Nuclear Quadrupole Moment of Al^{27} in Al_2O_3

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The electric field gradient at the Al site in corundum has been estimated considering the Al-O_6 complex embedded in Al_2O_3. The complete metal-ion–ligand overlaps have been taken into account. Our results in conjunction with the observed quadrupole coupling constant yield the value 0.148 b for the quadrupole moment of Al^{27}, which is in very good agreement with the experimental value 0.149 b.

Quite recently, the overlap effects for the determination of the quadrupole moment of Al^{27} in Al_2O_3 have been investigated by Sawatzky and Hupkes.[1] An important shortcoming of their method, however, is that it considers the "local" approximation[2] which neglects the terms involving the anion orbitals in the matrix element for the field gradient. Since the neglected terms (especially those terms which consider the charge density localized near the ligands) are amplified by the influence of the Sternheimer factor, these terms are expected to be important. In our treatment, we have included the effect of all such terms. Moreover, besides considering the overlap distortion of the cation $2p$ orbital due to the $2s$ and $2p$ ligand orbitals, the overlap distortion of the $2s$ cation orbital has also been taken into account. (The $2s$ cation orbital does not contribute to the field gradient in the "local" approximation. However, it gives a nonzero contribution if this approximation is not assumed.)

The method we are going to pursue determines the electric field gradient at the Al site due to the electrons and nuclei in the complex Al-O_6, and due to the monopoles and dipoles on the rest of the ions in the crystal. The many-electron wave function for the electrons on the complex has been formed by Hund–Mulliken–Van Vleck[3] molecular-orbital linear combination of atomic orbitals considering only the overlap effects. Since we have a diamagnetic system with doubly occupied states, the many-electron wave function Ψ for the complex Al-O_6 may be taken, in the Hartree-Fock approximation, as a Slater determinant formed by the one-electron molecular orbitals Ψ_i. The electric field gradient due to the electrons on the complex is then given by

$$q_{\mathrm{el}} = 2e\sum_i \langle\Psi_i|[(3\cos^2\theta_i - 1)/r_i^3]|\Psi_i\rangle, \tag{1}$$

where a factor 2 is included since the states are doubly occupied; e is the charge of an electron. The molecular orbitals Ψ_i are the antibonding and bonding orbitals constructed from the cation and anion atomic orbitals. The antibonding orbitals may be written as

$$\Psi_i = N_i[\varphi_i - \sum_{gLM} S_{gLMi}\chi_{gLM}], \tag{2}$$

where φ_i are the cation orbitals and χ_{gLM} are the anion orbitals with quantum numbers L, M, located near the ligand site designated by g. The bonding orbitals (in the absence of charge-transfer covalency) are just the anion orbitals. The parameters S_{gLMi} are the overlap integrals $\langle\chi_{gLM}|\times|\varphi_i\rangle$ obtained from the condition that the bonding and antibonding orbitals are orthogonal.

The total contribution to the field gradient q is due to the electrons on the complex, the nuclei of the ligands, and the monopoles and dipoles on the remaining lattice. Thus,

$$q = (1-R)[\sum_i |N_i|^2\langle\varphi_i|\cdot|\varphi_i\rangle - 2\sum_{igLM} S_{gLM}\langle\varphi_i|\cdot|\chi_{gLM}\rangle] + (1-\gamma_\infty)[\sum_{igLML'M'} S_{gLMi}{}^* S_{gL'M'i}\langle\chi_{gLM}|\cdot|\chi_{gL'M'}\rangle + \sum_{gLM}\langle\chi_{gLM}|\cdot|\chi_{gLM}\rangle + G|e|\sum_g (3\cos^2\theta_g - 1)/r_g^3 + q_{RL}'], \tag{3}$$

where the symbol $|\cdot|$ stands for the operator $2e(3\cos^2\theta_i - 1)/r_i^3$. In Eq. (3), the first term is the "local" contribution (q_l); the second term is the "nonlocal" contribution[2] (q_{nl}); the third term is the "distant" contribution arising from the antibonding orbitals (q_d); the fourth term is the "distant" contribution arising from the bonding orbitals (q_{dB}); the fifth term is the contribution from the nuclear charges on the ligands (q_n); and the sixth term is the contribution from the ions on the rest of the lattice (q_{RL}). For the summation over i, we take into account the $2s$ and $2p$ cation orbitals whereas for L, M, (and L', M'), the $2s$ and $2p$ anion orbitals. Since the $1s$ orbital is very much localized near the ligand nucleus, it is accurately taken that the contribution from the two electrons on it completely cancels the contribution from the two positive charges on the ligand nucleus. The factor of 6 in the last term but one in Eq. (3) has been introduced appropriately on account of this. The factors $1-R$ and $1-\gamma_\infty$ are the appropriate antishielding factors. For the "nonlocal" terms the factor $1-R$, instead of $1-\gamma_\infty$, has been introduced simply because the electron density $\varphi_i^* \chi_{gLM}$ encountered in such terms is dominant in the region close to the cation site.

For the simplification and evaluation of the matrix elements and the overlap parameters in Eq. (3), use is made of the rotation groups to rotate the functions and Löwdin's α-function technique[4] to expand the functions from one center to the other. As for the crystal structure parameters,[5] they are taken the same as in Ref. 1 to facilitate comparison. The overlap and two-center integrals are calculated using Clementi's $2s$ and $2p$ wave functions[6] for Al^{3+} and Watson's $2s$ and $2p$ wave functions[7] for O^{2-} in a 2+ stabilizing potential well. The detailed calculations yield (denoting the results without antishielding by primes) $q_l' = 1.2656$, $q_{nl}' = -0.26481$, $q_d' = 0.02167$, $q_{dB}' = 1.4394$, $q_n' = -1.1547$, and $q_{RL}' = 0.03809$ (in 10^{14} esu). q_l' is the "local" contribution[8] to the field gradient due to the overlap between the $2p$ cation wave functions[9] and $2s$ and $2p$ anion wave functions. The value of q_{nl}' incorporates the effects of overlaps of the $2s$ and $2p$ anion wave functions with the cation wave functions. If the various contributions in q_{nl}' are separated (for comparison), we have -0.04587, -0.18213, and 0.02180 (in 10^{14} esu) for the overlap effects of the $2p$ cation wave functions with the $2s$, $2p_\sigma$, and $2p_\pi$ ligand wave functions and -0.00950 and -0.04911 (in 10^{14} esu) for those of the $2s$ cation wave functions with $2s$ and $2p_\pi$ ligand wave functions, respectively. As for q_d', various cross terms are also involved and, therefore, it is not possible to separate them into simple contributions. It must be noticed that q_{nl}' (which was neglected in Ref. 1) is about 20% of q_l' and is of opposite sign. The field gradient from the monopoles and dipoles on the ions in the remaining lattice, q_{RL}', has been obtained by subtracting off the nearest-neighbor contributions from the total contribution.[10]

Using $1-R = 1.005$[11] and $1-\gamma_\infty = 3.59$,[12] we then obtain $q = 2.2518 \times 10^{14}$ esu which gives $Q(Al^{27}) = 0.148$ b from the experimental value[13] of $eqQ = 2.40$ MHz for Al^{27} in Al_2O_3. The value of Q calculated here is in very good agreement with $Q = 0.149$ b determined from atomic beam experiments.[14] The values of $Q(Al^{27})$ reported earlier by Sawatzky and Hupkes[1] and by Artman[10] are 0.155 b and 0.377 b, respectively.

Thus, the molecular-orbital approach used here has been very successful in determining the electric field gradient and hence the quadrupole moment accurately. Such calculations are in progress for Fe_2O_3 and similar systems (e.g., $Al_2O_3{:}Fe^{3+}$). The preliminary results for these are also very encouraging. The results of the complete finding will be reported in subsequent publication.

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[8] The value of q_l' reported in Ref. 1 is 1.27×10^{14} esu which is to be compared with our value.

[9] As mentioned earlier, q_l' becomes identically zero for the $2s$ cation wave function because of the matrix element involved.

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