Influence of Covalency in the Dynamic Jahn–Teller Effect in Al_2O_3:Ti^{3+}

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A numerical evaluation of the Jahn–Teller potential energy is presented for the case of Ti^{3+} in Al_2O_3. It is found that the crystal-field theory is inadequate to explain the experimental results, whereas the inclusion of covalency effects leads to a good agreement between the experimental results and the theoretical ones.

The influence of a dynamic Jahn–Teller effect on the energy levels of a d^1 electronic system in Al_2O_3 has been considered by Macfarlane *et al.*[1] They obtained analytical expressions for the energy splittings δ_1 and δ_2, as well as the g values for the Zeeman splitting of the $E_{3/2}$, $_1E_{1/2}$, and $_2E_{1/2}$ levels (Fig. 1). The independent variables involved are the trigonal and spin-orbit coupling parameters v and ζ and the quenching factor $\gamma = e^{-3E_{JT'}/2\hbar\omega}$, where E_{JT} denotes the Jahn–Teller potential energy and $\hbar\omega$ is the energy of the vibronic mode responsible for the Jahn–Teller effect. The analytical expressions were then fitted to the experimental data concerning Al_2O_3 : Ti^{3+} and the experimental value of the Jahn–Teller energy $E_{JT'}$ was obtained[1,2] ($E_{JT}^{expt} = 200$ cm^{-1}). The purpose of this paper is to present theoretical estimates of the quantity E_{JT}. It turns out that the crystal-field model is inadequate to explain the experimental results, whereas the inclusion of covalency effects leads to good agreement between the experimental results and the theoretical ones.

A theoretical estimate of the value of E_{JT} in the framework of crystal-field theory is feasible if one restricts oneself to the octahedron composed of the Ti^{3+} ion plus its nearest neighbors and adopts a point-charge model. We start from the formula[1] $E_{JT} = a^2/2\beta$, where $a = \sqrt{2}\ \langle d_{xz} | \partial V/\partial Q_2 | d_{xz} \rangle$ and β denotes the force constant. By using the explicit expression of $\partial V/\partial Q_2$ reported in Ref. 3, one obtains the following formula for the coupling constant a:

$$a = \frac{ee'}{84}\left(\frac{54\langle r^2\rangle}{R^4} + \frac{125\langle r^4\rangle}{R^6}\right)\ \text{(in a. u.)}, \qquad (1)$$

where $\langle r^2\rangle$ and $\langle r^4\rangle$ denote, respectively, the mean-square and mean-fourth-power radius of the $3d$ orbit, R is the distance between the metal ion and the ligands, and e' denotes the effective charge of the oxygen ions. In order to estimate a numerically, e' was assumed to be -1 a.u., R was assumed to be the lattice constant of the pure Al_2O_3 crystal,[4] and the free-ion values of $\langle r^2\rangle$ and $\langle r^4\rangle$ were used: $\langle r^2\rangle = 1.893$ a.u., $\langle r^4\rangle = 7.069$ a.u.[5] We obtain in this fashion the following value: $a = 9.3\times10^{-3}$ a.u.

The corresponding Jahn–Teller energy $E_{JT} = a^2/2\beta$ ($\beta = 6\times10^3$ dyn/cm)[3] turns out to be $E_{JT} = 2400$ cm^{-1}, which is too large compared with the experimental value $E_{JT}^{expt} = 200$ cm^{-1}.

In recent years, it has been shown that covalency effects play an important role in ion-phonon-interaction phenomena such as paramagnetic relaxation,[6–10] the phonon-field contribution to the hyperfine coupling of S-state ions in crystals,[11] and the positions of the energy levels of ions in crystals.[12] Moreover, it has been shown that covalency can substantially change the picture of the Jahn–Teller effect.[13–15] An evaluation of the quantity E_{JT} in the framework of molecular-orbital theory was therefore undertaken. The molecular-orbital method in its "linear combination of atomic orbitals" form was employed.[16] In the case of O_h symmetry, the proper set of ligand basis functions and their metal-ion counterparts are given in Ref. 16. The one-electron molecular orbitals to be considered here are

$$\Psi_\sigma(A_{1g}) = N_1[4s + (\lambda_1^{(\sigma)}/\sqrt{6})(z_1+z_2+z_3+z_4+z_5+z_6)],$$

$$\Psi_\sigma(E_g) = N_2[3d_{x^2-y^2} + \tfrac{1}{2}\lambda_2^{(\sigma)}(z_1 - z_2 + z_4 - z_5)]$$

$$= N_2[3d_{z^2} + (\lambda_2^{(\sigma)}/2\sqrt{3})(2z_3 + 2z_6$$

$$- z_1 - z_2 - z_3 - z_4 - z_5)],$$
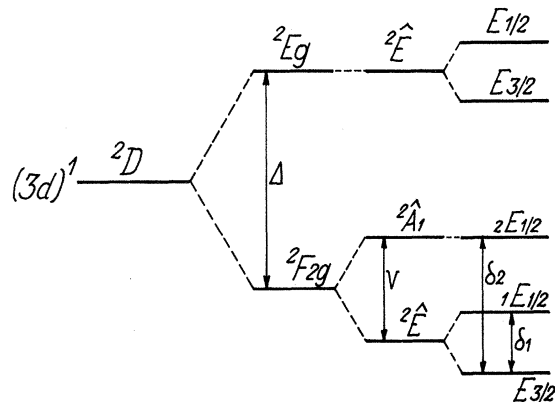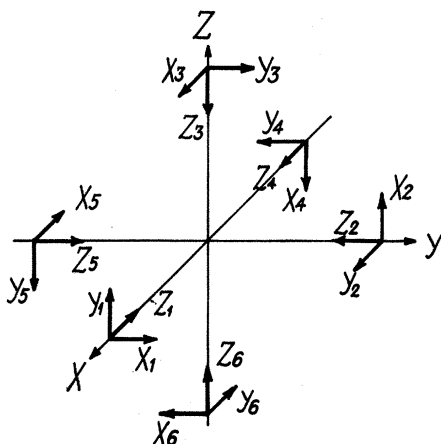

FIG. 1. Low-lying electronic energy of Al_2O_3 : Ti^{3+}.

FIG. 2. Coordinate system and numbering used in the molecular-orbital calculation.

$$\Psi_{\sigma,\tau}(F_{1u}) = N_3 \left[4p'_x + (\lambda_3^{(\sigma)}/\sqrt{2})(z_1 - z_4) + \tfrac{1}{2}\lambda_4^{(\tau)} \right.$$
$$\left. \times (x_3 + y_2 - x_5 - y_6) \right]$$

$$= N_3 \left[4p'_z + (\lambda_3^{(\sigma)}/\sqrt{2})(z_3 - z_6) + \tfrac{1}{2}\lambda_4^{(\tau)} \right.$$
$$\left. \times (x_2 + y_1 - x_4 - y_5) \right]$$

$$= N_3 \left[4p_y + (\lambda_3^{(\sigma)}/\sqrt{2})(z_2 - z_5) + \tfrac{1}{2}\lambda_4^{(\tau)} \right.$$
$$\left. \times (x_1 + y_3 - x_6 - y_4) \right],$$

$$\Psi_{\tau}(F_{2g}) = N_4 \left[3d_{yz} + \tfrac{1}{2}\lambda_5^{(\tau)}(x_2 + y_3 + x_6 + y_5) \right]$$

$$= N_4 \left[3d_{xy} + \tfrac{1}{2}\lambda_5^{(\tau)}(x_1 + y_2 + x_5 + y_4) \right]$$

$$= N_4 \left[3d_{xz} + \tfrac{1}{2}\lambda_5^{(\tau)}(x_3 + y_1 + x_4 + y_6) \right] , \quad (2)$$

where x, y, z refer to $3p_x$, $3p_y$, $3p_z$ oxygen orbitals. The coordinate system used is shown in Fig. 2. For each molecular orbital the averaged energy $(H)_{av}$ is calculated and the coefficients λ_i are varied so that $\delta(H)_{av} = 0$. This leads to a homogeneous system of linear equations from which the λ_i are evaluated. The condition that these equations are solvable provides the secular equation $|H_{ij} - G_{ij}E|$ $= 0$ from which the energy levels E are obtained. The extended Hückel theory, previously used by one of us for deriving the energy levels of KCl : Tl,[17] has been adopted in the present problem. Hartree's numerical values of O^{2-} (Ref. 18) and Ti^{3+} (Ref. 19) radial functions $R(r)$ were used for our computations. The numerical values of $R(r)$ were fitted with Slater functions. The overlap integrals G_{ij} were then evaluated in the usual way.[20] The diagonal terms H_{ii} in the secular equation $|H_{ij} - G_{ij}E| = 0$ were estimated as the sum of ionization potentials V_i plus the Madelung energy E_M. The quantities V_i were obtained from Moore's tables[21] of atomic spectra. For the off-diagonal terms H_{ij}, we have made use of the Wolfsberg–Helmholtz approxima-tion.[22] The computations were performed by means of the self-consistent procedure adopted in Ref. 17.

Figure 3 shows the molecular-orbital diagram. The configuration of the ground state is $(A_{1g})^2 (E_g)^4 (F_{1u})^6 (F_{2g})^1$. The corresponding covalency parameters λ_i turn out to be

$$\lambda_1^{(\sigma)}(A_{1g}) = 11, \quad \lambda_4^{(\tau)}(F_{1u}) = 3.5,$$

$$\lambda_2^{(\sigma)}(E_g) = 3.6, \quad \lambda_5^{(\sigma)}(F_{2g}) = 0.1, \quad (3)$$

$$\lambda_3^{(\sigma)}(F_{1u}) = 45.$$

Because of the small value of the parameter λ_5, the molecular orbitals transforming as F_{2g} are mostly centered on the metal-ion orbitals d_{xy}, d_{xz}, d_{yz}. Therefore, with a good approximation they can be taken to be coincident with the pure-$3d$ orbitals. Moreover, since $\lambda_4^{(\tau)}$ is one order of magnitude smaller than $\lambda_3^{(\sigma)}$, it turns out that π-bonding ef-fects can be neglected also for the case of molec-ular orbitals transforming as F_{1u}. Therefore, the computations have been performed neglecting the contribution of π bonds and by using accordingly renormalized orbitals. This leads to $\lambda_3 = 47.7$ and $\lambda_4 = \lambda_5 = 0$. Following the procedure adopted in Refs. 7–10, the parameter a was then expressed in terms of auxiliary functions $C_{\alpha\beta}^{\gamma\delta\epsilon}(\rho_a, \rho_b)$ given by

$$C_{\alpha\beta}^{\gamma\delta\epsilon}(\rho_a, \rho_b) = \tfrac{1}{2}\rho_b{}^{\alpha+\beta+\gamma+\delta+2\epsilon+1} \int_1^{\infty} d\xi \int_{-1}^{1} d\eta\, e^{-\rho\xi - \tau\rho\eta}$$

$$\times (\xi + \eta)^{\alpha} (\xi - \eta)^{\beta} (1 + \xi\eta)^{\gamma}$$

$$\times (1 - \xi\eta)^{\delta}(\xi^2 - 1)^{\epsilon}(1 - \eta^2)^{\epsilon}, \quad (4)$$

where

$$\rho = \tfrac{1}{2}(\rho_a + \rho_b), \quad \tau = (\rho_a - \rho_b)/\rho_a + \rho_b).$$

The corresponding expression of a turns out to be

$$\frac{a}{\sqrt{2}} = \frac{U_1 \chi_0^2}{192}\left[C_{-21}^{121}(0, \chi_0 R) - \tfrac{1}{4} C_{-21}^{102}(0, \chi_0 R) \right]$$

$$+ \frac{K_1}{192}\left(\sum_{p=0}^{6} u_p \chi_0^{1-p} \left[C_{p-1,1}^{121}(R, \chi_0 R) - \tfrac{1}{4} C_{p-1,1}^{102}(R, \chi_0 R) \right] \right.$$
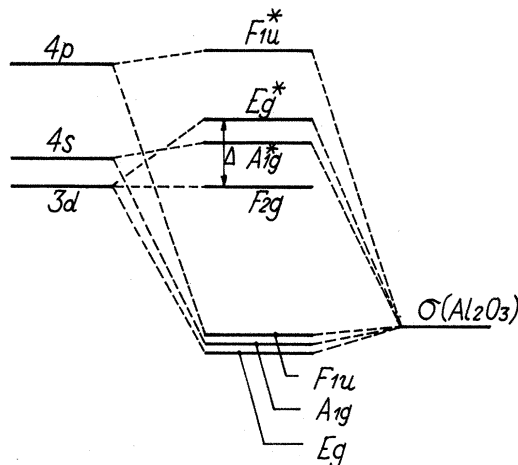

FIG. 3. Molecular-orbital energy-level diagram of $Al_2O_3 : Ti^{3+}$.

TABLE I. Observed and calculated splittings and g factors for the $^2F_{2g}$ ground term of Ti^{3+} in Al_2O_3.

	Observed	Crystal-field calculations	Molecular-orbital calculations
$\delta_1{}^a$ (cm^{-1})	37.8	0.8×10^{-3}	47
$\delta_2{}^a$ (cm^{-1})	107.5	4.4×10^{-3}	142
$g_{11}{}^a$	1.07	1.99	1.09

^{a}Reference 1.

$$-\sum_{p=0}^{4} (p-1)u_p\chi_0^{2-p}[C^{121}_{p-2,1}(R,\chi_0 R)$$

$$-\tfrac{1}{4}C^{102}_{p-2,1}(R,\chi_0 R)]\Bigg)$$

$$-\frac{K_1}{32}\left(15\chi_0^4[C^{321}_{-61}(0,\chi_0 R)-\tfrac{1}{4}C^{302}_{-61}(0,\chi_0 R)]\right.$$

$$-9\chi_0^4[C^{121}_{-41}(0,\chi_0 R)-\tfrac{1}{4}C^{102}_{-41}(0,\chi_0 R)]$$

$$-15\sum_{p=0}^{6}u_p'\chi_0^{4-p}[C^{321}_{p-6,1}(R,\chi_0 R)$$

$$-\tfrac{1}{4}C^{302}_{p-6,1}(R,\chi_0 R)]$$

$$+9\sum_{p=0}^{6}u_p'\chi_0^{4-p}[C^{121}_{p-4,1}(R,\chi_0 R)-\tfrac{1}{4}C^{102}_{p-4,1}(R,\chi_0 R)]$$

$$-3\sum_{p=0}^{6}u_p'\chi_0^{3-p}[C^{321}_{p-5,1}(R,\chi_0 R)-\tfrac{1}{4}C^{302}_{p-5,1}(R,\chi_0 R)]$$

$$+\sum_{p=0}^{6}u_p'\chi_0^{3-p}[C^{121}_{p-3,1}(R,\chi_0 R)-\tfrac{1}{4}C^{102}_{p-3,1}(R,\chi_0 R)]$$

$$+3\sum_{p=0}^{6}pu_p'\chi_0^{4-p}[C^{321}_{p-6,1}(R,\chi_0 R)$$

$$-\tfrac{1}{4}C^{302}_{p-6,1}(R,\chi_0 R)]$$

$$-\sum_{p=0}^{6}pu_p'\chi_0^{4-p}[C^{121}_{p-4,1}(R,\chi_0 R)-\tfrac{1}{4}C^{102}_{p-4,1}(R,\chi_0 R)]\Bigg),$$

$$(5)$$

with $\chi_0 = Z^*/Z_L^*$ where Z^*, Z_L^* are the effective charges Z and Z_L of titanium and oxygen, respectively, divided by principal quantum numbers. In

our case $Z=3.93$ a. u., $Z_L = 4.38$ a.u., $U_1 = Z_L - K_1$, $K_1 = 2\sum_i C^2_{1i}N_i^2\lambda_i$ and

$$u_p = 1 \quad \text{if } p=0,$$

$$u_p = \frac{1}{p!} - \frac{3!}{4!(p-1)!} \quad \text{if } 1 \le p \le 4,$$

$$u_p' = \frac{1}{p!} \quad \text{if } 0 \le p \le 4,$$

$$u_p' = \frac{1}{p!} - \frac{5!}{6!(p-5)!} \quad \text{if } 5 \le p \le 6.$$

The evaluation of $C^{\gamma\delta\epsilon}_{\alpha\beta}(\rho_a,\rho_b)$ has been made using a method of recurrent equations[23] by means of an electronic computer. One finds $a=3.2\times10^{-3}$ a.u. The corresponding value of the Jahn–Teller energy is $E_{JT}=270$ cm^{-1}. The strong reduction of E_{JT} in the molecular-orbital framework, in contrast to the point-charge model, may be understood on qualitative grounds by observing that in the former case the valence electrons are smeared out over all the complex. Therefore, the variation in the electrostatic energy of the F_{2g} electron in the field of the valence electrons arising from the displacements of the ligands may be expected to be smaller with respect to the case when the valence electrons are well localized as in the point-charge model. Analogous reduction factors of ion-phonon-interaction parameters due to covalency have been reported.[7] Upon substitution of $E_{JT}=270$ cm^{-1} into the analytical expressions of Macfarlane et al., the theoretical values of the energy splittings δ_1, δ_2 and g values were obtained.[24] They are reported in Table I along with the experimental results. The crystal-field results are also reported; it is seen that the results of the molecular-orbital calculations agree well with the experimental data, while calculations based on crystal-field theory lead to meaningless results.

The principal conclusion can then be drawn that covalency effects are of great importance in understanding the consequences of Jahn–Teller effect on the properties of metal ions in crystals.

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ERRATA

Antiferromagnetism. The Triangular Ising Net, G. H. Wannier [Phys. Rev. **79**, 357 (1950)]. It was kindly pointed out to me recently by Meijer[1] that the energy-versus-temperature plots differ by a small amount from similar plots constructed with the help of the formulas of Houtappel.[2] A short verification showed that the error is mine; it occurs in the first formula on p. 364: the sign of the two terms in κ^2 should be reversed. When this is done one obtains, in the place of Eqs. (34) and (35),

$$\frac{U}{-\tfrac{1}{2}NJ} = \frac{2}{1-\mu}\left(1 - 4\mu(3-\mu)\right.$$

$$\left.\times\frac{(2/\pi)K(k)}{4[|\mu|]^{1/2}+[(|\mu|+1)^3(3-|\mu|)]^{1/2}}\right),$$

where

$$k = \frac{4[|\mu|]^{1/2}-[(|\mu|+1)^3(3-|\mu|)]^{1/2}}{4[|\mu|]^{1/2}+[(|\mu|+1)^3(3-|\mu|)]^{1/2}}$$

$$= \frac{(|\mu|-1)^3(3-|\mu|)}{\{4[|\mu|]^{1/2}+[(|\mu|+1)^3(3-|\mu|)]^{1/2}\}^2},$$

with μ having its previous meaning, Eq. (36). The result is now numerically identical and analytically equivalent to the results of Houtappel. It differs formally from his answers by a Landen transformation. In this way, only one formula is needed

where Houtappel needs three. The same page contains an incorrect number for the zero-point entropy of the antiferromagnetic net. The number in Eq. (37c) is 0.323066; the series given there is correct. Both corrections do not change the major features and fixed points of the results or the qualitative conclusions. The energy-versus-temperature curves become somewhat more abrupt than those shown in Fig. 12.

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Spin Dynamics of Linear Heisenberg Magnetic Chains, F. B. McLean and M. Blume [Phys. Rev. B **7**, 1149 (1973)]. The expression for the diffusion constant D in Eq. (90) is missing a factor of 2. The correct expression is

$$D = \frac{2}{3N}\sum_{q'}\sin^2 q'\int_0^\infty dt'\, F_{q'}^2(t'). \qquad (90)$$

The values quoted for the diffusion constant at high temperature are also too small by a factor of 2. The second sentence after Eq. (90) should read, "The result from the numerical solutions is $D = 0.69$, or in terms of conventional units for a system of spin S the result is $D = 1.38\,Ja^2[S(S+1)]^{1/2}$." The low-temperature values for the diffusion constant given in the following paragraphs are correct as they stand.