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Low frequency transition between vibronic levels of V_2^{9+} in crystalline V_2O_5 from electron spin-lattice relaxation measurements

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Résumé. — Nous avons mis en évidence, dans V_2O_5 cristallin non dopé, une énergie caractéristique, Δ , de 0,0013 eV, en mesurant entre 1,3 et 50 K le temps de relaxation du défaut paramagnétique détecté à $g = 2$. Pour interpréter ce résultat, nous avons retenu, parmi les différents modèles proposés jusqu'ici pour décrire ce défaut (qui, tous, font intervenir un ion moléculaire V_2^{9+}), celui proposé par Perlstein ; nous prenons ainsi en compte les arguments récents de Clauws *et al.* L'énergie Δ ne peut correspondre à la séparation entre les niveaux liant et antiliant de V_2^{9+} , car un calcul montre que cette dernière vaut 0,16 eV. Dans notre interprétation, Δ est la séparation énergétique entre le niveau vibronique fondamental et le premier niveau vibronique excité de V_2^{9+} .

Abstract. — We have established the existence of a characteristic energy (0.0013 eV) in undoped crystalline V_2O_5 , by measuring, between 1.3 K and 50 K, the relaxation time of the paramagnetic defect detected at $g = 2$. In order to interpret this result, we have examined the different models which have been proposed in the past for this defect, and which all imply the existence of a V_2^{9+} molecular ion ; taking the recent arguments of Clauws *et al.* into account, we have finally adopted the model proposed by Perlstein. The energy Δ cannot correspond to the splitting between the bonding and antibonding levels of V_2^{9+} , since a calculation indicates that the separation between these levels is 0.16 eV. In our interpretation, Δ is the energy separation between the ground vibronic level and the first excited vibronic level of V_2^{9+} .

1. Introduction.

When an assembly of paramagnetic defects diluted in a diamagnetic solid has been perturbed by a strong r-f field, it returns towards its thermal equilibrium within a time T_1 , the spin-lattice relaxation (S.L.R.) time. Measurement of T_1 can provide information concerning the ground and first excited levels of the defect. We have used this technique to study the V_2^{9+} centre in crystalline V_2O_5 . The experimental results are presented in section 2. They are discussed in section 3, and interpreted with an Orbach process between two levels with an effective spin $S = 1/2$ and the same g value, separated by an energy Δ , with $\Delta/k = 15.5$ K. In section 4 we discuss the nature of

these levels, and conclude that they should not be electronic but rather vibronic.

2. Experimental results.

The lattice of crystalline V_2O_5 is orthorhombic ; the c axis is perpendicular to the cleavage planes.

At low temperature, and when the magnetic field was parallel to c , single crystals prepared from a powder of pure V_2O_5 (Johnson Matthey, specpur) showed an E.S.R. spectrum consisting of 15 hyperfine lines, identical with that previously obtained by Gillis and Boesman (Fig. 2 in ref. [1]). This spectrum is usually interpreted as originating from the interaction of one electron with two equivalent diamagnetic V^{5+} ions separated by an oxygen vacancy ; the corresponding effective spin $S_{\text{eff}} = 1/2$ is coupled with the nuclear moment $I = 7/2$ of both nuclei. The mecha-

(*) E.R.A. 375.

(**) L.A. 302.

nism of charge compensation is still controversial (cf. our discussion in section 4). One must emphasize that, in our E.S.R. experiments, the electron may be considered bound to a given pair of vanadium ions, as the conductivity of crystalline V_2O_5 is rather low in this temperature range ($\sigma = 5 \times 10^{-8} \Omega^{-1} \cdot \text{cm}^{-1}$ at 100 K). In the following, we will call this paramagnetic centre V_2^{9+} .

In our S.L.R. measurements, because of the small size of the single crystals, we preferred to use pure crystalline powder, in order to get a better signal-to-noise ratio. The S.L.R. time of V_2^{9+} was measured by the pulse saturation and recovery method up to 35 K, the experimental conditions being that of [2]. It was also measured by the continuous saturation method between 30 and 50 K.

The recovery signal was not exponential but corresponded to a sum of two exponential terms whose time constant kept a constant ratio of some units when the temperature was varied. We were unable to explain this non-exponential behaviour. The variation of the longer time constant *versus* T has been plotted in figure 1. The relaxation rate T_1^{-1} between 1.3 K and 2 K varies linearly with temperature, showing the existence of a direct process. When the temperature is raised from 2 K, one first observes a steep increase of the relaxation rate, then a tendency

Fig. 1. — Thermal variation of T_1^{-1} for V_2^{9+} in crystalline V_2O_5 (● pulse saturation, ○ continuous saturation). The solid curve corresponds to the expression $T_1^{-1} = 12.5 T + 300 / \sinh \frac{15.5}{T}$, the dashed curve to the expression $T_1^{-1} = 12.5 T + 3550 / (e^{14/T} - 1)$.

to a linear variation. From our study we fit the experimental results with the following analytical expressions :

$$T_1^{-1} = 12.5 T + 300 / \sinh \frac{15.5}{T} \quad (T_1 \text{ s, } T \text{ K}) \quad (1a)$$

$$T_1^{-1} = 12.5 T + 3550 / (e^{14/T} - 1) \quad (T_1 \text{ s, } T \text{ K}). \quad (1b)$$

Within experimental accuracy ($\pm 15\%$), the product of the integrated intensity of the E.S.R. absorption signal with the temperature T was found to be the same at 4 and 50 K. This was obtained using a dual sample cavity, and the VARIAN strong pitch kept at room temperature as a reference signal.

3. Interpretation of the T_1 measurements.

The description of the lattice is simpler in crystalline V_2O_5 than in the amorphous material; in contrast, the electron properties are more complex in the crystalline oxide : in amorphous V_2O_5 , the paramagnetic centre is V^{4+} , while in the crystalline material, it is the more complex V_2^{9+} centre. Little information is available on the energy levels of V_2^{9+} in the crystal. We used S.L.R. experiments to get information on these energy levels. Before discussing the results of these experiments, we briefly recall the laws usually found for the thermal variation of T_1 , in crystalline materials. At low temperatures, one has a one phonon process leading to $T^{-1} \propto T$ so long as the Zeeman energy $\ll kT$. As the temperature increases, the Raman process becomes more efficient. One then gets different field and temperature dependences according to whether the transition is of Kramers or non-Kramers type. However when $T \gtrsim T_D$ (Debye temperature) in all cases $T_1^{-1} \propto T^2$. If the paramagnetic defect has an electronic level separated from the ground multiplicity by an energy $\Delta < kT_D$, the Orbach process may be effective : in the simplest case of a ground doublet, even if a direct transition between the two ground sublevels is forbidden, a two-step transition is possible (Orbach process) leading to $T_1^{-1} \propto [\exp(\Delta/kT) - 1]^{-1}$. At high temperature ($kT \gtrsim 3\Delta$), $T_1^{-1} \propto T$. One must note the difference in the asymptotic behaviour of T_1^{-1} between Raman and Orbach processes : in the Raman process, the temperature dependence appears only in the product of the two phonon occupation numbers; this product results from a second order perturbation of a linear strain term, or from a first order perturbation of a quadratic strain term. The Orbach process, on the contrary, is really a sequence of two first order processes [3, 4] both with one phonon having an energy $\hbar\omega \sim \Delta$. If one prefers to consider this last process as resulting from second order perturbation, as is usually done [5], one must then keep in mind that the temperature dependence appears not only in the product of the two phonon occupation numbers, but also in the lifetime $\hbar/\Gamma$ of the intermediate level.

We now turn to our experimental results. We first eliminate the possibility of a Raman process above 2 K : at low temperatures, the experimental law is far from a T^7 or a T^9 dependence, and at high temperatures one tends to a linear rather than to quadratic variation.

We then examine the possibility of an Orbach process between the ground level ($S_{\text{eff}} = 1/2$) and some excited level with $S_{\text{eff}} = 1/2$ (we postulate its existence and will discuss its origin in section 4). However, as the Orbach process is usually considered between a ground doublet ($S_{\text{eff}} = 1/2$) and a single excited level ($S_{\text{eff}} = 0$) [5], we will discuss thoroughly the rate equations for a pair of doublets. Let us call (Fig. 2) $W_+ = An$ and $W_- = A(n+1)$ the probabilities for the S.L.R. transitions without change of the spin state, $W'_+ = Bn$ and $W'_- = B(n+1)$ those with change of the spin state, where $\bar{n} = (e^x - 1)^{-1}$ and $x = \Delta/kT$. We call $p = p_1 - p_2$ and $p' = p_3 - p_4$ the population differences for the ground and excited levels respectively. The rate equations for p and p' are :

$$\begin{aligned}\dot{p} &= -(W_+ + W'_+)p + (W_- - W'_-)p' \\ \dot{p}' &= +(W_+ - W'_+)p - (W_- + W'_-)p'\end{aligned}$$

We first assume that $A = B$. Then the two equations for p and p' are no longer coupled.

If the g factors for the ground and excited levels are different, the experimental signal is proportional to p ; then

$$T_1^{-1} = aT + \frac{2A}{e^{\Delta/kT} - 1} \quad (2)$$

where Δ is the energy separation between the ground and excited levels. Such an analytical expression can fit the experimental results for T_1 . But if the assump-

Fig. 2. — Diagram showing the various quantities implied in the electron spin-lattice relaxation in a system with two effective-spin doublets. The $1 \leftrightarrow 2$ and $3 \leftrightarrow 4$ transitions probabilities have been neglected. The $2 \leftrightarrow 4$ and $1 \leftrightarrow 4$ transition probabilities, not shown in the figure, are equal to the $1 \leftrightarrow 3$ and $2 \leftrightarrow 3$ transition probabilities respectively.

tion of different g factors were verified, the product of the integrated absorption with the temperature would differ by a factor of two between a temperature $T \ll \Delta/k$ (15 K) and a temperature $T \gg \Delta/k$, while we did not observe such a variation between 4 and 50 K.

Let us thus suppose that the g factors are the same, all the other assumptions being kept : the experimental signal will then be proportional to $p + p'$; the recovery after equalization of the populations at $t = 0$ will be given by

$$p + p' = p_0[(1 - e^{-t/\tau}) + e^{-x}(1 - e^{-t/\tau'})]$$

$$\text{with} \quad \tau^{-1} = \frac{2A}{e^x - 1} = (\tau')^{-1} e^{-x}.$$

At high temperature ($x \ll 1$), $\tau \simeq \tau'$; at low temperatures ($x \gg 1$) $\tau \gg \tau'$ but the amplitude of the shorter time constant τ' , which corresponds to the recovery of the excited level, will be much smaller than that of the ground doublet ($e^{-x} \ll 1$); when $x = 1$, $\tau \sim 3\tau'$ and the amplitudes of both exponential contributions will be in a ratio of 3. We thus conclude that one will experimentally get the longer time constant. The thermal variation of the S.L.R. will thus be given by expression (2). The integrated absorption will obey the Curie law. Thus both experimental results ($T_1(T)$ and integrated absorption) will approximately agree with the theoretical predictions.

Up to now, we have assumed $A = B$; let us now suppose that $A \gg B$ (i.e. that the transitions without spin flip are more likely than those with a spin flip), and that the g factor is the same for both levels (the need for such an assumption is the same as before); one then finds $\tau^{-1} \sim A \coth \frac{x}{2}$, $(\tau')^{-1} \sim \frac{2B}{\sinh x}$ and $\tau \ll \tau'$; the experimental signal is proportional to

$$p + p' \simeq p_0(1 + e^{-x})[1 - e^{-t/\tau'}].$$

Thus

$$T_1^{-1} = aT + \frac{2B}{\sinh x} \quad (3)$$

and the integrated absorption will follow the Curie law. In fact a model developed by Murphy [6] is just this situation in the $B/A \rightarrow 0$ limit. Murphy considered two vibrational levels separated by Δ , each with $S_{\text{eff}} = 1/2$, and having the same g factors. He assumed that, while p and p' recover, $p_1/p_3 = p_2/p_4 = e^{-x}$ at any time. The E.S.R. signal is proportional to $p + p' = p[1 + e^{-x}]$ and is exponential since $\dot{p} = -\frac{2Bp}{\sinh x}$. Thus T_1^{-1} follows (3).

From this discussion, we conclude that our experimental results are satisfactorily explained under the following assumptions :

— the ground and first excited levels of V_2^{9+} in crystalline V_2O_5 both have an effective spin $S_{\text{eff}} = 1/2$, and the same g ;

- their energy separation is such that $\Delta/k = 15.5$ K ;
- the transition probabilities without spin flip are at least equal to those with spin flip ($A \geq B$). This agrees with the intuitive feeling that transitions without spin flip are more likely than transitions with spin flip.

4. Discussion upon the origin of the lowest V_2^{9+} energy levels.

We now turn to the discussion of the lowest energy levels of V_2^{9+} in V_2O_5 . At the present time, the exact nature of this centre is not known. We hope that the present discussion will stimulate further investigations. We first recall the various models proposed up to now; we then try to make a determination of the energy separation for the lowest levels of the molecular ion V_2^{9+} , neglecting the motion of the nuclei; we finally consider the change from electronic to vibronic spectra, caused by this motion.

In 1966, Gillis and Boesman [1] proposed two models for the paramagnetic centre they had observed in E.S.R. ($g = 2$, $S_{\text{eff}} = 1/2$, 15 hyperfine lines). Both consist of an unpaired electron delocalized over two equivalent vanadium ions (V^{5+}) separated by an oxygen vacancy; in the first model (Fig. 3a), the two vanadium ions are along c (their distance being 4.37 Å); in the second one (Fig. 3b), the two

Fig. 3. — Two paramagnetic defects in crystalline V_2O_5 , as proposed by Gillis and Boesman; the internuclear axis of the V_2^{9+} molecular ion is parallel to c (3a) or to b (3b) (○ vanadium ion; ● vanadium ion belonging to V_2^{9+} ; ○ oxygen ion; ○ oxygen vacancy).

vanadium ions are along b ($R = 3.5$ Å). They considered that, in both cases, electrical neutrality is realized through the formation of V^{3+} ions.

Later on, Perlstein [7] claimed that the creation of V^{3+} ions was unlikely and suggested a model which was hoped consistent with electrical neutrality, E.S.R. and electrical conductivity experiments. V_2O_5 has a lamellar structure because the bonds between adjacent ab planes are weak; Perlstein suggested that an ab plane could slip 0.2 lattice spacing along a and 0.5 lattice spacing along b , with the formation of interstitial oxygen ions; one thus gets two vanadium nuclei along c ($R = 3.42$ Å) ⁽¹⁾ (Fig. 4).

More recently Vanhaelst and Clauws [8] found a new E.S.R. spectrum in V_2O_5 , called E_1 ($g_x = 1.33$, $g_y = 2.51$, $g_z = 1.01$; $S_{\text{eff}} = 1$), besides the E.S.R. spectrum observed at $g = 2$ and called E_2 . They tried to correlate the E.S.R. spectra, and previous optical absorption spectra of V_2O_5 which had been interpreted as the sum of two distinct spectra called F_1 and F_2 [9]. In order to establish this correlation, they recorded the E.S.R. and optical spectra of V_2O_5 single crystals grown under various atmospheres (O_2 , N_2 , air). They concluded that E_1 and F_1 originate from the same defect, and that E_2 and F_2 could come from the same defect whose origin is not unambiguously defined [10, 11], but could be the defect suggested by Perlstein.

Fig. 4. — Paramagnetic defect in crystalline V_2O_5 , as proposed by Perlstein; an ab plane has slipped 0.2 lattice spacing along a , and 0.5 lattice spacing along b , with the formation of interstitial oxygen ions (○ vanadium ion; ● vanadium ion belonging to V_2^{9+} ; ○ oxygen ion; (i) interstitial oxygen ion).

⁽¹⁾ After Wyckoff [22], this value should be presently the most accurate. For simplicity, our calculations in appendix use the same value $R = 3.5$ Å for that centre and the second centre considered by Gillis and Boesman.

We will retain the suggestion made by Clauws *et al.*, and consider that the V_2^{9+} centre consists of an electron delocalized over two nuclei, each along *c* (Perlstein's model, Fig. 4). In this defect, the crystal field acting on a vanadium ion is created by four ligands about 1.8 Å from this ion (Fig. 5), while the electron couples two V^{5+} ions 3.4 Å apart from each other. It is therefore sound to assume that the coupling between the two vanadium ions is a perturbation of this crystal field. The E.S.R. spectrum of the V_2^{9+} ion will then look like that of a V^{4+} ion; the main difference will appear in the hyperfine structure (15 instead of 8 hyperfine lines, and a reduction of the *A* components by a factor of two if the electron has the same probability to be on either site). The values of the *g* and *A* tensor components in crystalline and amorphous V_2O_5 are reported in table I [12]; in amorphous V_2O_5 , the paramagnetic centre consists of a single V^{4+} ion, and comparison between these values in crystalline and amorphous oxide support our assumption.

Fig. 5. — The molecular ion V_2^{9+} and its oxygen ligands, according to the model proposed by Perlstein. Distances are given in angström.

Table I

	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}(G)$	$A_{\perp}(G)$
Crystalline oxide	1.915 ± 0.002	1.987 ± 0.002	88.3 ± 0.5	29 ± 1
Amorphous oxide	1.913 ± 0.001	1.981 ± 0.002	176 ± 0.5	66 ± 1

In O_h symmetry, the $3d^1$ configuration (V^{4+} ion) splits into a ground triplet (t_{2g}) and a doublet (e_g). In C_{4v} symmetry, the triplet is split into a singlet (b_2 ; d_{xy}) and a doublet (e ; d_{xz} and d_{yz}) (Fig. 6). The E.S.R. spectrum of V^{4+} in the *amorphous* oxide is usually interpreted (cf. [2] and references therein) as arising from an electron in the ground state b_2 . This is consistent with the axial symmetry of the E.S.R. spectrum, and the fact that a spin in a ground orbital doublet would be more strongly coupled to the lattice, and could not be detected by E.S.R. at room-temperature (broadening of the E.S.R. line because of a very short T_1). The same arguments are still valid in the crystalline oxide.

We will now try to get an estimate of the energy separation between the two lowest levels of V_2^{9+} in the crystalline oxide. Our molecular ion V_2^{9+} has a single 3d electron and we will treat this problem by analogy with H^{2+} [13]. The two vanadium ions and their surroundings are kept in their equilibrium positions (adiabatic approximation). The molecular wave functions describing approximately the two lowest orbital levels of V_2^{9+} are

$$\psi_{\pm} = \frac{d_{xy}(1) \pm d_{xy}(2)}{\sqrt{2(1 \pm S)}}$$

In this expression, $d_{xy}(i)$, ($i = 1, 2$) is the d_{xy} atomic orbital of vanadium ion *i*, and *S* is the overlap integral.

Fig. 6. — Splitting of the 3d level by a crystal field from negatives charges; the main part of this field has O_h symmetry, the remaining part has C_{4v} symmetry and is supposed to lead to a b_2 ground level.

The calculation of the corresponding energies is presented in the appendix. We find that the separation between the bonding and antibonding levels is 0.16 eV. It should be emphasized that this value is very close to that of 0.15 eV postulated by Perlstein, from electrical conductivity measurements, for the breaking of the bond between the two vanadium ions of V_2^{9+} . On the other hand, the spin-lattice relaxation cannot proceed through the antibonding excited level, since the characteristic energy of the relaxation process found experimentally is far smaller (1.3×10^{-3} V).

We thus have to look for a mechanism leading to a small splitting of the ground level.

A possibility for such a splitting could come from the following : the previous treatment, where we took account of the coupling between the two vanadium ions is in fact more complex than appears at first sight : since we are dealing with a *non-linear molecule* (which consists here of the two vanadium ions and the surrounding ligands) in an orbitally degenerate unperturbed level ⁽²⁾, the electron and nuclear motions cannot be separated (breakdown of the adiabatic approximation) [14, 15]. A model for this problem has recently been proposed by Piepho, Krausz and Schatz [16-18] (hereafter called P.K.S.). In our case, the P.K.S. vibronic hamiltonian $\mathcal{H}_{\text{vib}}$ writes :

$$\mathcal{H}_{\text{vib}} = \mathcal{H}_{\text{el}} + (T_{1N} + T_{2N})$$

where T_{iN} is the sum of the kinetic energy of the vanadium ion at site i and of its surrounding ligands. The electronic hamiltonian $\mathcal{H}_{\text{el}}$ writes : $\mathcal{H}_{\text{el}} = \frac{k}{2}(Q_1^2 + Q_2^2) + \frac{p^2}{2m} + V(r_1, r_2, Q_1, Q_2)$ where Q_1 and Q_2 are the breathing modes of site 1 and 2 respectively ⁽³⁾, $\frac{p^2}{2m}$ is the kinetic energy of the 3d electron, and $V(r_1, r_2, Q_1, Q_2)$ is an electrostatic energy containing the repulsion between the two V^{5+} ions, the attraction of the electron with each V^{5+} ion (at distances r_1 and r_2), and the electrostatic interaction between the electron and the ligands (crystal field). P.K.S. develop the crystal field around the equilibrium configuration for the higher oxidation state (5^+ in our case); the crystal field from the ligands surrounding the V^{4+} ion will then contain a term lQ_i ($i = 1$ or 2). As a first step, the electronic Hamiltonian is treated by the variational method; there are two important quantities : ε , proportional to a transfer integral and measuring the ability for the electron to be delocalized over both sites, and λ , proportional to l and favouring localization. P.K.S. show that if $\varepsilon/\lambda^2 \gg 1$ the electron is delocalized, while if $\varepsilon/\lambda^2 \ll 1$ it is localized on one site. The next step is to consider the full Hamiltonian using vibronic functions. As a result, the ground electronic level is replaced by a set of low-lying unequally spaced vibronic levels. For instance, for the ruthenium complex $[(\text{bpy})_2\text{ClRu-Pyr-RuCl}(\text{bpy})_2]^{3+}$ [18], the values of ε and λ are first deduced from absorption spectra; knowing ε and λ , P.K.S. then predict very low vibronic energy levels at 1.7, 27, 355, 440 cm^{-1} . We think that our

E.S.R. experiments have shown the existence of such vibronic levels for the V_2^{9+} centre in crystalline V_2O_5 , 10 cm^{-1} apart from each other. At the present time it is not possible to calculate the position of the vibronic levels of V_2^{9+} using P.K.S. model, since we still do not possess any information about the intervalence band absorption spectrum, which should peak around 1 300 cm^{-1} (0.16 eV).

5. Conclusion.

We have measured the spin-lattice relaxation time of the paramagnetic centre detected in pure crystalline V_2O_5 around $g = 2$, with $S_{\text{eff}} = 1/2$ and axial symmetry, showing 15 hyperfine lines. This spectrum originates from a V_2^{9+} molecular ion, consisting of an electron delocalized over two equivalent vanadium ions ($^{51}\text{V} : I = 7/2$). Between 1.3 and 50 K, $T_1^{-1} = 12.5 T + 3\,100/\sinh \frac{15.5}{T} (T_1 \text{ s}, T \text{ K})$. We tried to find the meaning of the energy 15.5 K (1.3×10^{-3} eV). We described this V_2^{9+} centre according to Perlstein's model, which is supported by experiments from Clauws *et al.* Assuming that the crystal field energy is stronger than the bonding energy between the two vanadium ions, we found that this bonding energy is 0.16 eV, which compares favourably with the value of 0.15 eV postulated by Perlstein from electrical conductivity measurements. Our results suggest that the optical absorption spectrum of V_2O_5 single crystals should show an intervalence band around 0.16 eV. On the other hand, a direct measurement of the absorption between the two vibronic levels 1.3×10^{-3} eV apart seems much more delicate (transition in the far Infrared).

Appendix.

DETERMINATION OF THE SPLITTING FOR THE GROUND LEVEL OF V_2^{9+} . — We treat this problem along the methods used for H_2^+ [13]. The vanadium nuclei and their ligands are kept fixed at their positions. We neglect the small deviation from C_{4v} symmetry for the crystal field acting on a given vanadium ion. One can relate the local symmetry around a vanadium ion to the **a**, **b**, **c** crystal axes : the fourfold symmetry axis OZ is parallel to **c**, and two twofold symmetry axes OX and OY are parallel to **a** and **b** respectively. We take the quantification axis Oz along the internuclear axis. The reference frame Oxyz and the coordinates r_1, r_2, φ , are defined in figure 7. Approximate electron wave functions are :

$$\psi_{\pm} = \frac{d_{XY}(1) \pm d_{XY}(2)}{\sqrt{2(1 \pm S)}}. \quad (4)$$

⁽²⁾ One should not confuse the ground level of V^{4+} in C_{4v} symmetry, which is orbitally non-degenerate (d_{XY}), and the ground unperturbed level of V_2^{9+} (no coupling between the two ions) which is orbitally degenerate ($V^{4+}(1) - V^{5+}(2)$ and $V^{5+}(1) - V^{4+}(2)$ have the same energy).

⁽³⁾ P.K.S. explain that the other modes may be discarded.

We use a Slater wave function for the radial part $R(r)$ of the atomic orbital $d_{XY}(i)$ of ion i : $R(r) = \frac{(2\beta)^{7/2}}{(6)^{1/2}} r^2 e^{-\beta r}$ [19], where $\beta = \frac{Z_{\text{eff}}}{3a_0}$ with $Z_{\text{eff}} = 5$ [20]. The overlap integral is $S = \langle d_{XY}(1)/d_{XY}(2) \rangle$.

Fig. 7. — Coordinate systems used in our calculation of the splitting for the ground level of V_2^{2+} in Perlstein's model.

The energies E_+ and E_- corresponding to ψ_+ and ψ_- are :

$$E_{\pm} = \frac{H_{11} \pm H_{12}}{1 \pm S}$$

with

$$H_{ij} = \left\langle d_{xy}(i) \left| \frac{p^2}{2m} - \frac{Z_{\text{eff}} e^2}{4\pi\epsilon_0} \left(\frac{1}{r_1} + \frac{1}{r_2} \right) + \frac{(Z_{\text{eff}} e)^2}{4\pi\epsilon_0 R} \right| d_{xy}(j) \right\rangle.$$

When $S \ll 1$, the energy difference $E_- - E_+$ is given by :

$$E_- - E_+ \simeq -2 \left[\frac{S}{(r_2)_{11}} - \frac{1}{(r_2)_{21}} \right].$$

where $\frac{1}{(r_2)_{ij}} = \left\langle d_{xy}(i) \left| \frac{Z_{\text{eff}} e^2}{4\pi\epsilon_0 r_2} \right| d_{xy}(j) \right\rangle.$

The two-centre integrals are calculated using the spheroidal coordinates $\lambda = \frac{r_1 + r_2}{R}$, $\mu = \frac{r_1 - r_2}{R}$, φ . The jacobian for the change from x, y, z to λ, μ, φ variables is $\frac{R^3}{8}(\lambda^2 - \mu^2)$ [13]. In the calculations, extensive use is made of the integral

$$\int_y^\infty x^n e^{-ax} dx = \frac{n! e^{-ay}}{a^{n+1}} \left[1 + ay + \frac{(ay)^2}{2!} + \dots + \frac{(ay)^n}{n!} \right].$$

The main results of our calculations are given in table II. In this table, we also give the corresponding results for the two defects proposed by Gillis and Boesman, under the same assumptions (crystal field greater than the coupling between the vanadium ions; ground state wave functions given by (4)). In the third model, the coupling between the ions is of the order of the crystal field so this result must not be taken too confidently.

Our whole treatment rests upon the assumption that the crystal field is greater than the coupling between the two vanadium ions. It is natural to wonder what would be the energy separation for the *free* V_2^{2+} ion.

We have made a similar calculation using d_{z^2} instead of d_{xy} , because it is the only 3d function which will make a σ bond leading to the maximum overlap. For $R = 3.5$ Å, we find that $S = 7 \times 10^{-2}$ and $E_- - E_+ = 2.97$ eV ($24\,000$ cm^{-1}). Our previous treatment is thus valid only if the cubic part of the crystal is at least $24\,000$ cm^{-1} . This quantity is not known in crystalline V_2O_5 . From a comparison with $VOSO_4(5H_2O)$ [21], one can hope that this be the case : in $VOSO_4(5H_2O)$, $10 Dq = 16\,000$ cm^{-1} , and this quantity should be greater in V_2O_5 , since the ligands are nearer (1.8 instead of 2.3 Å) and the field is created by point charge instead of dipoles.

Table II.

Model	Position of the vanadium ions	R (Å)	S	$\left(\frac{1}{r_2}\right)_{11}$ eV	$\left(\frac{1}{r_2}\right)_{21}$ eV	$(E_- - E_+)_{\text{eV}}$
Perlstein	along c	3.5	5.51×10^{-3}	19.94	0.19	0.16
Gillis-Boesman 1	along c	4.37	0.73×10^{-3}	16.07	0.021	1.92×10^{-2}
Gillis-Boesman 2	along c	3.5	-3.75×10^{-2}	20.85	-1.41	-1.26

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