5. The magnetic field dependence of the transition at 15.8 cm$^{-1}$ was measured quantitatively only at 1.5 K up to 8 T as shown in figure 6. Detailed measurements of the high temperature absorption at 35.2 cm$^{-1}$ which also is magnetic field dependent failed because of the low signal to noise ratio. The (001) direction of this crystal was 10$^o$ out of the direction of the external magnetic field. On the other hand with our crystals we could not see any absorption in the 3 000-6 000 cm$^{-1}$ energy range which should correspond to the electronic transition between the E$_g$ and T$_2g$ orbital states.

![Fig. 4. — F.I.R. spectra of CaF$_2$ crystals doped with 2 700 ppm Fe$^{2+}$ at 1.5 and 19 K.](image)

![Fig. 5. — T-dependence of the F.I.R. absorptions due to the electronic transitions of Fe$^{2+}$. $\bullet$ represent experimental results for the 15.8 cm$^{-1}$ transition. $\times$ represent experimental results for the 35.2 cm$^{-1}$ transition. Solid line represents the fit for the temperature dependence of the 15.8 cm$^{-1}$ line taking account of the contribution of the two predominate magnetic dipole transitions $\Gamma_1-\Gamma_4$ and $\Gamma_4-\Gamma_3$ in the 1.5-35 K temperature range. Dashed line represents the fit of the $\Gamma_4-\Gamma_3$ temperature dependent transition.](image)

![Fig. 6. — Magnetic field dependence of the 15.8 cm$^{-1}$ line ($\Gamma_1-\Gamma_4$ transition) at 1.5 K (crystallographic (001) direction 10$^o$ from the direction of $H$).](image)

4. Discussion. — According to the energy level scheme of figure 1, the system is in the lowest spin-orbit state $\Gamma_1$ at low temperatures. Since this state is a singlet and since the symmetry is cubic, no electric field gradient at the $^{57}$Fe nucleus is expected. This is exactly what is observed at the lowest temperature 4.2 K where no quadrupole interaction is present (see Fig. 3). The quadrupole interaction $\Delta E_Q$ can only be different from zero in the $\Gamma_4$ and $\Gamma_3$ spin-orbit triplets within the E$_g$ ground state. According to Ham a quadrupolar doublet due to first excited triplet $\Gamma_4$ contribution can appear when the relaxation is slow between the three sublevels of this triplet split by the strain field. This implies that the system is at a temperature low enough to avoid relaxation averaging but where the first excited spin-orbit level $\Gamma_4$ can be populated. These conditions are fortunately fulfilled for the CaF$_2$ : Fe$^{2+}$ system. As shown in figure 3
the quadrupole doublet can be seen from 8 K to 14 K. One can therefore interpret the Mössbauer spectra in this temperature range as the superposition of two contributions: the main line comes from the \( \Gamma_1 \) state while the quadrupole doublet

\[ \Delta E_2 \approx 3.6 \text{-} 3.7 \text{ mm/s} \]

due to the population of the excited \( \Gamma_4 \) state. An estimate of the distance \( K \) between \( \Gamma_1 \) and \( \Gamma_4 \) can be obtained from the relative intensity of the quadrupole doublet \( \frac{I_2}{I_1 + I_2} \) given in table I. Assuming a Boltzmann population distribution, the relative population \( P \) of \( \Gamma_4 \) for a temperature \( T \) is given by

\[ P = \frac{3 e^{-K/4KT}}{1 + 3 e^{-K/4KT}}. \]

Relating the experimental intensities of table I to the above expression, one gets a set of approximate values for the spin-orbit distance \( K \) (Table II). From table II the mean value of \( K \) given by the temperature dependent Mössbauer measurements is \( K = 18 \text{ cm}^{-1} \).

| \( I_2 \) | 0.137 | 0.188 | 0.227 | 0.294 |
|\( I_1 + I_2 \) | 16.3 | 17.8 | 19.4 | 19.2 |

However we think that the values of \( K \) obtained from the Mössbauer data at 8 K and 10 K give the most reliable estimation for this distance because the two lines of the doublet are well defined and are not yet too broadened (2 \( \Gamma \sim 0.4 \text{-} 0.5 \text{ mm/s} \) confirming that at these temperatures the system is without any doubt in the slow relaxation regime. From the above arguments, it would be more suitable to take

\[ K = 17 \pm 2 \text{ cm}^{-1}. \]

If we refer to figure 2, we see that the only electronic transition observable at low temperature in the low frequency range is the \( \Gamma_1 \text{-} \Gamma_4 \) magnetic dipole transition. So we can attribute the 15.8 cm\(^{-1}\) absorption peak observed at 1.5 K (Fig. 4) to the electronic transition between the fundamental \( \Gamma_1 \) and first excited \( \Gamma_4 \) spin-orbit levels. This assumption is confirmed by the following: (i) The intensity of the 15.8 cm\(^{-1}\) line decreases as the temperature is raised from 1.5 to 35 K (Fig. 5) consistent with a Boltzmann population distribution within the set of electronic levels. The temperature dependence of the integral absorption \( I = \int \alpha(v) \text{d}v \) of this line can be fitted (Fig. 5) to the experimental results when we take into account only the \( \Gamma_1 \text{-} \Gamma_4 \) and \( \Gamma_4 \text{-} \Gamma_5 \) magnetic dipole transitions and the degeneracy of the levels as indicated in figure 2. (ii) The energy of this line is magnetic field dependent as shown on figure 6.

The 35.2 cm\(^{-1}\) line which appears at higher temperature (Fig. 4) can be attributed unambiguously to the \( \Gamma_4 \text{-} \Gamma_5 \) magnetic dipole transition. In fact as shown in figure 2 the only transition energy which approximates the interval energy value 2 \( K \) corresponds to the energy distance between the \( \Gamma_4 \) and \( \Gamma_5 \) spin-orbit levels. This is confirmed by the fact that the intensity of this additional line at 35.2 cm\(^{-1}\) increases with temperature: the integral absorption of this line can be fitted by taking into account only the magnetic dipole transition between these levels and their degeneracy.

One can notice here that no line has been observed at about 52 cm\(^{-1}\) which would correspond to the interval of energy 3 \( K \). As Slack et al. [7] attribute the higher relative oscillator strengths to the \( \Gamma_1 \text{-} \Gamma_5 \) and \( \Gamma_5 \text{-} \Gamma_2 \) transitions which would be observable at 19 K, we conclude that for Fe\(^{2+}\) in CaF\(_2\), no electric-dipole transition is observed in the F.I.R. Such transitions (see Fig. 2) could be observed for Fe\(^{2+}\) impurities with \( T_4 \) point-symmetry like Fe\(^{2+}\) in ZnS [5, 7]. They are not allowed in Fe\(^{2+}\) impurities with \( O_h \) point symmetry (see Table III). Such a conclusion is in fact predicted by group theory and is due to the different transformation properties of the \( E \) and \( H \) vectors in the \( T_4 \) and \( O_h \) groups (Table III). The difference between these two groups is due to the presence of an inversion centre in \( O_h \). The polar vector \( E \) is sensitive
to inversion which contrasts with the properties of the axial vector $B$. The dipole vector $E$ transforms like the odd representation $I_{4u}$ in the $O_h$ point group which possess an inversion centre. The electric dipole transitions between the spin-orbit levels ($I_{1g}$, $I_{4g}$, $I_{3g}$) in CaF$_2$:Fe$^{2+}$ given by the product

$$\langle I_{1g} | I_{4u} | I_{3g} \rangle = 0$$

are not allowed in contrast to the magnetic dipole transitions given by $\langle I_{1g} | I_{4g} | I_{3g} \rangle$. These arguments show that in CaF$_2$ we can only see magnetic dipole transitions in the F.I.R. region i.e. transitions of $K$ and $2K$ energies.

In the same way the electric dipole transitions between the $E_g$ and $T_{2g}$ orbital levels must be forbidden by group theory in the CaF$_2$:Fe$^{2+}$ system, but the magnetic dipole transitions given by the product $\langle E_g | T_{1g} | T_{2g} \rangle$ are allowed. If we consider the spin-orbit level scheme of the ground $E_g$ and excited $T_{2g}$ orbital states, we see on figure 7 that at low temperature, two magnetic dipole transitions

$$(I_{1g})_{E_g} \rightarrow (I_{4g})_{T_{1g}}$$

are allowed and should have been possible in N.I.R. One of the possible reasons for explaining their absence can be a smaller oscillator strength in N.I.R. compared to the F.I.R. case. This assumption is not valid if we refer to the work by Slack et al. [8] which shows that the oscillator strength of the electric and magnetic dipole transitions between $E_g$ and $T_{2g}$ is about of this same order of magnitude. A more plausible explanation for the absence of the N.I.R. transition consists to invoke the fact that the dynamic Jahn-Teller effects are more important in the excited $T_{2g}$ state and the $\langle E_g | T_{1g} | T_{2g,vib} \rangle$ oscillators strengths corresponding to phonon assisted lines are very small.

From F.I.R. measurements, we obtain the $\Gamma_4 \rightarrow \Gamma_4$ and $\Gamma_4 \rightarrow \Gamma_5$ energy distances:

$$E_{\Gamma_4 \rightarrow \Gamma_5} = 15.8 \text{ cm}^{-1} \quad \text{and} \quad E_{\Gamma_4-\Gamma_5} = 35.2 \text{ cm}^{-1}.$$ 

We observe here a slight difference in the spacing of the s.o. levels which is not explained if we refer to Ham's predictions even in case of a weak or moderate dynamic Jahn-Teller coupling in $E_g$ [8], [9]. Such an effect may in principle diminish the splitting interval $K$ without affecting the order of the levels or their uniform spacing. A non uniform spacing of the energy levels could be obtained by including higher order terms in perturbation theory [10]. The mean value of the splitting interval $K$ deduced from F.I.R. measurements is $K = 17 \text{ cm}^{-1}$. This value is in good agreement with that obtained by Mössbauer spectroscopy and will be retained for the calculation of $\Delta$.

We have seen above that we did not observe any absorption in the N.I.R. region. So no direct measure of the distance $\Delta$ between the $E_g$ and $T_{2g}$ orbital states is possible. If we refer to the expression of $K$ as a function of $\lambda$ and $\Delta$,

$$K = 6 q \left( \lambda^2 + \rho \right),$$

we can calculate $\Delta$ with the following assumptions: first we suppose that the dynamic Jahn-Teller effect is weak in the $E_g$ ground doublet as proposed by Ham. One can then use the value of the reduction factor $q = 1$. This approximation is reasonable if we refer to the estimation of the corresponding reduction factor for Fe$^{2+}$ in ZnS: $q = 0.91$ [11]. Second taking into account the strong ionicity of Fe$^{2+}$ in CaF$_2$, we can take for $\lambda$ the free ion value

$$\lambda_{CaF_2:Fe^{2+}} \approx \lambda_{Fe} = -100 \text{ cm}^{-1}.$$ 

Then one can develop the calculation of $\Delta$ in the two following approximations:

(i) In the simplest theory we neglect spin-spin interactions and spin-orbit interactions with higher $LS$ terms of the 5d configuration. The s.o. levels should be equally spaced by an amount $K = 6 \lambda^2/\Delta_1$. The value of $\Delta$ obtained with $\lambda = -100 \text{ cm}^{-1}$ and $K = 17 \text{ cm}^{-1}$ is $\Delta_1 = 3.530 \text{ cm}^{-1}$.

(ii) If we take into account spin-spin and spin-orbit interactions the spacing is given by

$$K = 6 \left( \frac{\lambda^2}{\Delta_2} + \rho \right).$$

Fig. 7. — The energy levels (schematic) of Fe$^{2+}$($3d^6$) as predicted by static crystal-field theory for cubic coordination ($O_h$). The arrows indicate the optical transitions from the lowest level ($\Gamma_1$) of $^5E_g$ which are magnetic-dipole allowed.
Taking for \( p \) the free ion value calculated by Pryce [12]
\[ p = 0.95 \text{ cm}^{-1} \], we obtain the energy distance
\[ \Delta_2 = 5 \text{ 320 cm}^{-1} \].

As \( \Delta \) depends strongly on the covalency of \( \text{Fe}^{2+} \) in
the matrix, we see immediately that the second value of \( \Delta \) seems to be more acceptable if we compare to the
\( \Delta \) values measured for the following similar systems
given in order of decreasing covalency strength:

\[
\begin{align*}
\Delta (\text{CdTe} : \text{Fe}^{2+}) &= 2 \text{ 480 cm}^{-1}, \\
\Delta (\text{ZnS} : \text{Fe}^{2+}) &= 3 \text{ 470 cm}^{-1}, \\
\Delta (\text{MgAl}_2\text{O}_4 : \text{Fe}^{2+}) &= 4 \text{ 470 cm}^{-1} [8], \\
\Delta (\text{CdF}_2 : \text{Fe}^{2+}) &= 4 \text{ 950 cm}^{-1} [13].
\end{align*}
\]

The value of the isomer shift measured at 300 K for
\( \text{Fe}^{2+} \) in \( \text{CaF}_2 \), \( \delta_2 = 1.48 \text{ mm/s} \) (relative to iron metal)
may be compared to the corresponding value,
\( \delta_2 = 1.44 \text{ mm/s} \), for \( \text{Fe}^{2+} \) in \( \text{CdF}_2 \) [14]. It confirms
that the \( \text{CaF}_2 : \text{Fe}^{2+} \) system is slightly more ionic.
Therefore we can expect a \( \Delta \) value of the same order of magnitude or slightly higher than that measured in
\( \text{CdF}_2 \). So we propose for \( \Delta \) in \( \text{CaF}_2 \), the calculated
value \( \Delta = 5 \text{ 320 cm}^{-1} \) i.e. that we must take into
account in the \( \Delta \) calculation of the spin-spin interac-
tions and spin-orbit interactions with higher \( LS \) terms.

On the other hand the F.I.R. experiments obtained
in the presence of an external magnetic field (Fig. 6)
confirm that the 15.8 cm\(^{-1}\) line whose position shifts
with the field is due to an electronic transition. When
spin-orbit interaction between the \( \varepsilon_5 \) and \( \varepsilon_2 \) states
is neglected, we have for the Zeeman interaction
simply \( \mathcal{H}_Z = \mu B \cdot 2 \cdot S \). This Zeeman Hamiltonian is modified if one takes into account the spin-orbit
interaction [5, 7]. For magnetic fields small compared to
\( K \) one should expect a linear Zeeman splitting of the
\( \Gamma_{4,5} \)-triplets with an isotropic \( g \)-factor of 1 if corrections
of the order of \( \lambda / \Delta \) are neglected. In our case the
effective \( g \)-factor up to about 3 T was measured to be
\( g = 1.18 \pm 0.06 \). At higher magnetic fields the levels
are mixed, leading to a non linear field dependence.
Vallin et al. [5] have given the matrix representation of
\( \mathcal{H}_Z \) for arbitrary directions of the vector \( B \). From their
calculation, it is possible to obtain the values of
\( g_1 = 2 - (4 \lambda / \Delta) \) and \( g_2 = - (4 \lambda / \Delta) \)
which provide a second estimation of \( \Delta \). Unfortunately up to now we have not determined the crystallographic directions with respect to the external magnetic field.

5. Conclusion. — In summary the agreement
between the results of the present measurements
and the predictions of crystal field theory (order of the
s.o. levels, measure of \( K \), estimation of \( \Delta \)) is good
despite the small discrepancy which we have noted for
the slight non uniform spacing of the s.o. levels within
the \( \varepsilon_2 \) state. The average value of \( K = 17 \text{ cm}^{-1} \)
measured by Mössbauer and far infrared experiments
is consistent with the experimental values obtained
for \( \text{Fe}^{2+} \) in tetrahedral sites and is also not much
reduced from the higher value of \( K \) proposed by Ham,
\( K = 20 \text{ cm}^{-1} \). Therefore dynamical Jahn-Teller effects
are not likely to be present in \( \varepsilon_2 \) at least to any
significant extent and crystal field theory may be
considered to give a fairly good description of the \( \varepsilon_2 \)
ground state for \( \text{Fe}^{2+} \) in \( \text{CaF}_2 \).

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References
Regnard, J. R. and Ray, T., Phys. Rev. 14 (1976) 1805 and refe-
rences therein.
(1976) C6-611.
281.
[6] Bonville, P., Chappert, J., Garcin, C., Imbert, P. and
Regnard, J. R., to be published in Proceedings of the
International Conference on Mössbauer Spectroscopy,
Portoroz (1979).
(1967) 170.
152 (1966) 376.
(1969) 511.
21 (1977) 545.