Intermediate Jahn-Teller effect within an orbital triplet - I - Theoretical analysis of the paramagnetic resonance

A. Nahmani, R. Buisson, R. Romestain

Classification
Physics Abstracts
76.30

Intermediate Jahn-Teller effect within an orbital triplet
I — Theoretical analysis of the paramagnetic resonance

A. Nahmani, R. Buisson and R. Romestain

Laboratoire de Spectrométrie Physique (*), Université Scientifique et Médicale de Grenoble,
B.P. 53X, 38041 Grenoble Cedex, France

Résumé. — Nous étudions de manière détaillée l'évolution des propriétés spectroscopiques d'un triplet orbital en symétrie octaédrique en fonction de l'intensité du couplage Jahn-Teller. Jusqu'à présent, seuls les cas statique et dynamique avaient été distingués. Nous montrons que, dans le cas d'un triplet orbital $^3T_1$ couplé à des modes de vibration E_g, une situation intermédiaire existe entre ces deux cas bien connus et qu'elle conduit à des spectres de résonance paramagnétique très différents de ceux caractéristiques des effets Jahn-Teller statique et dynamique. Nous montrons également qu'un fort champ magnétique devrait stabiliser le système et que des situations existent pour lesquelles les spectres de résonance présentent une symétrie apparemment orthorhombique.

Abstract. — We analyze in detail how the spectroscopic properties of an orbital triplet in octahedral symmetry vary because of the Jahn-Teller coupling. Up to now, only static and dynamic cases were distinguished. We show, in the case of a $^3T_1$ triplet coupled to E_g modes of vibration that an *intermediate* situation does exist between these well known cases, and that this *intermediate* situation leads to paramagnetic resonance spectra very different from those obtained in the static and dynamic cases. We show also that a high magnetic field could stabilize the system and that situations exist for which resonance spectra have an apparent orthorhombic symmetry.

1. **Introduction.** — The study of the spectroscopic consequences of the dynamic coupling between a paramagnetic ion and the surrounding lattice, mainly those resulting from the Jahn-Teller (J.T.) effect, has led to a considerable amount of publications. A recent review of this study in which 372 references can be found was recently published by C. Bates [1]. When the ion in cubic symmetry has an electronic level belonging to E representation and when the dominant coupling is with E_g modes of vibration, three kinds of situations have been distinguished : the dynamic J.T. effect when the ion-lattice coupling is not too large, the static J.T. effect which occurs when this coupling is strong and when the so called *warping terms* are of importance [2], and the *intermediate* case between these two limiting cases [3]. Although the distinction between static and dynamic depends on the way the system is studied (more precisely on the time scale of the experiment), it is still a common vocabulary. Real systems have been found which illustrate these different cases (see for instance ref. [1] and [2] and for the intermediate coupling ref. [3]).

When the 3d ion has a T_1 or T_2 electronic triplet, one distinguishes first between strong and weak coupling depending on the relative values of J.T. and spin-orbit (S.O.) couplings. When these couplings have comparable values, the problem can be solved only by numerical calculation, the vibronic wave functions being not simple. Such calculations have been done for instance by Ham *et al.* [4] and Parot *et al.* [5]. Within the so called strong coupling case, one still get strongly different E.P.R. spectra corresponding to the *static* and *dynamic* J.T. effects. In this work we will analyse in details how the spectroscopic properties of an orbital triplet vary because of the J.T. coupling. We show that an *intermediate* situation does exist between the static and dynamic cases, as for the E orbital doublet. In order to illustrate this situation, we select the particular case of the $^3T_1$ triplet coupled to E_g modes. The results of this study will be used to interpret acoustic paramagnetic resonance (A.P.R.) spectra obtained with V^{3+} : CaO and described in the next paper [6] (hereafter referred as II). This system is the first one reported as representing the *intermediate* case. Although the study done here concerns the $^3T_1$ orbital triplet, the conclusions are roughly valid for any triplet ^nT_i ($i = 1, 2$ and n = spin degeneracy). Recently, Uba and Baranowski [7] have analysed the situation for the $^4T_1$ multiplet and claim they have illustrated the transition

between static to dynamic J.T. effect. We will come back to this point later.

After introducing the problem in section 2, we give the results of calculations in part 3. Part 4 is a general discussion of the results. Particularly, it is shown that this intermediate situation, which remains dynamic in its fundamental nature, could be stabilized by a high magnetic field. Furthermore, this situation can lead to spectra which look orthorhombic. It is shown that a cautious experimental analysis should be necessary to show that they are only pseudo-orthorhombic.

2. **Position of the problem.** — The case of the orbital triplet only coupled to E_g modes was the first one investigated by Ham [8] in his series of papers. This is the simplest case mathematically, and it can be used as a model for the more complex situations. Using Ham's notation and keeping only linear coupling terms, one writes the Hamiltonian of the problem :

$$\mathcal{H} = \mathcal{H}_c + \mathcal{H}_V + \mathcal{H}_{JT} + \mathcal{H}_{SO} + \mathcal{H}_Z$$

where $\mathcal{H}_c$ is the electronic Hamiltonian of the ion in the static crystal field

$$\mathcal{H}_V = \frac{1}{2\mu}[P_\theta^2 + P_\varepsilon^2 + \mu^2 \omega^2(Q_\theta^2 + Q_\varepsilon^2)]$$

$$\mathcal{H}_{JT} = V_E(Q_\theta \, \mathcal{E}_\theta + Q_\varepsilon \, \mathcal{E}_\varepsilon)$$

$$\mathcal{H}_{SO} = \lambda_f(\mathbf{L}.\mathbf{S})$$

$$\mathcal{H}_Z = \mu_B \mathbf{H}.(\mathbf{L} + 2\mathbf{S}) .$$

In these expressions $(Q_\theta, Q_\varepsilon)$ and $(P_\theta, P_\varepsilon)$ are the coordinates and momenta of the E_g modes, ω is their circular frequency, μ is their effective mass. V_E defines the ion-mode coupling, λ_f is the spin orbit constant of the free ion and μ_B the Bohr magneton. $\mathcal{E}_\theta$ and $\mathcal{E}_\varepsilon$ are two standard electronic orbital operators belonging to E and having the following matrix form in the real basis ψ_X, ψ_Y, ψ_Z :

$$\mathcal{E}_\theta = \begin{pmatrix} \frac{1}{2} & . & . \\ . & \frac{1}{2} & . \\ . & . & -1 \end{pmatrix}, \quad \mathcal{E}_\varepsilon = \begin{pmatrix} -\frac{\sqrt{3}}{2} & . & . \\ . & \frac{\sqrt{3}}{2} & . \\ . & . & . \end{pmatrix}.$$

Since $\mathcal{H}$ is not easily diagonalized, one has to use perturbation theory in order to solve the problem. Two cases can be distinguished : weak and strong coupling. In the case of weak coupling $E_{JT} \ll \lambda_f$ and $\hbar\omega$; so, $\mathcal{H}_{JT}$ is applied after $\mathcal{H}_{SO}$. This is the case studied by Ham et al. [4] for Fe^{2+} in MgO, where the coupling with both E_g and T_{2g} modes was taken into account. Such a calculation was recently extended by Uba and Baranowski [7] who made numerical diagonalization using a large number of excited vibrational levels. The case of strong coupling $E_{JT} \gg \lambda_f$ is much easier to handle since the three leading terms of $\mathcal{H}$ can be simultaneously diagonalized [8], and vibronic wavefunctions easily written [9]. Then, one can write an effective Hamiltonian for the spin orbit coupling and Zeeman effect valid within the fundamental vibronic triplet. These Hamiltonians established by Ham [8] up to second order of perturbation to take into account excited vibronic levels are written :

$$\mathcal{H}_{SO}^{eff} = \lambda_f \, cg_L \, K(T_1) \, \mathbf{l}.\mathbf{S} + K_1(\mathbf{l}.\mathbf{S})^2 +$$
$$+ K_2(l_x^2 \, S_x^2 + l_y^2 \, S_y^2 + l_z^2 \, S_z^2) \quad (1)$$

$$\mathcal{H}_Z^{eff} = \mu_B(cg_L \, K(T_1) \, \mathbf{H}.\mathbf{l} + g_S \, \mathbf{H}.\mathbf{S}) +$$
$$+ \mu_B \, g_1[(\mathbf{l}.\mathbf{S}) \, (\mathbf{l}.\mathbf{H}) + (\mathbf{l}.\mathbf{H}) \, (\mathbf{l}.\mathbf{S})]$$
$$+ \mu_B \, g_2(l_x^2 \, S_x \, H_x + l_y^2 \, S_y \, H_y + l_z^2 \, S_z \, H_z) \quad (2)$$

c is a reduction factor due to covalency and g_L the Wigner Eckart constant connecting L to the fictitious orbital momentum $\mathbf{l}$ ($l = 1$) defined in the T_1 triplet : $\mathbf{L} = g_L \, \mathbf{l}$. The other quantities are defined by the following equations :

$$K(T_1) = \exp\left(-\frac{3}{2} S_E\right); \quad S_E = \frac{E_{JT}}{\hbar\omega}; \quad E_{JT} = \frac{V_E^2}{2\mu\omega^2}$$

$$K_1 = -\frac{\lambda_f^2 \, g_L^2 \, c^2}{\hbar\omega} f_a; \quad g_1 = -\frac{\lambda_f \, g_L^2 \, c^2}{\hbar\omega} f_a$$

$$K_2 = -\frac{\lambda_f^2 \, g_L^2 \, c^2}{\hbar\omega}(f_b - f_a); \quad g_2 = -\frac{2\lambda_f \, g_L^2 \, c^2}{\hbar\omega}(f_b - f_a)$$

$$f_a = \exp(-3 \, S_E) \, G\left(\frac{3}{2} S_E\right) \sim \frac{\exp(-\frac{3}{2} S_E)}{\frac{3}{2} S_E}\left(1 + \frac{1}{\frac{3}{2} S_E}\right)$$

$$f_b = \exp(-3 \, S_E) \, G(3 \, S_E) \sim \frac{1}{3 \, S_E}\left(1 + \frac{1}{3 \, S_E}\right)$$

$$\text{for} \quad S_E \gtrsim 3$$

where the function G has been defined by Ham [8].

When the coupling is not very large, the fine structure levels resulting from spin orbit coupling are well separated and it is possible to calculate the

Zeeman effect using perturbation theory : this is the typical situation of the dynamic J.T. effect, which corresponds to many experimental cases. When the coupling is very strong, the fine structure levels are close to each other and Zeeman interaction is no longer a perturbing term. One has then to simultaneously diagonalize both effective Hamiltonians within the vibronic triplet.

3. Particular study of $^3T_1$ triplet.

— For a $^3T_1$ triplet, the spin orbit coupling lifts the degeneracy and leads to 4 multiplets Γ_3, Γ_5, Γ_4, Γ_1 classified in the order of increasing energies when $\lambda_f < 0$. The splitting between Γ_3 and Γ_5 is created by admixture with vibronic excited states associated to the $^3T_1$ triplet itself but also to other excited electronic states. In the case of V^{3+} : CaO, to which the results obtained here will be applied in II, it is sufficient to consider the $^3T_2$ crystal field level coming from the ^3F term of the d^2 configuration. This was done for V^{3+} : MgO [10], but the calculation was very simplified (although the sign of the coupling in the excited state was wrong it did not lead to any consequence for the rest of the study). In the appendix, we give a more rigorous treatment of the problem. Though it particularly applies to the d^2 configuration, it can be adapted to other situations.
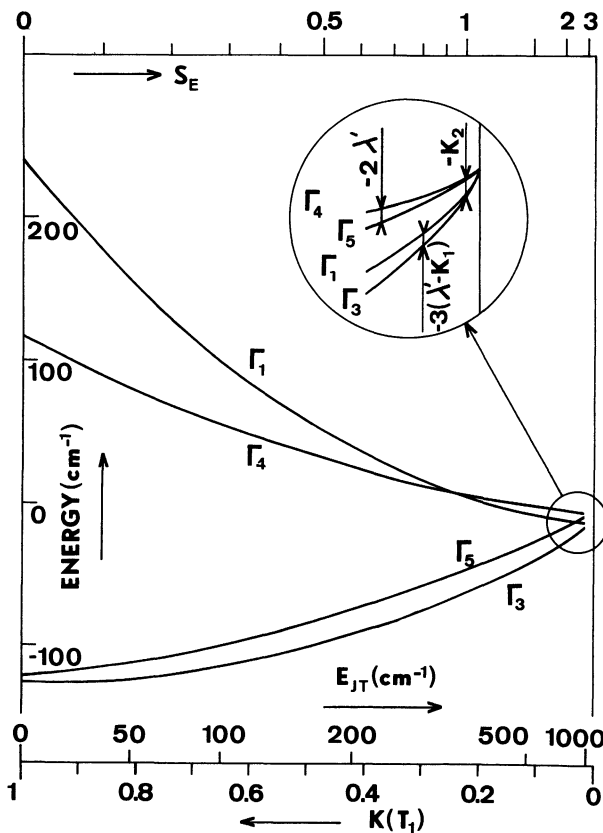
On figure 1, we have represented the evolution of the multiplets position as a function of the strength of the J.T. coupling with numerical values corresponding to V^{3+} : CaO. For strong coupling, we find the well known situation of the static J.T. effect with a quasi triplet $(\Gamma_1 + \Gamma_3)$ separated from a quasi sextuplet $(\Gamma_4 + \Gamma_5)$ by K_2. We see on this figure that for usual values of magnetic field, $\mathcal{H}_Z^{eff}$ can be considered as a perturbation as long as $K(T_1) \gtrsim 0.1$ $(E_{JT} \gtrsim 550 \text{ cm}^{-1})$. In this case, the g factors of the Γ_4 and Γ_5 triplets are easily found to be

$$g(\Gamma_4) = 1 + \tfrac{1}{2} c g_L K(T_1) - g_1$$

$$g(\Gamma_5) = 1 + \tfrac{1}{2} c g_L K(T_1) + g_1 .$$

The last result was used to interpret the APR spectra of V^{3+} : MgO [10] $(K(T_1) = 0.6)$ and Ti^{2+} : CaO [11] $(K(T_1) = 0.2)$. These two equations show that $g(\Gamma_4)$ and $g(\Gamma_5)$ should go to 1 when the coupling becomes very large though one finds usually $g = 2$ for this limit (the orbit is then quenched and only the spin paramagnetism is left). This comes from the fact that they were established by supposing a magnetic field sufficiently small not to mix the wave functions of the S.O. multiplets. However, if experimental g
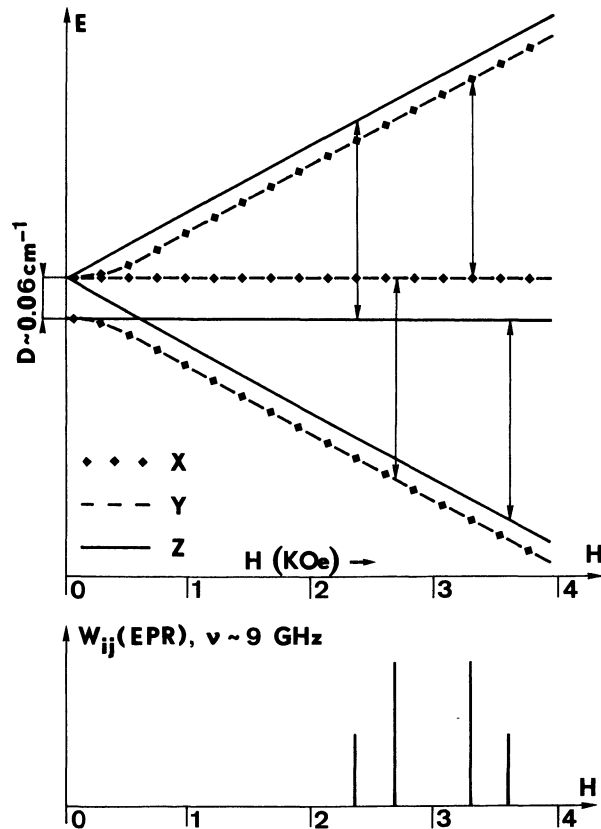

Fig. 1. — Energy of S.O. levels derived from $^3T_1$ orbital ground level versus Ham reduction factor $K(T_1)$, Jahn-Teller energy E_{JT} or Huang and Rhys factor S_E $(\lambda_f = -104 \text{ cm}^{-1}$, $c g_L = -1.2$, $\hbar\omega = 350 \text{ cm}^{-1})$.

Fig. 2. — F centers in CaO : an example of static J.T. effect $(|\lambda| = 15 \text{ cm}^{-1}, K(T_1) \sim 10^{-3}, \hbar\omega = 200 \text{ cm}^{-1}, E_{JT} \sim 900 \text{ cm}^{-1}, S_E \sim 4.2$ [12b]).
● Upper part : Zeeman effect on the sublevels of the $^3T_1$ orbital triplet for $H//Oz$ axis ; the three wells are denoted X, Y and Z.
● Bottom part : transition probability versus magnetic field for an EPR experiment at 9 GHz.

value is found close to 1, that proves that the coupling is relatively large but also that the $(\Gamma_4 - \Gamma_5)$ splitting has not been reduced to a value small as compared to the Zeeman effect. In that case, a complete calculation with simultaneous diagonalisation of the S.O. and Zeeman Hamiltonians is necessary.

We have done this numerical diagonalization for two situations corresponding, one to the static J.T. effect, the other to an *intermediate* case (the dynamical case is simple and well known). In the general case of a $^3T_1$ triplet (without taking into account other electronic levels) we have three parameters : λ_f, V_E, ω. In order to illustrate the different situations, we have selected some sets of values for these parameters but obviously other sets would lead to similar results. For the static case, we have chosen approximately the values found for the F centre in CaO [12]. Energy levels as a function of H are represented on figure 2 when $H \mathbin{/\mkern-6mu/} [001]$. Those belonging to the same *well* are drawn with the same line. For the intermediate case we use the set of values which best explain the APR spectrum of V^{3+} in CaO described in II. Levels are represented on figure 3 for $H \mathbin{/\mkern-6mu/} [001]$ with two different scales for the magnetic field. In addition we calculated the eigenvectors corresponding to these levels and transition probabilities for EPR experiments. Theoretical spectra (neglecting, however, the very important effect of random strains) are sketched under energy levels.

4. **Discussion.** — We first point out from our results that spectra obtained at three different frequencies for a given system are different and interpreted differently. It is clear from figure 3a that an
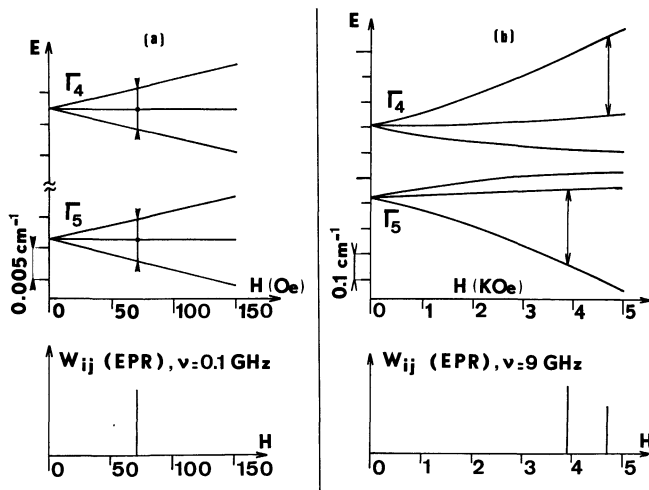
EPR experiment using a very low frequency would be interpreted as a consequence of a usual dynamic J.T. effect. Figure 4 shows that an experiment at a very high frequency would rather be interpreted as a consequence of a static J.T. effect. These results well confirm the idea that J.T. effect is unique but the method of measurement makes it appear as being static or dynamic. Of course, between these two *limits*, and for the same coupling, an intermediate case exists as shown on figure 3b (for this particular situation, only two lines are observed by EPR technique whereas APR experiment gives more significant results since inter-triplet transitions are allowed as shown in II). Concerning this point, we must stress the fact that Uba and Baranowski [7] improperly interpreted their results as an illustration of a transition from a dynamic towards a static J.T. effect. Actually, the evolution of the adiabatic potentials which they present, rather illustrates the transition from a weak to a strong coupling (as mentionned above, this distinction is mainly needed in the perturbation calculation). It is well known that, even when the
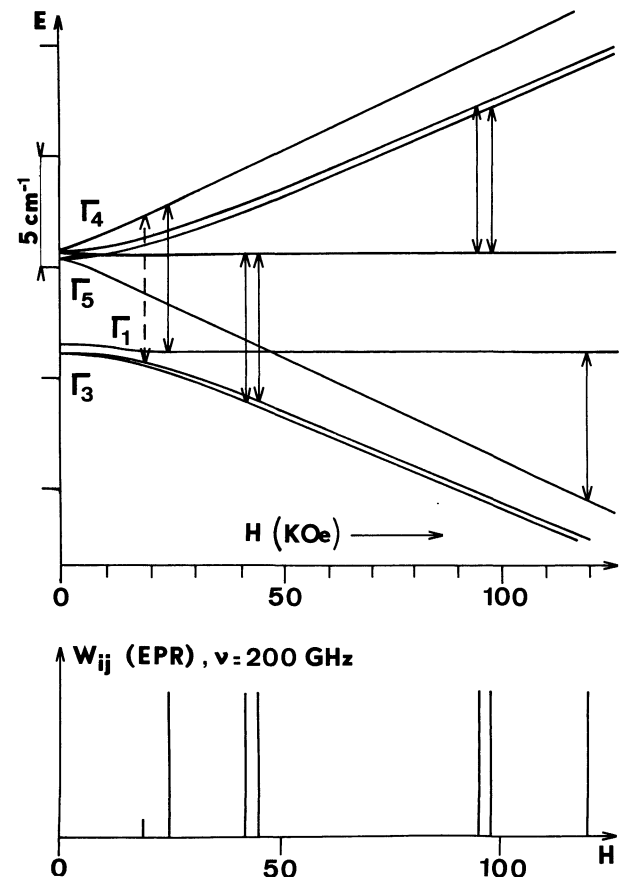

Fig. 4. — V^{3+} in CaO : an example of intermediate Jahn-Teller coupling (see II) ($\lambda_f = - 104 \mathrm{cm}^{-1}$, $K(T_1) \sim 10^{-3}$, $\hbar\omega = 350 \mathrm{cm}^{-1}$, $E_{JT} \sim 1\ 600\ \mathrm{cm}^{-1}$, $S_E \sim 4.6$). Zeeman effect on the S.O. levels derived from the $^3T_1$ orbital ground level and corresponding spectrum in the case of an EPR experiment at 200 GHz interpreted on the basis of *pseudo static* Jahn-Teller effect, the stabilization being induced by the magnetic field. The weak field variation of the energy levels is shown with more details on figure 4 of II.

Fig. 3. — V^{3+} in CaO : an example of intermediate Jahn-Teller coupling (see II) ($\lambda_f = - 104 \mathrm{cm}^{-1}$, $K(T_1) \sim 10^{-3}$, $\hbar\omega = 350 \mathrm{cm}^{-1}$, $E_{JT} \sim 1\ 600\ \mathrm{cm}^{-1}$, $S_E \sim 4.6$). Zeeman effect on the S.O. triplets Γ_4 and Γ_5 and corresponding spectra for EPR experiments at two frequencies : a) : $\nu = 0.1$ GHz leading to a spectrum interpreted on the basis of dynamic Jahn-Teller effect. b) : $\nu = 9$ GHz leading to a spectrum interpreted on the basis of intermediate Jahn-Teller effect.

adiabatic potential energy surfaces display three well characterized wells, the J.T. effect may still remain dynamic. Therefore it is not their existence which is a proof of a static J.T. effect but rather, as we have shown in our case, the admixture of states by the magnetic field. Needless to say, static J.T. effect cannot exist if the three wells are not well separated.

One has to keep in mind that the previous analysis applies to the theoretical case where the site of the ion is purely cubic. It is well known that the *stabilization* by a magnetic field, proposed long ago in the E doublet case [13], has always been hidden by the stabilization by random strains [14] which hinder the tunneling by destroying the equivalence between the three wells. In the case of V^{3+} : CaO studied in II, we qualitatively estimate from the experimental results that the effect of strains would be sufficiently weak not to hide the stabilization of the system by a magnetic field of 50-100 kG. Thus, a difficult experiment with such a magnetic field and a microwave frequency in the range of 200-250 GHz would certainly be the first illustration of this magnetic stabilization of the J.T. effect.

Another surprising and interesting result is emphasized from the calculations. When the coupling is strong but not very strong, the EPR spectrum shows more lines than expected for the static J.T. case. This can be seen by comparison between figures 4 and 2. To study in more detail this situation, we have chosen another set of values for the parameters λ_f, $E_{JT}, \hbar\omega$. This set ($\lambda_f \sim -30$ cm^{-1}, $E_{JT} \sim 1\,600$ cm^{-1}, $\hbar\omega \sim 350$ cm^{-1}) permits to attain this situation at lower magnetic fields, making negligible first order and part of second order Zeeman orbital effect. It is then possible, for a magnetic field of the order of 20 kG, to do a perturbation calculation where the electronic Zeeman effect is the dominant term, the terms in $\lambda' = \lambda_f\,cg_L\,K(T_1)$, K_2 and g_2 are perturbing terms, and terms in K_1, $G_1 = \mu_B\,cg_L\,K(T_1)$ and g_1 are ignored. The energy levels are shown on figure 5 for two magnetic field orientations; the points show the position of the lines for various orientations, the radius of the full circles being representative of the transition probability.

For H along [001] as well as along [101], the spectrum looks qualitatively as if it was due to a $S = 1$ system in orthorhombic sites with the $\langle 100 \rangle$ directions as principal axis. We determine the D and E values of the well known orthorhombic Hamiltonian

$$\mathcal{H}_{ORT} = DS_z^2 + E(S_x^2 - S_y^2)$$

which fit best the positions of the lines for H along [001]. These values are *nearly* $D \sim K_2$ and $E \sim \lambda'$. We then calculate the theoretical angular variation of the lines within the hypothesis of an orthorhombic symmetry in order to compare with the positions calculated above within a moderately strong J.T. coupling. The lines on figure 5 represent this angular variation. This comparison is of interest
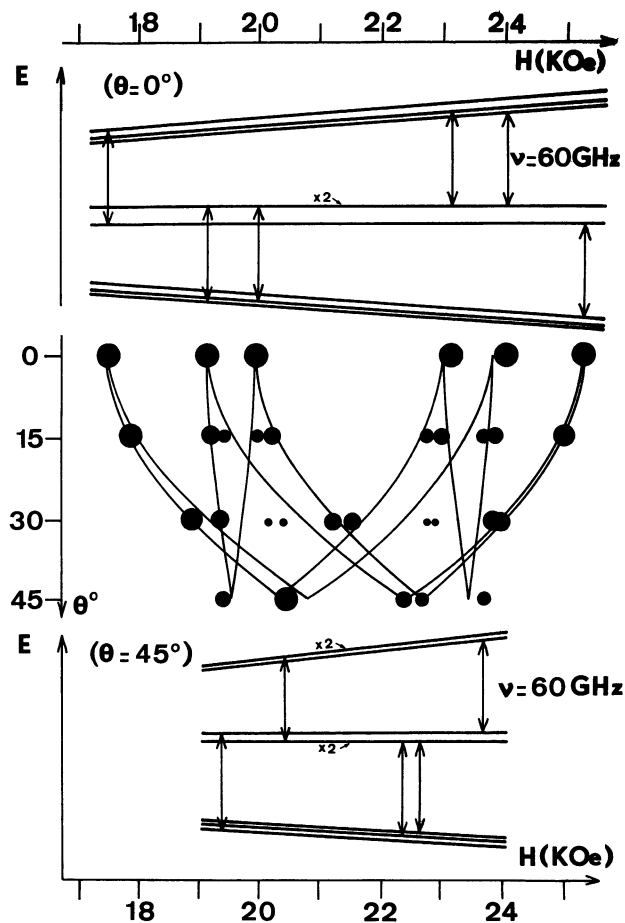
Fig. 5. — An example of pseudo orthorhombic symmetry due to intermediate Jahn-Teller coupling ($\lambda_f = -30$ cm^{-1}, $K(T_1) \sim 10^{-3}$, $\hbar\omega = 350$ cm^{-1}, $E_{JT} \sim 1\,600$ cm^{-1}, $S_E \sim 4,6$). Upper and lower parts show the energy levels of the system for respectively H along [001] ($\theta = 0^\circ$) and H along [101] ($\theta = 45^\circ$). Central part : the points show the position of the lines calculated within the intermediate coupling scheme (the area of the points is proportional to the line intensity) ; the lines show the angular variation for a true orthorhombic symmetry whose D and E parameters are fitted from the $\theta = 0^\circ$ spectrum.

because when obtaining an EPR or APR spectra, looking as orthorhombic, one can be tempted to explain it by the existence of a defect (vacancy, charge compensation) near the resonant ion. Indeed, if one has only the spectra for H along [001] and [101], the conclusion for an orthorhombic symmetry is quite natural. On the contrary, a good analysis of the full angular variation permits to distinguish the two situations.

Orthorhombic spectra have already been reported [15] in cubic crystals but the principal axis were along [001], [101] and [10$\bar{1}$] instead of the cubic $\langle 100 \rangle$ axis found here. This could be related to calculations performed by Bacci *et al.* [16] : they showed that quadratic J.T. coupling to both E_g and T_{2g} modes can lead to orthorhombic distortions of the lattice. Recently, an orthorhombic spectrum having the cubic $\langle 100 \rangle$ axis as principal axis was reported for the excited state $^3T_1$ of Ga^+ in KBr

and KCl [17]. However, in this case the coupling is very large, the Ham reduction factor $K(T_1)$ is smaller than 10^{-10} and thus the λ' value responsible of a rhombic symmetry is extremely small. A non linear coupling between two different sets of E_g modes can possibly explain the existence of such a symmetry [18]. Thus, the situation studied here has not yet been experimentaly observed.

5. **Conclusion.** — In this work, we have analysed the situation which arises when the ion lattice coupling strength between a system with a cubic orbital triplet and the E_g vibrational modes is *intermediate* between the two well known extreme situations of weak and strong coupling. To this situation correspond EPR (or APR) spectra which differ from the usual static or dynamic J.T. spectra. When the coupling is intermediately weak, transitions between S.O. vibronic levels appear in addition to the intra-triplet transitions

of the usual dynamic situation. It is proved in the following paper, that V^{3+} : CaO is the first illustration of this situation. We have shown here that this situation, which remains dynamic in nature, could be stabilized by a magnetic field. When the coupling is intermediate, the spectrum looks as orthorhombic. We show that there are some differences with the true orthorhombic case resulting from a rhombic crystal field. A careful examination of the spectra together with a detailed analysis of their angular variation is however necessary to distinguish between them. Finally, we show that in this intermediate situation the distinction between static and dynamic is ambiguous, depending from the time scale of the experiment and not, as was claimed recently, from the comparative values of the vibrational frequency and the coupling.

Appendix

The ground term ^3F of the d^2 configuration is split by a cubic crystal field into a ground $^3T_1$ triplet, an excited $^3T_2$ triplet and an excited $^3A_2$ singlet. This singlet can be discarded, the matrix elements of S.O. coupling being zero between it and the ground $^3T_1$ triplet. A correct calculation of the 2nd order terms of the S.O. coupling inside the ground $^3T_1$ triplet must take into account the vibronic levels associated with the $^3T_2$ excited triplet. Even if the ground triplet is generally more strongly coupled with the E_g than with the T_{2g} vibrational modes, it is not necessarily the case for the $^3T_2$ excited triplet. Table I shows the ratios of the coupling coefficients calculated from a point charge model in various situations.

In order to simplify the analysis, we first suppose that the coupling with E_g modes is dominant for both triplets. The vibronic wavefunctions of these triplets have then a vibrational part which is that of a displaced two dimensional harmonic oscillator, the displacements being different for the two triplets. On figure 6, we have shown the intersection by the

Table I. — *Ratios of different coupling coefficients $V_i(j)$ of the electronic multiplet i with the vibrational mode j, calculated from a point charge model for V^{3+} : MgO, V^{3+} : CaO and Ti^{2+} : CaO systems.*

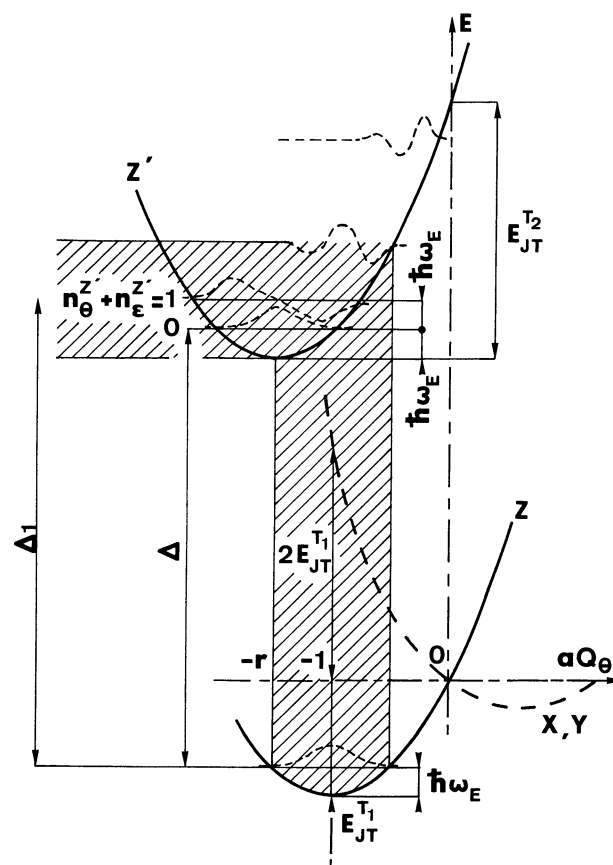| Free ion	Lattice	$\dfrac{V_E(T_1)}{V_{T_2}(T_1)}$	$\dfrac{V_E(T_2)}{V_{T_2}(T_2)}$	$\dfrac{V_E(T_2)}{V_E(T_1)}$
V^{3+}	MgO	− 5,85	1,34	1,34
V^{3+}	CaO	− 14,7	0,99	0,91
Ti^{2+}	CaO	− 3,21	1,72	1,94

Fig. 6. — Intersection by the $Q_\varepsilon = 0$ plane of the energy surfaces (plotted as a function of the reduced quantity aQ_θ) associated to $^3T_2$ and $^3T_1$ electronic states derived from ^3F term when only the coupling with a pair of E_g vibrational modes Q_θ, Q_ε is considered. The constants r and a are given by

$$r = \frac{V_E(T_2)}{V_E(T_1)} \quad \text{and} \quad a = \frac{\mu\omega_E^2}{V_E(T_1)}$$

(see Table I).

$Q_\varepsilon = 0$ plane of the corresponding energy surfaces. The matrix elements involved have the following general form

$$A_{ij} = -\lambda_f^2 \sum_\alpha \frac{\langle v^i T_1 | \mathbf{L.S} | v^\alpha T_2 \rangle \langle v^\alpha T_2 | \mathbf{L.S} | v^j T_1 \rangle}{\Delta + n_E \hbar\omega_E}$$

where $| v^i T_1 \rangle$ is the ground vibronic state associated with the well i ($i = X, Y, Z$), $| v^\alpha T_2 \rangle$ is a vibronic state associated with the T_2 triplet, Δ is the zero-phonon splitting between the triplets and $n_E \hbar\omega_E$ the vibrational energy of the $| v^\alpha T_2 \rangle$ state. If the couplings $V_E(T_1)$ and $V_E(T_2)$ are sufficiently strong, the three minima of each potential surface are well separated and the vibrational wavefunctions have the shape indicated in figure 6. Since, for the excited states, the wavefunction is greater near the potential curve, we can say only those contained in the hatched region of the figure will give a noticeable contribution in the summation $\sum_\alpha$. We can then approximate the denominator $\Delta + n_E \hbar\omega_E$ by a constant value Δ_1 (in ref. [10] the crudest approximation $\Delta_1 \sim \Delta$ was done) and use the closure relation for the vibrational part of the operator $| v^\alpha T_2 \rangle \langle v^\alpha T_2 |$. It thus remains for $\sum_\alpha$ only the summation on the electronic part of $| v^\alpha T_2 \rangle \langle v^\alpha T_2 |$.

The case where the couplings with both E_g and T_{2g} modes have to be taken into account is less easy to handle, but the final result is the same : by the above approximation consisting to replace the denominator (which would be now $n_E \hbar\omega_E + n_{T_2} \hbar\omega_{T_2}$) by a constant value, say Δ', one can use closure relation for the vibrational part of the T_2 wavefunctions. The matrix element (A_{ij}) can then be written as

$$A_{ij} = -\frac{\lambda_f^2}{\Delta'} \langle \psi^i, m^i | \mathcal{A} | \psi^j, m^j \rangle \langle i00 | j00 \rangle$$

where $| \psi^i \rangle$ and $| m^i \rangle$ are the orbital and spin parts of the wavefunctions, and where $| i00 \rangle$ stands for the ground vibrational wavefunction of the well i. The term $\langle i00 | j00 \rangle$ is the usual $K(T_1)$ Ham reduction factor. The operator $\mathcal{A}$ is defined as

$$\mathcal{A} = \sum_u L_u S_u \left(\sum_\alpha | \psi^\alpha \rangle \langle \psi^\alpha | \right) \times$$
$$\times \left(\sum_\alpha | m^\alpha \rangle \langle m^\alpha | \right) \sum_v L_v S_v .$$

It looks like the usual 2nd order spin orbit operator and, from symmetry considerations, can be transformed in an effective Hamiltonian inside the ground $^3T_1$ triplet [8]

$$\mathcal{H}_{SO}^{(2)} = -\frac{\lambda_f^2 c^2}{\Delta'} [W_1(\mathbf{l.S})^2 +$$
$$+ W_2(l_x^2 S_x^2 + l_y^2 S_y^2 + l_z^2 S_z^2)] K(T_1)$$

where, for completness, we have included the covalency reduction factor c. The Wigner Eckart constants W_1 and W_2 can easily be calculated. The energy of the levels issued from $^3T_1$ by spin-orbit coupling are then, including first order, second order due to vibronic states of T_1 and second order due to excited vibronic states of T_2 respectively :

$$E(\Gamma_1) = -2 \lambda_f cg_L K(T_1) +$$
$$+ 4 K_1 + 2 K_2 - \frac{15 \lambda_f^2 c^2}{2 \Delta'} [1 - K(T_1)]$$

$$E(\Gamma_4) = -\lambda_f cg_L K(T_1) + K_1 + K_2 - \frac{15 \lambda_f^2 c^2}{4 \Delta'}$$

$$E(\Gamma_5) = \lambda_f cg_L K(T_1) + K_1 + K_2 - \frac{15 \lambda_f^2 c^2}{4 \Delta'}$$

$$E(\Gamma_3) = \lambda_f cg_L K(T_1) +$$
$$+ K_1 + 2 K_2 - \frac{15 \lambda_f^2 c^2}{4 \Delta'} [2 + K(T_1)] .$$

References

[1] BATES, C. A., Phys. Rep. 35C (1978) 187.
[2] HAM, F. S., in Electron Paramagnetic Resonance, edited by S. Geschwind (Plenum Press, New York) 1972.
[3] See the references (232) to (238) of the review of BATES, C. A. [1], or the more recent work : BOATNER, L. A., REYNOLDS, R. W., CHEN, Y. and ABRAHAM, M. M., Phys. Rev. B 16 (1977) 86.
[4] HAM, F. S., SCHWARTZ, W. M. and O'BRIEN, M. C. M., Phys. Rev. 185 (1969) 548.
[5] PARROT, R., NAUD, C. and GENDRON, F., Phys. Rev. B 13 (1976) 3748.
[6] NAHMANI, A. and BUISSON, R., J. Physique 41 (1980) 67.
[7] UBA, S. M. and BARANOWSKY, J. M., Phys. Rev. B 17 (1978) 69.
[8] HAM, F. S., Phys. Rev. A 138 (1965) 1727.
[9] MOFFIT, W. and THORSON, W., Phys. Rev. 108 (1957) 1251.
[10] BUISSON, R. and NAHMANI, A., Phys. Rev. B 6 (1972) 2648.
[11] NAHMANI, A. and BUISSON, R., Solid State Commun. 18 (1976) 297.

[12] a) EDEL, P., HENNIES, C., MERLE D'AUBIGNÉ, Y., ROMESTAIN, R. and TWAROWSKY, Y., Phys. Rev. Lett. 28 (1972) 1268 ;
b) LE SI DANG, MERLE D'AUBIGNÉ, Y. and RASOLOARISON, Y., J. Physique 39 (1978) 760.
[13] O'BRIEN, M. C. M., Proc. R. Soc. A 281 (1964) 323.
[14] HAM, F. S., Phys. Rev. B 4 (1971) 3854.
[15] WOODBURY, W. H. and LUDWIG, G. W., Phys. Rev. 126 (1962) 466.
[16] BACCI, M., RANFAGNI, A., FONTANA, M. P. and VILIANI, G., Phys. Rev. B 11 (1975) 3052.
BACCI, M., RANFAGNI, A., CEITA, M. and VILIANI, G., Phys. Rev. B 12 (1975) 5907.
[17] ROMESTAIN, R., LE SI DANG, MERLE D'AUBIGNÉ, Y. and FUKUDA, A., Semiconductors and Insulators 3 (1978) 175.
LE SI DANG, Thèse de Doctorat ès Sciences, Grenoble (1978).
[18] ROMESTAIN, R., to be published.