Intermediate Jahn-Teller effect within an orbital triplet - II - Application to the acoustic paramagnetic resonance of V3+ in CaO

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Intermediate Jahn-Teller effect within an orbital triplet
II — Application to the acoustic paramagnetic resonance of V^{3+} in CaO

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Résumé. — Les résultats expérimentaux de Résonance Paramagnétique Acoustique de l'ion V^{3+} dans CaO sont présentés. Les spectres obtenus ne peuvent pas être interprétés comme étant dus à l'effet Jahn-Teller statique ou dynamique. Par contre, ils sont bien expliqués sur la base d'une situation *intermédiaire* décrite dans le précédent article. Ainsi, l'ion V^{3+} dans CaO apparaît-il comme le premier système représentant le cas d'un couplage Jahn-Teller *intermédiaire* pour un triplet orbital. D'autre part, une analyse générale du couplage hyperfin pour les systèmes de configuration d^2 soumis à l'effet Jahn-Teller est présentée. Elle permet de comprendre de manière satisfaisante pourquoi la structure hyperfine n'est pas observée sur les spectres du système *intermédiaire* V^{3+} : CaO. Appliquée, cependant, au système dynamique V^{3+} : MgO précédemment étudié, elle conduit à une valeur inacceptable du terme de contact.

Abstract. — Experimental results of Acoustic Paramagnetic Resonance of V^{3+} in CaO are presented. The spectra cannot be interpreted as due to the well known static or dynamic Jahn-Teller effect. On the other hand, they are well explained by the intermediate situation described in the preceding paper. Thus, V^{3+} : CaO appears as the first system representing the *intermediate* case of Jahn-Teller coupling for an orbital triplet. In addition, a general analysis of the hyperfine coupling for d^2 systems submitted to Jahn-Teller coupling is presented. It explains satisfactorily why the hyperfine structure is not observed for the *intermediate* V^{3+} : CaO system. However, when applied to the dynamic V^{3+} : MgO system previously studied, it leads to an unacceptable contact term value.

1. **Introduction.** — The acoustic paramagnetic resonance (APR) of V^{3+} : MgO, reported many years ago [1, 2], was interpreted [3, 4] as due to a dynamic Jahn-Teller effect (see for instance ref. [5] for a review of the general Jahn-Teller problem). The anisotropic spectra, which showed a tetragonal symmetry, were well explained as due to V^{3+} ions in sites whose point symmetry is cubic on average but distorted by random strains. The Jahn-Teller coupling being higher with the E_g modes than with the T_{2g} modes, the distortions of E_g type have the major effect and thus lead to the tetragonal symmetry indicated by the spectra. As the isoelectronic system Ti^{2+} : CaO has shown a very similar behaviour [6], it has seemed interesting to study the analogous V^{3+} : CaO system.

The APR spectra obtained with vanadium doped CaO crystals are strongly different from those obtained with V^{3+} : MgO and Ti^{2+} : CaO. Below, we shall give arguments to attribute these spectra to V^{3+} ion but, since the typical hyperfine structure of vanadium does not appear, we have to cautiously justify these arguments. In section 2, we show from EPR and APR experiments that, among the impurities of the crystals studied, V^{3+} is the only reasonable ion which can be responsible for the spectra. After a brief description of these spectra, we show in section 3 that they can be interpreted neither by a static nor by an usual dynamic Jahn-Teller effect. We show that they are well explained by supposing an *intermediate* coupling, whose theoretical aspects have been analysed in the previous paper [7] (hereafter referred as I). Thus, V^{3+} : CaO is the first illustration of this intermediate situation in the case of an orbital triplet. In section 4, we discuss the problem of the hyperfine structure, showing that it is not surprising not to observe it for V^{3+} : CaO. However, an analysis of the case of V^{3+} : MgO, where this structure was clearly observed, shows that the core polarisation field should have a value outside the range of values reported for this ion in other materials.

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2. **Experimental results.** — 2.1 CRYSTAL TREAT-
MENT. — The best CaO crystals we have studied have
been produced by Spicer Limited (England). The
spectra described in this paper have been observed
with two samples cut from a crystallised part of the
best *melt* obtained. Although the vanadium nominal
concentration was 1 000 ppm, a chemical analysis
of two other samples cut in the same crystallised
part have given 50 ppm of V, 40 ppm of Ti and 5 ppm
of Cr. With the *as received* crystals, we observe
only V^{2+} and Mn^{2+} impurities by EPR and no
absorption by APR. After heating at 1 400 °C in
an oxygen atmosphere, EPR V^{2+} spectra disappear
while the APR spectra described below are obtained.
About six months later, these spectra are no longer
visible but the EPR V^{2+} spectra can again be observed.

The APR spectra of Cr^{2+} and Ti^{2+} in CaO have
been reported [8, 6]. They are strongly different from
those described here. V^{4+} and Ti^{3+} ions of d^1 configu-
ration, which have never been observed in octahedral
symmetry, could be responsible for the spectra.
A simple analysis shows that the resonance of these
ions should be observed inside a ground multiplet [9].
Since our spectra are visible in the liquid hydrogen
temperature range and not at liquid helium tempe-
rature, we can eliminate this possibility. V^+ ion,
isoelectronic of Cr^{2+} has never been observed
previously. Due to the oxidizing treatment of the
crystal, we think this ion has not been produced.
In addition, in light of the results obtained with
Cr^{2+} [8], the V^+ spectra should be more compli-
cated than those reported here. Thus, the only ion
to which the spectra can be ascribed is V^{3+}.

Fig. 1. — Angular variation of the V^{3+} : CaO APR spectra at
$T = 20$ K. The orientations of H and k with respect to the cubic
axis are indicated. The attenuations are in arbitrary units. The
different resonance lines are labelled by capital letters in order
to make easier the discussion.

2.2 DESCRIPTION OF THE SPECTRA. — APR spectra
shown in figures 1, 2, 3 have been observed at 9.3 GHz
with a spectrometer previously described [10]. The
k vector of the longitudinal waves is along a $\langle 100 \rangle$
direction of the crystal. The magnetic field orientation
with respect to the $\langle 100 \rangle$ axis is indicated in the
figures. We have labelled the lines : A, B, ..., E.
Most of our spectra have been obtained at 14 K
or 20 K. At 4.2 K, only the $\Delta m_s = 2$ of the Fe^{2+}
ion and a weak line at the field of the line A of figure 1
are observed. It is thus clear that our spectra are due
to resonance in an excited multiplet.

As usual, the APR spectra depend on the orienta-
tion of both the magnetic field and the k vector
of the hypersonic wave. This is well illustrated in
figure 1 and 2 for $\theta = 45°$: line E is not observed
when k is perpendicular to H. We note that A, B,
C lines seem nearly isotropic, that E line is aniso-
tropic with a strongly anisotropic width and that D
line is also anisotropic and comes in coincidence with
C line when H is aligned with k along a $\langle 100 \rangle$ axis.
We note also the zero field absorption for all orien-
tations and the observation of C and D lines with
H parallel to k, an unusual result in APR which will
be important in the discussion.

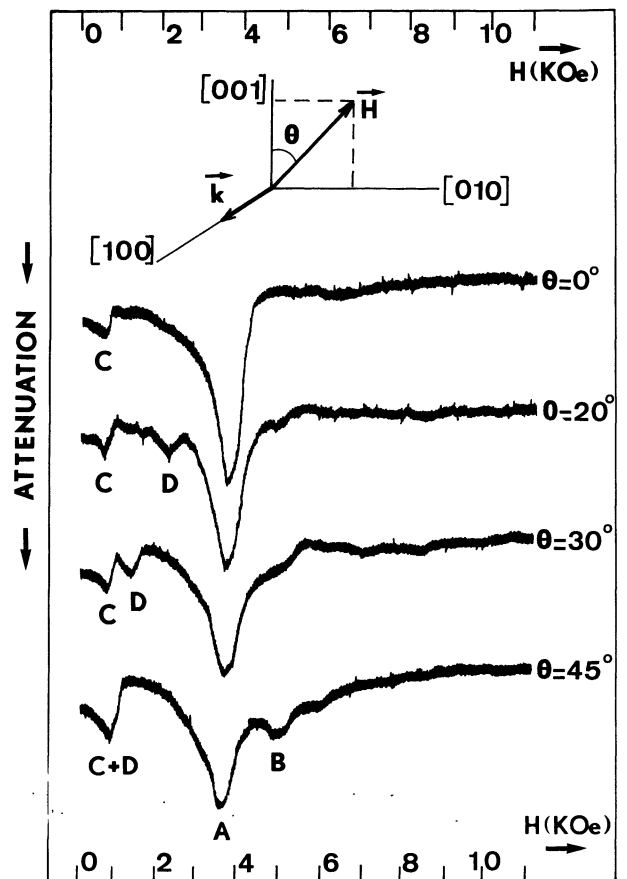3. **Interpretation.** — We recall briefly that V^{3+}
has a configuration $3d^2$ and that its ^3F ground term
is split by an octahedral field leaving a $^3T_1$ orbital
level as a ground state. The Jahn-Teller coupling
with E_g modes changes this *electronic* state into a
$^3T_1$ *vibronic* state whose degeneracy is lifted by
spin-orbit coupling leading to one Γ_1 singlet, one
Γ_3 doublet and two Γ_4 and Γ_5 triplets. The splitting
of these levels depends on the strength of the Jahn-
Teller coupling as shown in detail in the previous
paper.

We can first try to explain our spectra by assuming
a small or moderate Jahn-Teller coupling and using
the results of the analysis for V^{3+} in MgO [3]. Within
this model of a dynamic Jahn-Teller effect, the E line
and the nearly half field A line would be the $\Delta m_s = 1$
and $\Delta m_s = 2$ transitions within the excited Γ_5 triplet.
The random strains should not be too large, in oppo-
sition to what was observed for V^{3+} in MgO, so
that the isotropic behavior should be preserved.
The angular dependence of the transition proba-
bilities is approximately in agreement with this
interpretation ($\Delta m_s = 1$ line is forbidden if H is
perpendicular to k). However, B, C, D lines are not
explained in this model. In addition, the g value of

Fig. 2. — Angular variation of the V³⁺ : CaO APR spectra at T = 20 K. The orientations of H and k with respect to the cubic axis are indicated. The attenuations are in arbitrary units. The different resonance lines are labelled by capital letters in order to make easier the discussion.
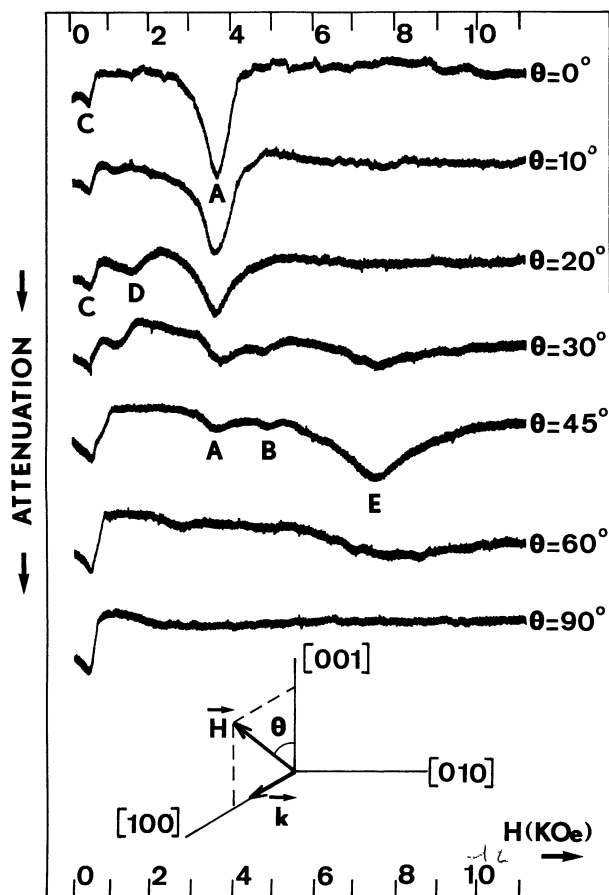
Fig. 3. — Angular variation of the V³⁺ : CaO APR spectra at T = 20 K. The orientations of H and k with respect to the cubic axis are indicated. The attenuations are in arbitrary units. The different resonance lines are labelled by capital letters in order to make easier the discussion.
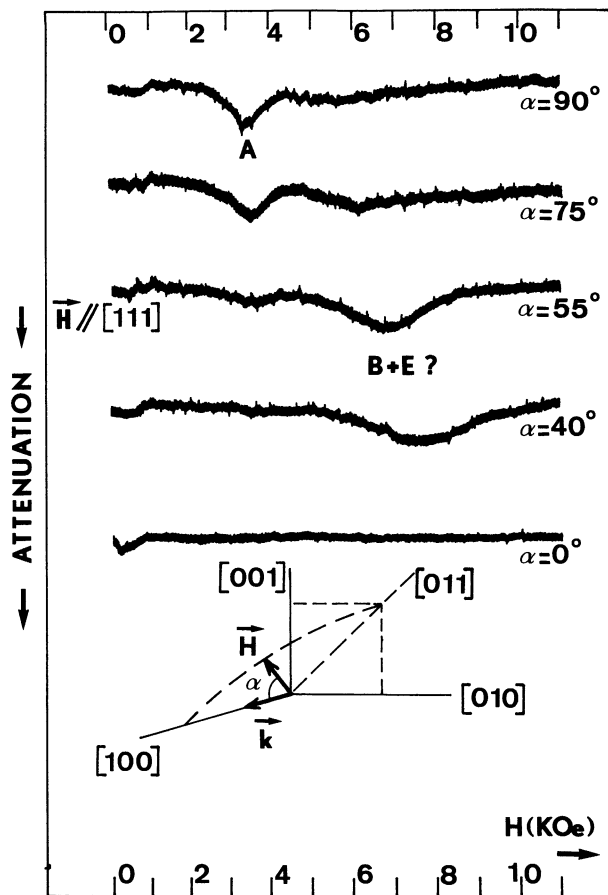
the Γ_5 triplet should be 0.93 very close to $g = 1$ which can be considered (see I, § 3) as the *frontier-value* between the weak and strong coupling cases. All that invalidates the use of the moderate coupling model for this system.

Since a static Jahn-Teller effect cannot explain our spectra any better, we think we are in the *intermediate* situation which has been studied in the previous paper I and that the Γ_4 and Γ_5 triplets coming from the $^3T_1$ vibronic level are sufficiently near one another to allow intertriplet transitions. Within this hypothesis and using $\lambda_f = -104 \text{ cm}^{-1}$, $\hbar\omega = 350 \text{ cm}^{-1}$ for the E_g modes energy [11] and $cg_L \sim -1.2$ (see the discussion of this value at the end of this section), the best value for the Jahn-Teller coupling energy compatible with our spectra is $E_{JT} \sim 1600 \text{ cm}^{-1}$, which implies a Ham reduction factor $K(T_1) \sim 10^{-3}$. In figure 4, we have plotted the variation of the 9 energy levels derived from $^3T_1$ versus magnetic field for H parallel to $\langle 100 \rangle$ and $\langle 110 \rangle$. These levels are labelled by a small letter in order to simplify the discussion. We have also calculated the APR transition probabilities for

the interesting transitions. In the following discussion, we shall use their values W_{ij} in arbitrary units.

It is well known that the random strains play a very important role for the lineshape and even for the spectra themselves. In some particular situations, it was possible to study in detail the effect of these strains, either by simulating them with a Monte Carlo calculation [3] or with a cautious analysis by perturbation calculations [12]. In our case, the two triplets in which the resonance occurs are so close that the perturbation method is not possible. A Monte Carlo calculation would be too cumbersome because at least the 6 levels of these triplets ought to be considered. So, we shall satisfy ourselves with a semi-quantitative approach based on perturbation theory usable for low magnetic fields and with a strain splitting of the levels smaller than the triplet separation. The strain Hamiltonian valid within the vibronic triplet $^3T_1$ may be expressed [13] either in terms of the strains e_θ and e_ε or in terms of the lattice coordinates of distortion Q_θ' and Q_ε' as :

$$\mathcal{K}_c = V_2[e_\theta \, \delta_\theta + e_\varepsilon \, \delta_\varepsilon] = V_2'[Q_\theta' \, \delta_\theta + Q_\varepsilon' \, \delta_\varepsilon]$$
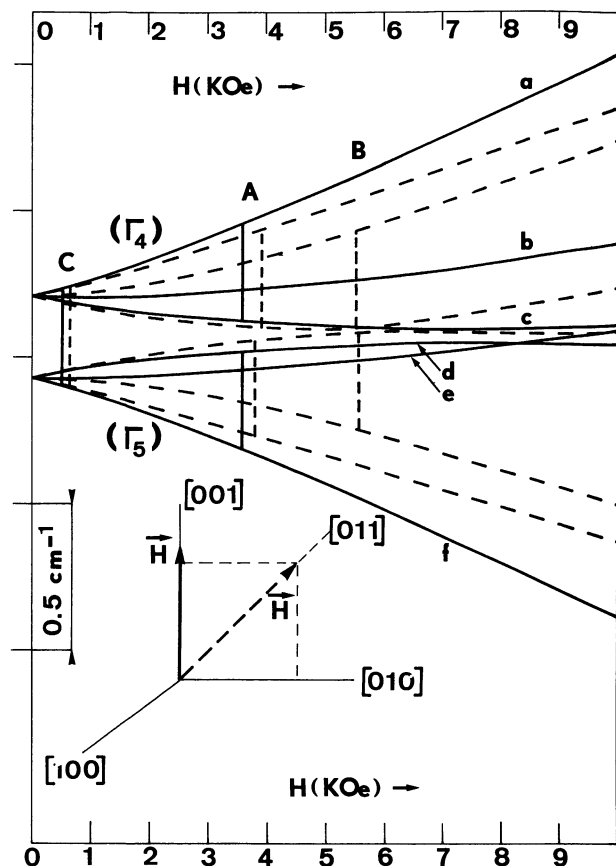
Fig. 4. — V^{3+} in CaO. Zeeman effect on the Γ_4 and Γ_5 S.O. triplets and allowed transitions for APR experiments at 9 GHz with $H/\!/[001]$ (continuous lines) and $H/\!/[011]$ (dotted lines). Capital letters identify the transitions responsible for the resonance lines of the preceding figures. Small letters are used to distinguish the sublevels of the triplets.
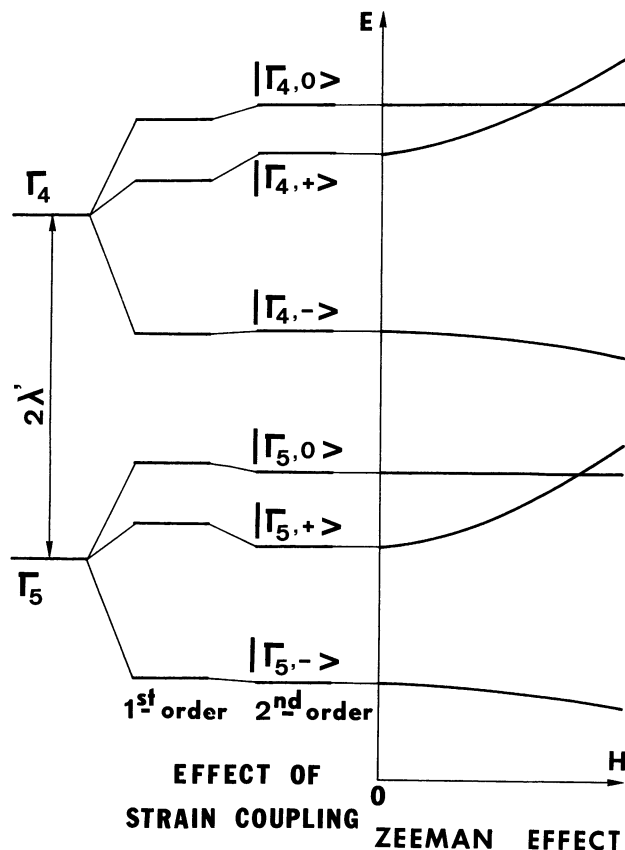

Fig. 5. — V^{3+} in CaO. Effect of tetragonal strain coupling at first and second order of perturbations and Zeeman effect on the Γ_4 and Γ_5 S.O. triplets for $H/\!/[001]$. The energies of the eigenstates $\Gamma(i,j)$ are given in the text.

with $Q'_\theta = \dfrac{2R}{\sqrt{3}}\,e_\theta$ and $Q'_\varepsilon = \dfrac{2R}{\sqrt{3}}\,e_\varepsilon$; V_2 and V'_2 are

the strain coupling coefficients, $\mathcal{E}_\theta$ and $\mathcal{E}_\varepsilon$ the usual operators belonging to E doublet.

From this Hamiltonian, we can deduce the corrections to first and second order of perturbation on the energies of S.O. levels :

$$E(|\,\Gamma_4, 0\,\rangle) = E(\Gamma_4) + G_\theta + \frac{(2\,G_\varepsilon)^2}{2\,\lambda'}$$

$$E(|\,\Gamma_4,\,\pm\,\rangle) = E(\Gamma_4) - \frac{G_\theta}{2} \pm G_\varepsilon + \frac{(1.5\,G_\theta \pm G_\varepsilon)^2}{2\,\lambda'}$$

$$E(|\,\Gamma_5, 0\,\rangle) = E(\Gamma_5) + G_\theta - \frac{(2\,G_\varepsilon)^2}{2\,\lambda'}$$

$$E(|\,\Gamma_5,\,\pm\,\rangle) = E(\Gamma_5) - \frac{G_\theta}{2} \pm G_\varepsilon - \frac{(1.5\,G_\theta \pm G_\varepsilon)^2}{2\,\lambda'}$$

where $G_\theta = \dfrac{V_2}{2}\,e_\theta$, $G_\varepsilon = \dfrac{\sqrt{3}\,V_2}{4}\,e_\varepsilon$

and $\lambda' = \lambda_f\,cg_L\,K(T_1)$.

These results are reported in figure 5 together with the effect of a small magnetic field, which is zero to

first order of perturbation theory. The qualitative evolution of the levels given in figure 5 is obtained by extrapolation of the results obtained in I (see fig. 3 of I). It must be pointed out that to first order, strains have the same effect on equivalent levels of each triplet : we shall see the importance of this point later.

With the help of figures 4 and 5 we can now interpret our spectra as follows. A line corresponds to c → a and f → d transitions ($W_{ca} \sim W_{fd} \sim 0.2$ for $H \perp k$). The position of this line, which of course depends on the Jahn-Teller energy, was used to determine this energy. The two transitions c → a and f → d which would be of $\Delta m_s = 2$ type if they were occurring within two well separated triplets, are induced at the same field for $\theta = 0°$. They are split by about 100 G for $\theta = 45°$. This behavior is in agreement with the spectra since A line is broader for $\theta = 45°$ than for $\theta = 0°$. The fact that it disappears for H parallel to k ($W_{ca} = W_{fd} = 0$) is in agreement with its $\Delta m_s = 2$ nature as is its asymmetry with a low field broadening induced by random strains (see fig. 5).

The $\Delta m_s = 1$ type transitions occurring within each triplet (see fig. 4) are the origin of the B and E lines. But, as usual, the random strains have a larger

effect on their broadening and, due to the extreme proximity of the levels, a perturbation calculation is impossible. Only the major property of these transitions is preserved, namely their interdiction when **H** is perpendicular to **k**. The fact that the peak of the E line is almost at a field twice that of A line is not in perfect agreement with this model, which predicts, in absence of random strains and for $\theta = 45°$, a line at about 6 kG instead of the 7.5 kG observed. We think that a complete (but complicated !) calculation taking account of the random strains could explain this discrepancy. Along the same qualitative arguments, we can attribute the B line to $\Delta m_s = 1$ transitions allowed (when **H** is perpendicular to **k**) by the random strains (see the spectrum for $\theta = 45°$ in fig. 1). A line analogous to that one was observed with Fe^{2+} : MgO (see the spectra of ref. [3]).

We attribute the C line to a transition between the two triplets at low field. In fact, the value of the transition probabilities tells us that only the d → c and the f → a are allowed ($W_{dc} \sim W_{fa} \sim 0.3$) and remain allowed even when **H** is parallel to **k**, in agreement with our results. The qualitative study of the effect of random strains illustrated on figure 5 tells us that C line can only be attributed to the f → a transition because the strain broaden this transition on the low field side whereas they broaden the d → c transition on the high field side. This attribution of the C line gives a very important spectroscopic result since it implies the equality :

$$hv = 2 \lambda' + 2 g\mu_B H_c$$

where H_c is the magnetic field of the sharp edge of C line and $g = 0.93$ is the approximate g factor at low field for the two triplets. By measuring H_c, we deduce the value of the reduced spin-orbit coupling $\lambda' = 0.12$ cm^{-1} with good precision.

The interpretation of D line can be given on the same basis as those used for explaining lineshapes of strongly random strain coupled ions [3, 12, 14]. When the broadening is important, only *turning points* give appearance of a line. We have seen that C line corresponds to a transition between ions in perturbed cubic sites. We say now that only the ions

in slightly perturbed sites give C line. Among the others, those which are in *nearly axial* sites have a resonance magnetic field nearly equal and give *lines* with axial symmetry. This is exactly the behaviour of D line. We find here, for inter-triplet transitions the behaviour observed previously for V^{3+} : MgO for transitions within an isolated triplet : both isotropic lines (for nearly cubic sites) and axial lines (for nearly axial sites) are observed. This is possible here for inter-triplet transitions because the two triplets have nearly identical behaviour on magnetic field and strains.

We can now summarize the spectroscopic information obtained from our experiments and compare the values of the various parameters to those obtained with similar systems. We have measured

$$\lambda' \sim 0.12 \text{ cm}^{-1} .$$

As $\lambda' = \lambda_f cg_L K(T_1)$ we could try to deduce a good value for $K(T_1)$ and thus for E_{JT}. However, there exists no optical experiments to give information on the term mixing from which a g_L value could be deduced, as was the case for V^{3+} : MgO [15]. Of course, the value of the covalency factor c is not known either. We thus can only verify that the order of magnitude $g_L \sim - 1.25$, $c \sim 0.9$ and $K(T_1) \sim 10^{-3}$ are compatible with our λ' and the known value $\lambda_f = - 104$ cm^{-1}.

From the shape of C line and from the fact that there is a zero field absorption, we can deduce that for $H = 0$, $hv \sim 2 \lambda' + 2 | \overline{G}_\varepsilon |$ and thus

$$| \overline{G}_\varepsilon | \sim 0.04 \text{ cm}^{-1} \quad \text{where} \quad G_\varepsilon = \frac{\sqrt{3}}{4} V_2 e_\varepsilon$$

must be taken with a value for e_ε representative of the strain distribution. Taking $e \sim 10^{-5}$, we get

$$V_2 = 10\ 000 \text{ cm}^{-1} ,$$

and assuming $V_2 e \sim V_2' Q'$, we deduce the Jahn-Teller coupling coefficient $V_2' = 0.7 \times 10^{-4}$ erg.cm^{-1}. This value must be compared with

$$V_E = 2.7 \times 10^{-4} \text{ erg.cm}^{-1}$$

deduced from the Jahn-Teller energy $E_{JT} = 1\ 600$ cm^{-1}

Table I. — *Values of different parameters for* V^{3+} : MgO, V^{3+} : CaO *and* Ti^{2+} : CaO *systems. In this table,* g *represents the experimental Landé factor,* λ_f *the spin-orbit coupling constant for the free-ion,* g_L *the orbital effective factor within the ground* T_1 *triplet, c the covalency factor,* $K(T_1)$ *the Ham reduction factor,* $\hbar\omega_E$ *the energy of* E_g *active modes, and* E_{JT} *the Jahn-Teller energy.*

	g	$\Gamma_3 - \Gamma_5$ splitting (cm^{-1})	$\Gamma_4 - \Gamma_5$ splitting (cm^{-1})	λ_f	g_L	$cg_L K(T_1)$	$\hbar\omega_E$ (cm^{-1})	$K(T_1)$	E_{JT} (cm^{-1})
V^{3+} : MgO	0.67	7	—	− 104	− 1.24 (*a*)	− 0.57	450	0.64	135
V^{3+} : CaO	0.93	—	0.24	− 104	− 1.25 (*b*)	− 1.15 × 10^{-3}	350	10^{-3} (*b*)	1 600
Ti^{2+} : CaO	0.85	5.5	—	− 60	− 1.34 (*b*)	− 0.24	350	0.2	350

(*a*) From optical spectra [15].
(*b*) Estimation (see the text).

obtained by the fitting with the A line position. Although these two quantities have not to be equal, we find they have values of same order of magnitude, a result often found in J.T. systems and expected in the idealized case of the cluster model.

As a conclusion of this section, we recall the main parameter values obtained with the two isoelectronic systems previously studied : V^{3+} : MgO and Ti^{2+} : CaO. They are given in table I along with those found here. It thus appears that a given ion has a greater Jahn-Teller coupling in CaO than in MgO. This unexpected result (since the V^{3+}-O distance is greater in CaO than in MgO) was already pointed out by Ham [13] from the g values of Fe^{2+} in these two matrices. We do not succeed in detecting Ti^{2+} in MgO and thus we cannot draw any conclusion about this ion. We can only note, by comparison of Ti^{2+} and V^{3+} in CaO, that the coupling is greater with the more positive ion, a result which is in contradiction with the values reported by Ham [13] for Fe^+ and Mn^0 in Si. This contradiction can however be partially explained because the Si matrix is more covalent than the oxides studied here.

4. Hyperfine coupling.

— We have given, in section 2, the experimental arguments which have led us to attribute the spectra observed to V^{3+} although the typical hyperfine structure was not visible. We study now how Jahn-Teller interaction can modify the hyperfine coupling both to justify again our interpretation and to discuss the case of V^{3+} : MgO which was not analysed before [3].

We start from the well known expression for the magnetic hyperfine Hamiltonian within a (L, S) term [16] :

$$\mathcal{H}_{HF} = P \left\{ \mathbf{L}.\mathbf{I} + [\xi L(L + 1) - \kappa] \mathbf{S}.\mathbf{I} - \frac{3}{2} \xi[(\mathbf{L}.\mathbf{S}) (\mathbf{L}.\mathbf{I}) + (\mathbf{L}.\mathbf{I}) (\mathbf{L}.\mathbf{S})] \right\} \quad (1)$$

with

$$P = 2 \mu_B \gamma_N \langle r^{-3} \rangle \quad \text{and} \quad \xi = \frac{1}{105}$$

for ^3F term of d^2 configuration. In this Hamiltonian, we have included the orbital term $(\mathbf{L}.\mathbf{I})$, the dipolar terms (ξ) and the contact term (κ). We establish, in the appendix, the effective spin Hamiltonian for this hyperfine coupling within a Γ_4 or Γ_5 isolated triplet derived from the $^3T_1$ vibronic state. This effective Hamiltonian takes the simple form $\mathcal{H}_I = A\mathbf{I}.\mathbf{s}$ with $s = 1$ and

$$A = -\frac{P}{2} \left\{ \kappa g_L K(T_1) - \kappa + \xi \left[L(L+1) + \frac{9}{2} K(T_1) \right] - \frac{2 \lambda_f g_L^2 c^2}{\hbar \omega_E} \exp(-3 S_E) G\left(\frac{3}{2} S_E\right) \right\} \quad (2)$$

where the last term of the bracket comes from the second order Jahn-Teller contribution.

4.1 V^{3+} : MgO. — We begin with this case for which expression (2) is directly applicable. From the spectra obtained with this system and previously published we found the value :

$$| A | = (40 \pm 1) \times 10^{-4} \, cm^{-1} .$$

Since all the factors in eq. (2) are known except κ, we can deduce its value. Using $c = 0.72$, $g_L = -1.24$, $K(T_1) = 0.64$, $\lambda_f = -104 \, cm^{-1}$, $\hbar \omega_E = 450 \, cm^{-1}$, $S_E = 0.3$ determined in ref. [3] and the values $\mu_I = 5.148$ nuclear magnetons, $\langle r^{-3} \rangle = 3.217$ atomic units we are led to the following equation for κ :

$$\pm 40 = -75 \{ -0.56 - \kappa + 0.14 - 0.07 \} \quad (3)$$

where we have left the numerical value of the various terms appearing in eq. (2). Depending on the sign of A, we deduce :

$$\kappa_{exp} = \quad 0.04 \quad \text{if} \quad A > 0$$

$$\kappa_{exp} = -1.02 \quad \text{if} \quad A < 0 .$$

This result is very surprising. Abragam and Bleaney [16] show both experimentally and theoretically (from calculations of Freeman and Watson), that the value of κ for iron group ions varies in a small range around 0.6. Pontnau and Adde [17], using the core polarisation hyperfine field per unit spin H_{cp} instead of κ for their discussion (these quantities are connected by $H_{cp} = -\mu_B \langle r^{-3} \rangle \kappa$), show that H_{cp} does not change by more of a factor of 3 among all the experimental values known for the iron group ions and does not change by more of a factor of 2 for a given ion in various matrices. For instance, κ goes from 0.69 for V^{3+} : ZnS to + 1.04 for V^{3+} : CdF_2 presumably due to covalency effect. It is clear that neither of our values of κ is in this range. Looking at eq. (3), we see that κ could have a more usual value if the orbital part of A were zero or even negative. We have carefully verified that the sign of this orbital part is the same (for κ positive), as that of the core polarisation part. Taking a nearly zero value for this orbital part would imply that the orbital quenching is complete and thus that the g value would be ~ 1, in strong disagreement with the well determined 0.7 experimental value. We have also calculated the correction to g_L due to the S.O. coupling via the $^3T_2$ excited level [18]. This correction has a negligible effect (less than 1 %). We thus have no explanation for the anomalous κ value.

4.2 V^{3+} : CaO. — For this system, we must show that the theoretical prediction for A is compatible with our experiments from which we have deduced

$$| A_{exp} | \lesssim 25 \times 10^{-4} \, cm^{-1} .$$

Since the Γ_4 and Γ_5 triplets are very near one another, we cannot use the result (2) established for an isolated triplet. We must then come back to the

total Hamiltonian $\mathcal{H}_t = \mathcal{H}_{SO} + \mathcal{H}_Z$ defined by eq. (1) and (2) of I, find the eigenstates and calculate, by perturbation, the matrix elements of the hyperfine Hamiltonian (1) between these eigenstates. When **H** is along the z axis, we find easily the eigenstates of a, c, d, f level :

$$| V_a \rangle = -\alpha \, | \tilde{1}, 0 \, \rangle + \beta \, | \tilde{0}, 1 \, \rangle$$

$$| V_c \rangle = -\alpha' \, | \tilde{0}, -1 \, \rangle + \tilde{\beta}' \, | -1, 0 \, \rangle$$

$$| V_d \rangle = \beta \, | \tilde{1}, 0 \, \rangle + \alpha \, | \tilde{0}, 1 \, \rangle$$

$$| V_f \rangle = \beta' \, | \tilde{0}, -1 \, \rangle + \alpha' \, | -\tilde{1}, 0 \, \rangle$$

where α, α', β, β' are positive quantities and where the kets are written in the basis $| \tilde{m}_1, m_s \rangle$, ℓ being the $\ell = 1$ orbital momentum of the vibronic T_1 triplet. Keeping only the two major terms of (1), namely the **l.I** and **S.I** terms, we find the energies of the hyperfine levels

$$E_{dI}(m_{I_z}) = E_d +$$
$$+ P \{ \beta^2 \, cg_L \, K(T_1) + \alpha^2 [\xi L(L + 1) - \kappa] \} \, m_{I_z}$$

$$E_{fI}(m_{I_z}) = E_f -$$
$$- P \{ \alpha'^2 \, cg_L \, K(T_1) + \beta'^2 [\xi L(L + 1) - \kappa] \} \, m_{I_z}$$

and similar results for a and c levels. We can deduce a hyperfine structure constant A defined by

$$E_{dI} - E_{fI} = 2 \, g\mu_B \, H_0 + 2 \, Am_{I_z}$$

which leads to

$$A = \frac{P}{2} \{ (\beta^2 + \alpha'^2) \, cg_L \, K(T_1) +$$
$$+ (\alpha^2 + \beta'^2) [\xi L(L + 1) - \kappa] \} \, .$$

At the field for which the A line is observed, we find $\alpha \sim \alpha'$, $\beta \sim \beta'$ and thus $\beta^2 + \alpha'^2 \sim \alpha^2 + \beta'^2 \sim 1$ with a precision of 10^{-4}. That means that the proximity

of the triplets does not affect the value of A we should have found using eq. (2) valid for an isolated triplet. Since $K(T_1) \sim 10^{-3}$ we get

$$A \sim \frac{P}{2} \{ \xi L(L + 1) - \kappa \} \, .$$

With κ in the range $0.5 \leqslant \kappa \leqslant 0.8$ expected for iron group ions, we deduce $29 \times 10^{-4} \leqslant A_{th} \leqslant 50 \times 10^{-4}$ as compared to our result $| A_{exp} | \lesssim 25 \times 10^{-4} \, cm^{-1}$. Thus, even without an (hypothetical) anomalous reduction such as that seen with $V^{3+} : MgO$, we note that the non-observation of the hyperfine structure of our spectra is approximately justified.

5. **Conclusion.** — APR spectra obtained with vanadium doped CaO crystals have been attributed to V^{3+} ion although they do not show the characteristic hyperfine structure. They cannot be interpreted as resulting either from an usual dynamic or a static Jahn-Teller effect. They are, on the contrary well explained if the coupling is supposed to be *intermediate*. It is the first time such a situation is observed for an orbital triplet coupled with E_g modes. Some lines observed at very low fields, are interpreted as due to transitions between the two triplets which result from the splitting of the $^3T_1$ vibronic level by spin orbit coupling. It is thus possible to deduce directly the reduction of the spin orbit coupling by the Jahn-Teller effect. The problem of the hyperfine structure for an ion submitted to Jahn-Teller effect is discussed and applied to V^{3+} in MgO and CaO. For $V^{3+} : MgO$, the observed hyperfine structure and g values lead to anomalously low core polarisation field. For $V^{3+} : CaO$, we can only verify that, even with normal core polarization fields, it is not surprising that the hyperfine structure was not observed.

Appendix

It is convenient, in order to transform the hyperfine Hamiltonian (1) valid in a (LS) term, to write it in terms of operators belonging to the irreducible representations of the O_h group :

$$\mathcal{H}_{HF} = P \left\{ O_{T_1}(L, I) - \kappa \mathbf{S.I} + \xi \left[L(L+1) \mathbf{S.I} - \right.\right.$$
$$\left.\left. - O_{A_1}(L, I, S) - \frac{1}{2} O_E(L, I, S) - \frac{3}{2} O_{T_2}(L, I, S) \right] \right\}$$

where

$$O_{A_1} = L^2(\mathbf{I.S})$$

$$O_E = (3 L_z^2 - L^2)(3 I_z S_z - \mathbf{I.S}) +$$
$$+ 3(L_x^2 - L_y^2)(I_x S_x - I_y S_y)$$

$$O_{T_1} = \mathbf{L.I}$$

$$O_{T_2} = (L_x L_y + L_y L_x)(I_x S_y + I_y S_x) +$$
$$+ \text{ circular permutations } .$$

Going to the crystal field orbital triplet $^3T_1$, the orbital operators $O_i(L, I, S)$ are transformed into operators $O_i(l, I, S)$ with an effective orbital momentum $l = 1$. The Wigner-Eckart coefficients for this transformation are respectively 6, 6, $-3/2$ and $-3/2$ for the representations A_1, E, T_1, T_2 if we neglect the term mixing. For the dominant term **L.I** we can take into account this mixing by changing $g_L = -3/2$ to $g_L = -1.25$. We can also introduce for that term a covalent reduction factor c. Within the vibro-

nic triplet $^3T_1$ resulting from the Jahn-Teller coupling, we have again to introduce the Wigner-Eckart coefficients calculated by Ham [13]. They are respectively 1, 1, $K(T_1)$, $K(T_2) = K(T_1)$ for the representations A_1, E, T_1, T_2. Going finally to the Γ_5 triplet derived from $^3T_1$ and taking into account second order vibronic coupling, we find the hyperfine constant A given in eq. (2). When comparing our eq. (2) with that obtained in ref. [4], we point out that the contact and orbital terms are the same but that the dipolar term is different, certainly due to an incorrect Jahn-Teller reduction.

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