Theoretical Investigations of the EPR Parameters of Ti^{3+} in Beryl Crystal

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The EPR parameters (g factors $g_\parallel$, $g_\perp$ and hyperfine structure constants $A_\parallel$, $A_\perp$) of Ti^{3+} ion at the sixfold coordinated Al^{3+} site with trigonal symmetry in beryl crystal are calculated by the third-order perturbation formulas of $3d^1$ ions in a trigonal octahedron. In the calculations, the crystal-field parameters are obtained by the superposition model, and the impurity-induced local lattice relaxation (which is similar to that found for Fe^{3+} in beryl) is considered. The calculated EPR parameters (and also the optical spectra) are in reasonable agreement with the experimental values.

Key words: Electron Paramagnetic Resonance; Crystal- and Ligand-Field Theory; Local Lattice Distortion; Ti^{3+}; Beryl.

1. Introduction

Beryl ($Be_3Al_2Si_6O_{18}$) crystals, doped with transition metal $(3d^n)$ ions, can have many colours. So they are important in the gem industry and increasingly in the laser industry. Many EPR experiments have been made to study the $3d^n$ ions in beryl crystals [1 – 7]. In these studies it is found that $3d^n$ ions in beryl often substitute the sixfold coordinated Al^{3+} site with D_3 point symmetry [1 – 7] (note: in a few cases, $3d^n$ ions, e.g., Ti^{3+}, can occupy the irregular tetrahedral Si^{4+} site [6]). For example, the EPR spectra due to Ti^{3+} $(3d^1)$ substituted in the trigonally distorted Al^{3+} site of beryl were measured by several groups, and the EPR parameters (g factors $g_\parallel$, $g_\perp$ and hyperfine structure constants $A_\parallel$, $A_\perp$) were given [5 – 7]. These EPR parameters, obtained by different groups, are very similar. Until now, besides a simple and rough analysis based on the first approximation (where only the T_{2g} orbitals and splittings in an octahedral and trigonal field are considered [5]), no satisfactory theoretical explanation related to the local geometry of the Ti^{3+} impurity center in beryl has been given. In this paper we calculate the EPR parameters $g_\parallel$, $g_\perp$, $A_\parallel$ and $A_\perp$ of Ti^{3+} in beryl crystal from third-order perturbation formulas of the EPR parameters (where the contribution due to the ^2E_g orbitals and the covalency reduction effect are included). In the calculations, the crystal-field parameters are calculated by the superposition model and the impurity-induced local lattice relaxation is considered. The results are discussed.

2. Calculation

When Ti^{3+} $(3d^1)$ is in an octahedral field, the energy level ^2D is split into ^2E_g and $^2T_{2g}$ levels. If the octahedron is distorted along the C_3 axis, the energy level ^2E_g remains unsplit and the level $^2T_{2g}$ is further split into an orbital doublet ^2E_g and an orbital singlet $^2A_1$ [5, 8]. For the studied compressed trigonal octahedron, the ground state is the singlet $^2A_1$. Thus, from the method in [8], the third-order perturbation formulas of the EPR parameters $g_\parallel$, $g_\perp$, $A_\parallel$ and $A_\perp$ for a $3d^1$ ion in a trigonal octahedral site can be written as

$$g_\parallel = g_s - (g_s + k)\zeta^2/E_2^2,$$

$$g_\parallel = g_s - 2k\zeta/E_2 - 4k\zeta/E_1 - (g_s - 2k)\zeta^2/(2E_2^2),$$

$$A_\parallel = P\left[-K + \frac{4}{7} - \frac{1}{7}(g_\perp - g_s)\right],$$

$$A_\perp = P\left[-K - \frac{2}{7} + \frac{15}{14}(g_\perp - g_s)\right], \quad (1)$$

	$g_\parallel$	$g_\perp$	$A_\parallel(10^{-4}\ \mathrm{cm}^{-1})$	$A_\perp(10^{-4}\ \mathrm{cm}^{-1})$
Calculation	1.987	1.844	0.1	24.7
Calculation [5]	1.987 ± 0.001	1.842 ± 0.002	0.0 ± 0.1	18.0 ± 0.1
Experiment [6]	1.9895 ± 0.001	1.8416 ± 0.001	-2.0 ± 0.5	19.5 ± 0.5

Table 1. The EPR parameters (g factors $g_\parallel$, $g_\perp$ and hyperfine structure constants $A_\parallel$, $A_\perp$) for Ti^{3+} at the trigonal octahedral Al^{3+} site in beryl crystal.

where g_s (≈ 2.0023) is the free-electron value, k the orbital reduction factor, ζ and P are, respectively, the spin-orbit coupling parameter and the dipolar hyperfine structure constant in crystals. Considering the covalency reduction effect [9–11], we have $\zeta \approx N^2\zeta_0$, $P \approx N^2 P_0$, where the covalency reduction factor $N^2 \approx k$ and ζ_0 and P_0 are the corresponding parameters in free state. For a free Ti^{3+} ion we have $\zeta_0 \approx 154\ \mathrm{cm}^{-1}$ [12] and $P_0 \approx -25.6 \cdot 10^{-4}\ \mathrm{cm}^{-1}$ [13]. The value of K, the core polarization constant (we take $K \approx 0.6$ here), is close to that (≈ 0.725 [14]) for Ti^{3+} in ZnS crystal. E_1 is the energy difference between the ground state ${}^2A_1$ and ${}^2E_g$ in cubic symmetry, and E_2 is that between ${}^2A_1$ and ${}^2E_g$ (${}^2T_{2g}$) caused by a trigonal crystal-field. By diagonalizing the 2×2 ${}^2E_g$ energy matrix we have

$$\begin{aligned} E_1 &= 5D_q + \frac{5}{2}D_\sigma + \frac{15}{2}D_\tau + \frac{1}{2}\sqrt{Q}, \\ E_2 &= 5D_q + \frac{5}{2}D_\sigma + \frac{15}{2}D_\tau - \frac{1}{2}\sqrt{Q} \end{aligned} \tag{2}$$

with

$$\begin{aligned} Q = {} & (10D_q)^2 - \frac{20}{3}D_q(3D_\sigma - 5D_\tau) \\ & + (3D_\sigma - 5D_\tau)^2, \end{aligned} \tag{3}$$

in which D_q is the cubic field parameter, and D_σ and D_τ are the trigonal field parameters.

According to the superposition model [15], for the studied system the trigonal field parameters can be expressed as

$$\begin{aligned} D_\sigma &= -\frac{3}{7}\bar{A}_2(R)\sum_{i=1}^{2}\left(3\cos^2\theta_i - 1\right), \\ D_\tau &= -\bar{A}_4(R)\sum_{i=1}^{2}\left[\frac{1}{7}\left(35\cos^4\theta_i - 30\cos^2\theta_i + 3\right)\right. \\ &\qquad \left. + \sqrt{2}\sin^3\theta_i\cos\theta_i\right], \end{aligned} \tag{4}$$

where $\bar{A}_2(R)$ and $\bar{A}_4(R)$ are the intrinsic parameters with the metal-ligand distance R (note: for beryl crystal, $R_1 \approx R_2 \approx R \approx 1.904$ Å [16], where the subscripts 1 and 2 denote the three oxygen ligands in the upper and lower triangles, respectively). For $3d^n$ ions in an octahedron with cubic approximation, $\bar{A}_4(R) = \frac{3}{4}D_q$ [15, 17], and $\bar{A}_2(R) \approx (9 \sim 12)\bar{A}_4(R)$ obtained for $3d^n$ ions in many crystals [18–20]. We take $\bar{A}_2(R) \approx 12\bar{A}_4(R)$. The cubic field parameter D_q is often estimated from the optical spectra, so we estimate D_q of Ti^{3+} in beryl as follows: Considering that Ti^{3+} in both beryl and Al_2O_3 replace the octahedral Al^{3+} sites, and that the average metal-ligand distance R in beryl is slightly smaller than that in Al_2O_3 (≈ 1.912 Å [21]), we can reasonably estimate $D_q \approx 1950\ \mathrm{cm}^{-1}$ in beryl:Ti^{3+} from the value of $D_q \approx 1910\ \mathrm{cm}^{-1}$ in $Al_2O_3:Ti^{3+}$ [22]. θ_i is the angle between the R_i and C_3 axis. In pure beryl crystal, $\theta_1^h \approx 55.30°$ and $\theta_2^h \approx 59.68°$ [16]. Since the impurity can induce a local lattice relaxation in the impurity centers in crystals, as in the case of Fe^{3+} in beryl crystal [23], the angle θ_i in the Ti^{3+} center may be different from the corresponding value in the pure beryl crystal. So, θ_i can be assumed as adjustable parameters. To decrease the number of adjustable parameters, we take only θ_2 as adjustable. Thus, in the above formulas, the factors k and θ_2 are unknown. By fitting the calculated EPR parameters to the experimental values, we obtain

$$k \approx 0.918, \quad \theta_2 \approx 56.5°. \tag{5}$$

Obviously, the local angle is smaller than that in the host crystal. In Table 1 the calculated and experimental EPR parameters are shown.

3. Discussion

The above studies suggest that by considering a suitable local lattice relaxation the EPR parameters $g_\parallel$, $g_\perp$, $A_\parallel$ and $A_\perp$ for Ti^{3+} at a trigonal octahedral Al^{3+} site of beryl crystal can be reasonably explained (see Table 1) from the third-order perturbation formulas of a $3d^1$ ion in trigonal symmetry. In addition, based on the local lattice distortion, the calculated transition energy E_1 of ${}^2A_1 \rightarrow {}^2E_g({}^2D)$ is $20680\ \mathrm{cm}^{-1}$, which agrees with that obtained from the absorption spectrum of Ti^{3+} at the Al^{3+} site in beryl ($\approx 20200\ \mathrm{cm}^{-1}$ [6]). The calculated $E_2 \approx 1960\ \mathrm{cm}^{-1}$ [note: $E_2 \approx -v$ if the interaction between the irreducible representations ${}^2E_g({}^2D)$ and ${}^2E_g(2T_{2g})$ is neglected] is also close to the trigonal field parameters $\nu \approx -1780$ and $-2564\,\mathrm{cm}^{-1}$ obtained in [6]. So, the impurity-induced local lattice relaxation and the above calculated formulas are reasonable.

The impurity-induced local lattice relaxation (characterized by the decrease in θ_2) of the Ti^{3+} center in beryl is qualitatively consistent with that of the Fe^{3+} center in beryl (in which the angle θ_2 is also smaller than θ_2 in the pure crystal [23]) obtained from the simple superposition model analysis of zero-field splitting b_2^0 [23], but the decrease in angle θ_2 for the Ti^{3+} center in beryl is smaller than that for the Fe^{3+} center in beryl ($\theta_2 \approx 55.44^\circ$ [23]). It appears that the local structure in an impurity center is different not only from the host one, but also from impurity to impurity.

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[1] A. Edgar and D. R. Hutton, J. Phys. C **11**, 5051 (1978).
[2] M. Dvir and W. Low, Phys. Rev. **119**, 1587 (1960).
[3] J. C. R. Mittani, S. Watanbe, M. Matsuoka, D. L. Baptista, and F. C. Zawislak, Nucl. Inst. Methods Phys. B **218**, 255 (2004).
[4] D. R. Hutton, F. A. Darmann, and G. J. Troup, Aust. J. Phys. **44**, 429 (1991).
[5] D. R. Hutton, J. R. Pilbrow, G. J. Troup, and J. O. Warne, Aust. J. Phys. **45**, 253 (1992).
[6] V. P. Solntsev and A. M. Yurkin, Cryst. Rep. **45**, 128 (2000).
[7] L. V. Bershov, Zh. Strukt. Khim. **10**, 141 (1969).
[8] A. Abragam and B. Bleaney, Electron Paramagnetic Resonance of Transition Metal Ions, Oxford University Press, London 1970.
[9] Z. Y. Yang, C. Rudowicz, and J. Qin, Physica B **318**, 188 (2002).
[10] M. G. Zhao, J. A. Xu, G. R. Bai, and H. S. Xie, Phys. Rev. B **27**, 1516 (1983).
[11] W. C. Zheng, Q. Zhou, X. X. Wu, and Y. Mei, Spectrochim. Acta A **61**, 1243 (2005).
[12] J. S. Griffith, The Theory of Transition-Metal Ions, Cambridge University Press, London 1964.
[13] B. R. McGarvey, J. Phys. Chem. **71**, 51 (1976).
[14] U. Kaufmann, A. Rauber, and J. Schneider, J. Phys. C **8**, L381 (1975).
[15] D. J. Newman and B. Ng, Rep. Prog. Phys. **52**, 699 (1989).
[16] B. Morosin, Acta Crystallogr. B **28**, 1899 (1972).
[17] W. L. Yu and M. G. Zhao, Phys. Rev. B **37**, 9254 (1988).
[18] C. Rudowicz and Y. Y. Zhou, J. Magn. Magn. Mater. **111**, 153 (1992).
[19] A. Edgar, J. Phys. C **9**, 4304 (1976).
[20] T. H. Yeom, S. H. Chon, M. L. Du, and M. S. Jang, Phys. Rev. B **53**, 3415 (1996).
[21] D. S. McClure, J. Chem. Phys. **38**, 2289 (1963).
[22] S. Garcia-Revilla, F. Rodriguez, R. Valiente, and M. Pollnau, J. Phys.: Condens. Matter **14**, 447 (2002).
[23] R. Buscher, K. P. Such, and G. Lehmann, Phys. Chem. Mirerals **14**, 553 (1987).