Classification

Physics Abstracts

78.30 — 75.10D — 76.30D — 78.60

Ground state Jahn-Teller effects for $V^{3+} : Al_2O_3$

M. Abou-Ghantous (*) and C. A. Bates (**)

Service Basses Températures, Centre d'Etudes Nucléaires de Grenoble, 85X, 38041 Grenoble, France

(Reçu le 5 septembre 1979, révisé le 25 mars, accepté le 10 avril 1980)

Résumé. — Une analyse à l'ordinateur de l'ensemble des données expérimentales actuelles sur l'état fondamental du système $V^{3+} : Al_2O_3$ est présentée. On montre que ces données sont expliquées de manière satisfaisante par un modèle de l'effet Jahn-Teller du réseau dans lequel le couplage aux modes $E(E_g)$ est prépondérant.

Abstract. — A computer analysis of the current experimental data available for ground states of V^{3+} ions in Al_2O_3 has been undertaken. It is shown that the new data are satisfactorily accounted for on a multimode lattice Jahn-Teller model in which coupling to the $E(E_g)$ modes dominates.

1. Introduction. — Many experimental and theoretical investigations have been carried out on the ground states of the $3d^2 V^{3+}$ impurity ion in Al_2O_3 . In an earlier paper [1] we concluded that a multimode full-lattice model of the Jahn-Teller effect (JTE) was needed to account for all the experimental data available at that time (1976). Since then further experiments have been carried out and substantial changes in the experimental values for the spin-phonon G -tensors have been found. As the interpretation of [1] was based on experimental data which are now known to be partially wrong, a completely new analysis has been undertaken in view of the current interest shown in this system [2-5].

2. Summary of changes in and additions to the experimental data. — Challis and Williams [6] have investigated the concentration dependence of the size of the frequency crossing signals from $V^{3+} : Al_2O_3$ and from their measurements they obtained the strengths of both the $\Delta M = 1$ and $\Delta M = 2$ transitions in the same sample. However, the strengths quoted in [6] have since been revised because of further measurements and more detailed analyses [5]. Abou-Ghantous and de Goër [7] have corrected the value of G_- deduced from the APR measurements described in [1]. Further APR experiments using CdS transducers producing both longitudinal and transverse waves have also been carried out and lower limits for G_- and G_{15} have been deduced [8]. Devismes and de Goër [9] have undertaken a comprehensive analysis of phonon scattering data including low

temperature thermal conductivity measurements. They [9] also concluded that it was impossible to reconcile the revised data with either the JT model of [1] or with a detailed crystal field model in which admixtures of excited states were taken into account. Finally, independent cross-relaxation measurements by Vasson *et al.* [10] have shown that the ion-lattice coupling constant V_E for $V^{3+} : Al_2O_3$ is larger than that for the $3d^1$ ions $V^{4+} : Al_2O_3$ and $Ti^{3+} : Al_2O_3$. As JTE's are important in $3d^1$ ions, they are likely to be significant for V^{3+} as well.

3. The model. — In view of the conclusions reached in [5] and [9], we again begin with the effective Hamiltonian derived in [1] for a full-lattice, dynamic JT model for the 3T_1 cubic ground state of a strain-free V^{3+} ion in zero magnetic field, namely

$$\mathcal{H} = \frac{1}{3} v(3 l_z^2 - 2) + \gamma \lambda [\alpha l_z S_z + \alpha' (l_x S_x + l_y S_y)] + \mathcal{H}_{\text{trig-SO}}^{(2JT)} + \mathcal{H}_{\text{SO-SO}}^{(2JT)}. \quad (1)$$

$S = 1$, $l = 1$, γ is the first-order JT reduction factor and α , α' are the isomorphic constants (adjusted from $-3/2$ to allow for admixtures of excited states like ${}^3T_2(\text{te})$, ${}^1E(t^2)$, ${}^1T_1(t^2)$, etc.). v is the diagonal

(*) Permanent Address : Department of Physics, Faculty of Science, Lebanese University, Al-Hadet, Beirut, Lebanon.

(**) Permanent Address : Department of Physics, University of Nottingham, University Park, Nottingham NG7 2RD, England.

trigonal field parameter and λ is the spin-orbit coupling constant. $\mathcal{H}_{\text{trig-SO}}^{(2\text{JT})}$ and $\mathcal{H}_{\text{SO-SO}}^{(2\text{JT})}$ are the second-order JT terms which include the additional reduction factors F_a and F_b ; $\mathcal{H}_{\text{trig-trig}}^{(2\text{JT})}$ has been included in the first term of (1). In the JT model used, coupling to the $E(E_g)$ modes only is included.

The eigenstates of (1) split into an upper set of six states at an energy of V relative to the lower set of three states. In the presence of a magnetic field $\mathbf{H}$, the lowest set are conveniently described by a spin-Hamiltonian ($s = 1$) :

$$\mathcal{H}_s = D \left(s_z^2 - \frac{2}{3} \right) + g_{\parallel} \beta H_z s_z + g_{\perp} \beta (H_x s_x + H_y s_y) . \quad (2)$$

In [1], perturbation theory was used to obtain expressions for the $s = 1$ states, D , $g_{\parallel}$ and $g_{\perp}$. Perturbation theory is now regarded as inaccurate as the various contributions have approximately the same order of magnitude. Instead, we write the eigenstates in the form :

$$\begin{aligned} |M_s = 0\rangle &= \eta |0, 0\rangle + \varepsilon | -1, 1\rangle + \varepsilon |1, -1\rangle \\ |M_s = \pm 1\rangle &= \rho |0, \pm 1\rangle + \psi |\pm 1, 0\rangle \\ &\quad \pm \varphi |\mp 1, \mp 1\rangle \end{aligned} \quad (3)$$

where $|0, 0\rangle \equiv |m_l = 0, m_s = 0\rangle$, etc. and obtain $\eta, \varepsilon, \rho, \dots$ by diagonalization of the three (3×3) matrices of (1) within the $|m_l, m_s\rangle$ basis.

Then

$$\begin{aligned} g_{\parallel} &= 2[\rho^2(1 + C) + \rho\psi(B + C) - \psi\varphi C - \\ &\quad - \varphi^2(1 + \frac{1}{2}\alpha\gamma + A + C) + \frac{1}{2}\psi^2(\alpha\gamma + 2A)] \\ g_{\perp} &= 2(\rho\eta + \varepsilon\psi) + (\alpha'\gamma - A)(\psi\eta + \varepsilon\rho) + \\ &\quad + C[2\eta\rho + \varepsilon(\varphi + 2\psi - \rho)] + B[2\eta\rho + \varepsilon(3\psi - \rho)] \end{aligned} \quad (4)$$

where D is defined in (1) and where $A = -\frac{1}{3}\alpha F_a v$, $B = -\alpha^2 \lambda F_a$ and $C = -\frac{2}{3}\alpha^2 \lambda (F_b - F_a)$.

Small modifications are also needed in the expressions for the spin-phonon coupling constants. In the expressions for G_{-} and G_{15} in eq. (18) of [1], φ is multiplied by ρ while in the expressions for G_{51} and G_{44} in equations (19) of [1], $(\varepsilon - \psi)$ is replaced by $(\varepsilon\rho - \eta\psi)$ but $\varphi\varepsilon$ is unchanged.

4. The « experimental » parameters. — Suppressing the variations in JT energy $E_{\text{Ee}}^{\text{JT}}$ as in [1], we are left with nine unknown basic « theoretical » parameters, namely $\gamma, F_a, F_b, v, V, \lambda\alpha, \lambda\alpha', V_E$ and V_{T_2} (the ion-lattice coupling constant for $E(T_2)$ -type displacements) which need to be determined. (The v' of [1] is here absorbed into V .) Information is available on the « experimental » parameters $g_{\parallel}, g_{\perp}, D, G_{-}, G_{15}, G_{51}$ and G_{44} only. (At this stage we exclude optical and infrared transitions to states outside the lowest nine states as their incorporation further complicates the analysis by introducing further « theoretical » parameters.)

Unfortunately, these « experimental » parameters are known only imprecisely and often inconsistently between different measuring technique. For $g_{\parallel}$ and D we use the values quoted by Pontnau and Adde [11] as before, but for $g_{\perp}$, less accurately known, we take the value deduced by Challis and Williams [12]. In contrast, values for the G -tensors now available from the most recent measurements [5] show big changes. More APR experiments have been carried out using CdS transducers [8] so that both longitudinal and transverse ultrasound could be generated in the same sample. With $\mathbf{k}$ along $\mathbf{a}$, longitudinal waves gave $G_{-} = 150 \pm 25 \text{ cm}^{-1}$, while transverse waves along $\mathbf{c}$ gave $G_{15} = 55 \pm 12 \text{ cm}^{-1}$. In a different sample with $\mathbf{k}$ along $\mathbf{a}$, transverse waves gave $G_{-} \sim 80 \text{ cm}^{-1}$ and $G_{15} \sim 40 \text{ cm}^{-1}$. The samples themselves were very similar and the differences between the results have been attributed to the different geometries of the crystals relative to the cavity. In the latter case, only a fraction of the total number of V^{3+} ions in the crystal are sampled by the ultrasound phonons so that the G_{-} values obtained ($\mathbf{k}$ along $\mathbf{a}$) represent lower limits on the true values. Frequency crossing experiments [6] measured a weighted average of G_{-} and G_{15} and also a weighted average of G_{51} and G_{44} , but in the same sample. Independent measurements of G_{51} and G_{44} have also been made by Kinder [13] using tunnel-junction phonon spectroscopy. However, the values quoted in [13] have been recalculated [6, 9] and agree with those obtained from frequency crossing experiments. Unfortunately, there appears to be no measurement of the ratios G_{-}/G_{15} and G_{44}/G_{51} . The most recent frequency crossing experiments [5] give values for all the G -tensors which are consistent with the most recent APR values [8].

Table I summarizes the values for the experimental parameters determined by the different techniques, and those used finally in our computer program.

5. The « theoretical » parameters. — Table II gives the values of the computed « theoretical » parameters which give the best fit to the « experimental » parameters. The fitting procedure used was to diagonalize the matrices on a Telemechanic T1600 computer and vary the « theoretical » parameters to minimize Q , where Q is the root mean square difference between the calculated and measured value for all the « experimental » parameters weighted by the experimental uncertainty. Results were regarded as acceptable when they were independent of the initial starting values in the fitting procedure and within physically acceptable limits ⁽¹⁾. The error quoted is the last

⁽¹⁾ In principle, it is impossible to obtain a fit to nine « theoretical » parameters using only seven « experimental » parameters. However, the ten-dimensional space in which an absolute minimum for Q is being sought is severely limited by physical considerations for many of the parameters. These constraints provide the necessary additional data which produces only one fit.

Table I. — « Experimental » parameters.

Parameter	D (cm ⁻¹)	$g_{ }$	$g_{\perp}$	G_{-} (cm ⁻¹)	G_{15} (cm ⁻¹)	G_{51} (cm ⁻¹)	G_{44} (cm ⁻¹)
Experimental value	8.296 ± 0.016 [11] (**)	1.910 ± 0.005 [11] (**)	1.78 ± 0.04 [12] (**)	170 ± 70 [20] 150 ± 25 [8]	130 [20] > 55 [8]		
[Reference]	8.3 ± 0.2 [9]			180 ± 90 (*) [5] (**)	130 ± 65 (*) [5] (**)	100 ± 65 (*) [5] (**)	140 ± 90 (*) [5] (**)
Computed value	8.307	1.907	1.723	193	145	91	119
(Increment)	(0.001)	(0.000 6)	(0.000 6)	(0.6)	(0.8)	(0.3)	(0.9)

(*) G_{-} and G_{15} are measured in combination as given in [6]; the values quoted are deduced using the approximate theoretical relation $G_{-} = \sqrt{2} G_{15}$. Similarly, G_{51} and G_{44} are measured in combination.
(**) Denotes values used in the computer program.

Table II. — The « theoretical » parameters taking $\lambda = 95\text{ cm}^{-1}$.
(If λ is in error, α and α' should be adjusted keeping $\alpha\lambda$, $\alpha'\lambda$, B and C constant.)

Parameter	γ	$F_a/10^{-4}$ (cm ⁻¹) ⁻¹	$F_b/10^{-4}$ (cm ⁻¹) ⁻¹	v (cm ⁻¹)	V (cm ⁻¹)	α	α'	$ bV_E $ (cm ⁻¹)	$ bV_{T2} $ (cm ⁻¹)
Value	0.036 7	4.01	7.50	3 333	563	- 1.33	- 1.20	56 350	4 575
(Increment)	(0.000 5)	(0.001)	(0.015)	(5)	(0.5)	(0.000 7)	(0.008)	(200)	(50)

Parameter	η	ε	ρ	ψ	φ	A	B	C
Value	0.997	0.051 4	0.998	0.055 2	0.001 6	0.592	- 0.067 1	- 0.039 3
(Increment)	(0.000 03)	(0.000 2)	(0.000 02)	(0.000 2)	(0.000 02)	(0.001)	(0.000 2)	(0.000 3)

increment used in the fitting program ; if a parameter is changed by the increment, the fit is worse.

While tables I and II give details for what we consider to be the most reliable set of data, more than one hundred other sets of « experimental » parameters have been taken from table I and fitted. While the values so obtained for the « theoretical » parameters are different, all the various fits have the following properties :

1) Only a JT model fits the results as γ is always less or much less than unity. F_b is always close to $2 F_a$ and of magnitude $\leq 10^{-3}$ (cm⁻¹). The cluster model constraints between γ , F_a and F_b are not obeyed, confirming the need for a multimode lattice model [14].

2) $|V_E|$ is always greater or much greater than $|V_{T2}|$ so justifying the basic assumption in our theory that only $E(E_g)$ modes need to be considered in our JT Hamiltonian. Additionally, the contributions from T_{2g} modes are further quenched by the factor γ which always multiplies V_{T2} [14].

3) α and α' are different from each other but reasonably close to $-3/2$. Significant admixtures from 3T_2 states have been calculated previously [9] and further admixtures from other excited states like 1E , 1T_1 are anticipated.

4) The value deduced for V is within the range normally quoted (but never measured) by others.

5) The theory itself fits best to the final set of « experimental » parameter values given in table I in that Q ($= 0.73$) had a value close to the minimum for any other combination of experimental parameters. Furthermore, no other « fits » to these parameters have been found.

6. Discussion. — From table II, our computed value of $\gamma V_T/V_E$ is 3.0×10^{-3} . This can be compared directly to the value of $\sim 10^{-2}$ which has been deduced independently from measurements on the line widths in the frequency crossing experiments [5]. In view of the nature of the approximations made in [5], the two values for the ratio are in very good agreement.

A good deal of information on the energy levels of $V^{3+}:Al_2O_3$ has also been obtained by Duval and co-workers [19] by absorption and emission spectroscopy. Uniaxial stress effects on the absorption spectra [15] and on the near infrared emission spectra [16] have been thoroughly investigated while the Raman spectrum has been obtained [2] in conjunction with the emission spectrum of $V^{4+}:Al_2O_3$. Low-temperature optical absorption on the zero-phonon lines and stress-induced linear dichroism experiments on the broad bands involving the $^3A_2(^3T_1) \rightarrow ^3T_2$, V^{3+} transitions have also been carried out very recently [3, 17]. The data obtained by these techniques have not been incorporated into our model, for

reasons outlined in section 4, and it is necessary to compare the interpretation of these experimental results [18, 2, 3, 17] with our model.

Duval and co-workers interpret their results on a JT model in which the real trigonal field is included at the outset [19, 18] but second-order JT contributions are excluded. In their earlier work [19] a cluster approximation was used, but more recently [18] various excitations of the vibrational doublet were taken into account using a direct diagonalization procedure. $\text{Co}^{3+}:\text{Al}_2\text{O}_3$ is taken as an example. While we agree that the real trigonal symmetry of the cluster should be used in the Hamiltonian for the ion-lattice interaction, the incorporation of real-symmetry-adapted lattice phonons into the lattice Hamiltonian of section 3 makes the problem prohibitively difficult. In our view, it is necessary to use a multimode, full-lattice model (and to retain the second-order JT terms) even if the detailed model does not possess the real trigonal symmetry, as many techniques such as spin-lattice relaxation only work through the phonon spectrum. Thus we are forced to work with trigonally-adapted cubic Q 's [14] in our lattice Hamiltonian.

Champagnon and Duval [3] conclude that the ${}^3\text{E}({}^3\text{T}_1)$ levels of V^{3+} are subject to a JTE while the potential energy curve for the ${}^3\text{A}_2({}^3\text{T}_1)$ level is not displaced. The same conclusion is also obtained from their analysis of their stress-induced linear dichroism experiments [17]. In effect, the conclusions of Duval and co-workers are in agreement with many of the features discussed here, namely that a strong JTE is present in the ${}^3\text{T}_1$ ground states. One difference is that our model and [5] show that the $\text{E}(\text{E}_g)$ phonons

are largely responsible whereas Duval and co-workers conclude that the trigonal component of the E-vibration dominates. However, their experiments are generally not particularly sensitive as to whether or not a JTE is present in the ${}^3\text{A}_2$ ground states as the orbital contributions to the magnetic properties are very small. This is also true of the EPR data as $g_{\parallel}$ and $g_{\perp}$ are not drastically changed by the JTE from their crystal field values. However, the sizes of the G -tensors, the value deduced here for V_E and spin-lattice relaxation measurements [10] indicate conclusively that significant JTE's are also present in the ${}^3\text{A}_2$ ground states of $\text{V}^{3+}:\text{Al}_2\text{O}_3$.

While we anticipate that there may be further improvements in the « experimental » parameters as different and more accurate experiments are carried out, the general features of our conclusions are likely to remain as the resulting changes in the « theoretical » parameters are likely to be small. Finally, we have not attempted a new analysis of Cr^{4+} as the experimental information is insufficient.

Acknowledgments. — We wish to thank Dr. A.-M. de Goër and M. J. Doulat for their hospitality and arrangements made for our stay in Grenoble where the above computations were carried out. We also gratefully acknowledge the many helpful discussions we have had on various aspects of this work with Professor L. J. Challis and Drs. A.-M. de Goër and A.-M. Vasson. In addition, our thanks are due to Professor L. J. Challis and Drs. Ghazi, Jefferies and Wybourne for permission to quote their results *prior* to publication.

References

- [1] ABOU-GHANTOUS, M., BATES, C. A. and GOODFELLOW, L. C., *J. Phys. Chem. Solids* **37** (1976) 1059.
- [2] CHAMPAGNON, B. and DUVAL, E., *J. Phys. C. Solid State Phys.* **12** (1979) L425.
- [3] CHAMPAGNON, B. and DUVAL, E., *J. Phys. C. Solid State Phys.* **13** (1980) 131.
- [4] CHALLIS, L. J. and DE GOËR, A.-M., *J. Phys. C. Solid State Phys.* **13** (1980) 2171.
- [5] CHALLIS, L. J., GHAZI, A. A. and WYBOURNE, M., *J. Phys. C. Solid State Phys.*, submitted.
- [6] CHALLIS, L. J. and WILLIAMS, D. J., *J. Phys. C. Solid State Phys.* **11** (1978) 3816.
- [7] ABOU-GHANTOUS, M. and DE GOËR, A.-M., Centre d'Etudes Nucléaires de Grenoble, Internal Report (1977) SBT 447/77.
- [8] DAUDIN, B., Docteur-Ingénieur Thesis (1978), L'Université Scientifique et Médicale et l'Institut National Polytechnique de Grenoble; also DAUDIN, B. and DE GOËR, A.-M., Centre d'Etudes Nucléaires de Grenoble, Internal Report (1980) SBT 538/80.
- [9] DEVISMES, N. and DE GOËR, A.-M., *J. Phys. C. Solid State Phys.* **11** (1978) 3814.
- [10] VASSON, A.-M., VASSON, A. and BATES, C. A., *J. Phys. C. Solid State Phys.* **13** (1980) 2181.
- [11] PONTNAU, J. and ADDE, R., *J. Phys. Chem. Solids* **36** (1975) 1023.
- [12] CHALLIS, L. J. and WILLIAMS, D. L., *J. Phys. C. Solid State Phys.* **10** (1977) L 621.
- [13] KINDER, H., *Z. Phys.* **262** (1973) 295.
- [14] BATES, C. A., *Phys. Rep.* **35C** (1978) 187.
- [15] CHAMPAGNON, B., DUVAL, E. and LOUAT, R., *Phys. Status Solidi (b)* **69** (1975) 339.
- [16] CHAMPAGNON, B. and DUVAL, E., *J. Physique Lett.* **38** (1977) L-299.
- [17] CHAMPAGNON, B. and DUVAL, E., *J. Phys. C. Solid State Phys.* **13** (1980) 141.
- [18] LACROIX, R., WEBER, J. and DUVAL, E., *J. Phys. C. Solid State Phys.* **12** (1979) 2065.
- [19] DUVAL, E., CHAMPAGNON, B. and LACROIX, R., *J. Physique* **37** (1976) 1391.
- [20] GUERMEUR, R., JOFFRIN, J., LEVELUT, A. and PENNÉ, J., *Phys. Rev.* **187** (1969) 1153.