

Crystal Field Analysis of Cr^{3+} Doped SrAl_2O_4 Spinel

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The present work is devoted to the crystal field analysis of trivalent chromium doped in SrAl_2O_4 spinel in the frame of the exchange charge model of crystal field. Using the shell model and pair approximation, we optimize the geometric structure of the crystal. The approach enables the modeling of the crystal field parameters and thus calculates the energy level scheme of Cr^{3+} ions in spinel SrAl_2O_4 . The obtained results are compared with experimental data and discussed.

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1. Introduction

The spinel SrAl_2O_4 is generally regarded as a versatile material of great technological importance and physical behavior [1].

The crystal structure is related to AB_2O_4 spinel structure and belongs to the cubic space group $P2_1$ monoclinic, with eight formula units per cell. The A site has tetrahedral coordination, while the B site has distorted octahedral coordination [2].

The crystal structure of SrAl_2O_4 is derivative of the stuffed tridymite structure, in which all of the Si^{4+} is replaced by Al^{3+} and the charge compensating cation Sr^{2+} occupies the large open channels in the framework. This structure is less regular compared to the hexagonal structure of SrAl_2O_4 [3, 4].

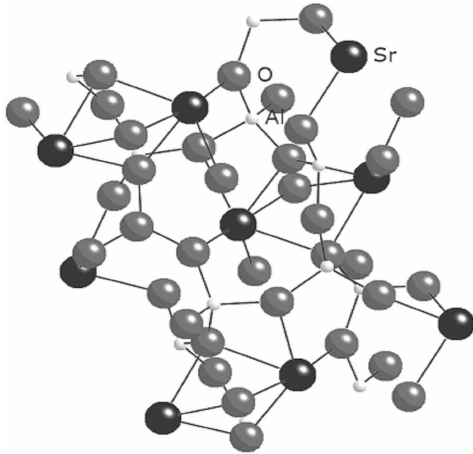


Fig. 1. The structure of SrAl_2O_4 .

A cationic site in the structure (Al^{3+}) is available for Cr^{3+} substitution and the new complex $[\text{CrO}_4]^{5-}$ is created [5]. The Cr^{3+} ion may occupy either an octahedral site or a tetrahedral site in the SrAl_2O_4 spinel (Fig. 1).

This work is devoted to crystal field analysis of trivalent chromium doped in SrAl_2O_4 spinel using exchange charge model (ECM) of crystal field. Based on the crystal structure data, modeled by shell model and pair approximation, our approach enables the modeling of the crystal field parameters (CFP) and thus calculates the energy level scheme of Cr^{3+} ions in spinel SrAl_2O_4 .

2. Crystal geometry optimization

For crystal structure calculations, we will use the GULP 3.0 computer program [6] and the shell model and pair approximation. First, we will do the optimization of the geometric structure of the crystal with impurity, and then the CFP and energy levels calculations. The lattice energy can be written as

$$U_{\text{lat}} = \frac{1}{2} \sum_i \sum_{k(\neq i)} V_{ik} + \frac{1}{2} \sum_i k_i \delta_i^2, \quad (1)$$

where $k_i \delta_i^2$ — the energy of the core-shell interaction of the i -th ion; V_{ik} — the interaction energy between the i -th and k -th ions, which can be expressed as

$$V_{ik} = \frac{X_i X_k}{|\mathbf{r}_i - \mathbf{r}_k|} + \frac{Y_i X_k}{|\mathbf{r}_i - \mathbf{r}_k + \delta_i|} + \frac{X_i Y_k}{|\mathbf{r}_i - \mathbf{r}_k - \delta_k|} + \frac{Y_i Y_k}{|\mathbf{r}_i - \mathbf{r}_k + \delta_i - \delta_k|} + f_{ik}(|\mathbf{r}_i - \mathbf{r}_k|) + g_{ik}(|\mathbf{r}_i - \mathbf{r}_k + \delta_i - \delta_k|), \quad (2)$$

where the functions

$$f_{ik}(r) = -A_{ik} \exp(-B_{ik}r)/r, \quad (3)$$

$$g_{ik}(r) = C_{ik} \exp(-D_{ik}r) - \lambda_{ik}/r^6. \quad (4)$$

$f_{ik}(r)$ describes the short-range screening of the electrostatic interaction between the ion cores; $g_{ik}(r)$ describes

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the short-range repulsion between the ion shells (which is written in the form of the Born–Mayer potential) and the Van der Waals interaction; X_i , Y_i are the core and shell charges of the i -th ion; \mathbf{r}_i is the vector defining the position of the ion core; δ is the vector defining the position of the ion shell relative to the ion core. The shell charges have been determined from the condition: $Z_i = X_i + Y_i$, where Z_i is the ion charge in the compound. To calculate Eqs. (1)–(4), we will use the parameters given in Tables I, II [7] and cell parameters are given in Table III.

TABLE I

The short-range interaction potential parameters (at. un.) [7].

| Pair | A | B | C | D | λ |
|--------------------------------|---------------------|------------------------|------|-----------------------|-----------|
| $\text{O}^{2-}-\text{O}^{2-}$ | 25.4 | 0.694 | 32.3 | 0 | 0 |
| $\text{O}^{2-}-\text{Al}^{3+}$ | 0.241×10^4 | 0.265 | 0 | 0 | 0 |
| $\text{O}^{2-}-\text{Sr}^{2+}$ | 0.196×10^4 | 0.325 | 0 | 0 | 0 |
| $k_{\text{O}} = 20.5$ | | $k_{\text{Sr}} = 21.5$ | | $k_{\text{Al}} = 404$ | |

TABLE II

The position of ions in the cell of SrAl_2O_4 and the charges of the ions [7].

| Atom | x | y | z | X_i | Y_i |
|-----------------|--------|--------|--------|-------|-------|
| Sr ₁ | 0.4905 | 0 | 0.2507 | 0.169 | 1.831 |
| Sr ₂ | 0.0292 | 0.9929 | 0.202 | 0.169 | 1.831 |
| Al ₁ | 0.1895 | 0.8314 | 0.7158 | 0.043 | 2.957 |
| Al ₂ | 0.7997 | 0.8394 | 0.7287 | 0.043 | 2.957 |
| Al ₃ | 0.7087 | 0.6685 | 0.2236 | 0.043 | 2.957 |
| Al ₄ | 0.6809 | 0.1707 | 0.7975 | 0.043 | 2.957 |
| O ₁ | 0.265 | 0.174 | 0.436 | 0.513 | 2.513 |
| O ₂ | 0.736 | 0.316 | 0.589 | 0.513 | 2.513 |
| O ₃ | 0.327 | 0.493 | 0.345 | 0.513 | 2.513 |
| O ₄ | 0.265 | 0.984 | 0.898 | 0.513 | 2.513 |
| O ₅ | 0.174 | 0.297 | 0.936 | 0.513 | 2.513 |
| O ₆ | 0.206 | 0.669 | 0.906 | 0.513 | 2.513 |
| O ₇ | 0.487 | 0.219 | 0.876 | 0.513 | 2.513 |
| O ₈ | 0.990 | 0.888 | 0.651 | 0.513 | 2.513 |
| Cr | – | – | – | 3 | – |

TABLE III

Cell parameters.

| | Exp. | Optimized | | Exp. | Optimized |
|-------------------|-------|-----------|----------|---------|-----------|
| α [degree] | 90 | 90 | a [nm] | 0.84470 | 0.8650255 |
| β [degree] | 93.42 | 92.0691 | b [nm] | 0.88160 | 0.9119741 |
| γ [degree] | 90 | 90 | c [nm] | 0.51630 | 0.5250639 |

To take into account we fixed the elementary cell side-bar according to measured values. The ions inside the cell could relax to minimal energy. For the calculations

of the structure of impurity centers, we used the Mott–Littleton method. In the calculations, the internal region around impurity ion consists of about 1300 ions. 40–85 thousands of ions in the adjoining region to the internal region could relax restrictedly.

3. Energy levels scheme

The energy levels of $3d$ electrons of the Cr^{3+} ions in a crystal field will be calculated diagonalizing the crystal field Hamiltonian. This Hamiltonian depends on CFPs, containing all the information about geometrical arrangement of the ligands around the impurity ion. In the ECM

TABLE IV

CFP (in cm^{-1}) for octahedrally coordinated Cr^{3+} ion in SrAl_2O_4 . Point charges contribution (PCC) and exchange charges contribution (ECC) are shown separately.

| Parameter | PCC | ECC | Total value |
|------------|-------|--------|-------------|
| B_2^{-2} | 670 | 2776 | 3446 |
| B_2^{-1} | 89 | 553 | 642 |
| B_2^0 | 524 | 1627 | 2151 |
| B_2^1 | –2698 | –9030 | –11728 |
| B_2^2 | 1962 | 7525 | 9487 |
| B_4^{-4} | 412 | 9121 | 9533 |
| B_4^{-3} | 47 | 13779 | 13826 |
| B_4^{-2} | –536 | –15392 | –15928 |
| B_4^{-1} | –355 | –11522 | –11877 |
| B_4^0 | –32 | –564 | –596 |
| B_4^1 | 405 | 10399 | 10804 |
| B_4^2 | –25 | –1897 | –1922 |
| B_4^3 | 976 | 41110 | 42086 |
| B_4^4 | –661 | –14071 | –14732 |

the CFPs B_p^k consist from two parts. The first arises from the electrostatic interaction between a $3d$ ion and ions of crystal lattice (treated as the point charges, without taking into account their electron structure), and the second one is proportional to the overlap of the wave functions of a central ion and ligands. Originally the ECM was proposed by Malkin [8] for rare earth ions, but later it has also been successfully applied to the transition metal ions in different hosts ([9–16] and references therein).

The overlap integrals between Cr^{3+} and O^{2-} ions functions were taken from [17]:

$$S(s) = \langle d0 | s0 \rangle = -1.5941 \exp(-0.74497r),$$

$$S(\sigma) = \langle d0 | s0 \rangle = 1.3496 \exp(-0.76490r),$$

$$S(\pi) = \langle d0 | s0 \rangle = 1.2614 \exp(-0.86530r).$$

To ensure the convergence of CFPs (especially those ones of the second rank), large clusters of 19577 ions (2779 ions of Sr^{2+} , 5605 ions of Al^{3+} and 11193 ions of O^{2-}) were considered.

TABLE V
Observed and calculated (this work) energy levels (in cm^{-1}) of Cr^{3+} ion in SrAl_2O_4 ($B = 559 \text{ cm}^{-1}$, $C = 2349 \text{ cm}^{-1}$, $G = 39.23$).

| Energy levels (O_h group notations) | This work | | [5] |
|-------------------------------------------|-------------------------|----------|----------|
| | Calculated | Averaged | Observed |
| 4A_2 | 0 | 0 | 0 |
| 2E | 6636 7749 | 7193 | 7210 |
| 2T_1 | 10676 11148 11746 | 11190 | — |
| 4T_2 | 10358 17944 19880 | 16060 | 16051 |
| 2T_2 | 20961 21185 21421 | 21189 | — |
| 4T_1 | 22468 23036 25184 | 23562 | 21598 |

The calculated CFPs values are shown in Table IV. The values of the ECM parameter G were determined from the positions of the first absorption band in the corresponding absorption spectra. The obtained values of CFPs were used to diagonalize the crystal field Hamiltonian in the space spanned by all 50 wave functions of 8 LS terms of Cr^{3+} (4F , 4P , 2H , 2G , 2F , 2^2D , 2P).

The spin-orbit interaction was not considered, since the absorption bands in the experimental spectra were broad and no fine structure was observed. Calculated energy levels are shown in Table V.

4. Conclusions

In this paper, the Cr^{3+} doped in SrAl_2O_4 covalent crystal at room temperature has been investigated theoretically.

Consistent crystal field analysis of the energy level splittings for the SrAl_2O_4 crystal doped with Cr^{3+} ions was performed within the ECM framework. Optimized crystal structure data were used to calculate the CFP val-

ues, which were used then to calculate the lowest terms of all considered ions.

By the diagonalization of crystal field Hamiltonian in 50 basis functions of d^3 configuration, the scheme of the energy levels of system was obtained.

The reasonable agreement between the calculated and experimental data has been obtained despite distorted octahedral site symmetry of Cr^{3+} .

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