

STATIC JAHN–TELLER MODEL FOR $\text{Cr}^{2+} (d^4)$ CENTRES OF TETRAHEDRAL SYMMETRY IN ZnS

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Abstract. The optical spectra of substitutional $\text{Cr}^{2+} (3d^4)$ in single crystals of ZnS can be understood by the application of the crystal field theory which requires modifications by introducing the Jahn–Teller effect. The structure of $\text{ZnS}(\text{Cr}^{2+})$ optical spectra has been interpreted with the help of a static Jahn–Teller model, spin–orbit, spin–spin, and the Tress interaction. The $|D|$ constant of the fine structure of ground-state Jahn–Teller energy levels has been established and two new transitions suggested.

Key words: Jahn–Teller model, crystal field, spin–orbit coupling.

1. INTRODUCTION

In recent years, the properties of Cr-doped ZnS have been investigated by means of various methods both theoretically and experimentally [^{1–10}].

The results show that chromium enters the lattice of ZnS in a substitutional position on the cation site. The effectively neutral charge state of the centre is Cr^{2+} with a $3d^4$ electron configuration, which is under the influence of the tetrahedral crystal field (T_d symmetry) of the ZnS host. It has been found that the crystal field theory [^{11, 12}] is a good starting point for giving an account of the energy levels of the d -shell electrons of these ions.

However, for a detailed comparison between theory and experiment, the lattice of ZnS will be treated as a dynamic system coupled to the electronic shell of the Cr^{2+} ion.

The failure of a static crystal field description and the effect of coupling between the ZnS lattice and the electronic d shell of the Cr^{2+} ion have led various authors to introducing static or dynamic Jahn–Teller models for the Cr^{2+} ground state and the excited states [^{13, 14}].

The main optical transitions, ${}^5E(D) \leftrightarrow {}^5T_2(D)$, of a Cr^{2+} ion appear as a doublet at 5218 and 5212 cm^{-1} , coinciding for emission and absorption

spectra, as a result of the splitting of the ground and the excited state multiplets under combined interactions. In a recent paper [10], a broad band (maximum near 1300 cm^{-1}) has been detected and interpreted as the ${}^5\hat{E}(T_2) \leftarrow {}^5\hat{B}_2(T_2)$ absorption between the sheets of the respective adiabatic potential surfaces in D_{2d} symmetry.

On the other hand, the new results on the near infrared absorption spectra recorded by high-resolution spectroscopy could not be interpreted in the energy-level scheme derived from the static Jahn–Teller effect.

The purpose of this paper is to discuss the influence of spin–orbit, spin–spin, and the Tress interactions [15] on the energy levels of Cr^{2+} ions. These interactions distort the tetragonal symmetry of the ZnS host and are manifested in the vibronic coupling of the electronic wavefunctions of Cr^{2+} with the modes of a certain symmetry [16], which indicates the presence of a Jahn–Teller effect.

2. STATIC JAHN–TELLER MODEL

The Hamiltonian for the $3d^4$ ion in a crystal can be written as

$$\mathcal{H} = \mathcal{H}_{fi} + \mathcal{H}_{CF} + \mathcal{H}_{JT} = \mathcal{H}_{es} + \mathcal{H}_{s-o} + \mathcal{H}_{s-s} + \mathcal{H}_{Tress} + \mathcal{H}_{CF} + \mathcal{H}_{JT} . \quad (1)$$

The free-ion Hamiltonian \mathcal{H}_{fi} (excluding the kinetic energy of electrons and their Coulomb attraction with the nucleus) consists of electrostatic repulsion between these $3d$ electrons:

$$\mathcal{H}_{es} = \sum_{i < j}^4 \frac{e^2}{r_{ij}} , \quad (2)$$

the spin–orbit interaction:

$$\mathcal{H}_{s-o} = \sum_{i=1}^4 \xi(r_i) \vec{s}_i \vec{l}_i , \quad (3)$$

the spin–spin interaction \mathcal{H}_{s-s} , and the Tress correction \mathcal{H}_{Tress} describing the two-body orbit–orbit polarization (see, e.g. [17]). \mathcal{H}_{CF} is the crystal (ligand) field Hamiltonian and \mathcal{H}_{JT} is the Jahn–Teller Hamiltonian. Since the ligand field is in the weak or the intermediate range, the basis of states in the $L - S$ coupling scheme can be taken as

$$|\psi \rangle = |d^4 \alpha S M_S L M \rangle , \quad (4)$$

where α is an extra quantum number (seniority) and the orbital quantum number $d = 2$. The matrix elements for the operators in Eq. (1) have been evaluated by Yeung and Rudowicz [18].

In a simple crystal field theory one assumes $\mathcal{H}_{JT} = 0$.

The terms of the $3d^4$ configuration of a free Cr^{2+} ion split into eleven $2S+1L$ multiplets, i.e. one spin quintet ($S = 2 : {}^5D$), five spin triplets

($S = 1 : {}^3P, {}^3D, {}^3F, {}^3G, {}^3H$) and five spin singlets ($S = 0 : {}^1S, {}^1D, {}^1F, {}^1G, {}^1I$). According to the Hund rules, the free ion ground state for $\text{Cr}^{2+}(3d^4)$ is 5D . A crystal field \mathcal{H}_{CF} of a tetrahedral (T_d) symmetry will split this state into an orbital doublet (5E) and an orbital triplet (5T_2), the latter being the ground state for Cr^{2+} . The spin-orbit, spin-spin, and the Tress interactions will then split the energy levels further.

As a result of a static Jahn-Teller interaction, the local symmetry of Cr^{2+} is reduced to D_{2d} , whereby the 5T_2 state is split into a ${}^5\hat{B}_2$ ground state and a ${}^5\hat{E}$ state elevated by $3E_{JT}(T_2)$ (E_{JT} represents the Jahn-Teller energy). The excited 5E state is split into ${}^5\hat{B}_1$ and ${}^5\hat{A}_1$ components, separated by $4E_{JT}(E)$:

$${}^5T_2 \rightarrow {}^5\hat{B}_2 + {}^5\hat{E}, \quad (5)$$

$${}^5E \rightarrow {}^5\hat{A}_1 + {}^5\hat{B}_1, \quad (6)$$

where:

$${}^5\hat{A}_1 : |e\theta\rangle; \quad {}^5\hat{B}_1 : |e\epsilon\rangle; \quad {}^5\hat{E} : |t_2\xi\rangle, |t_2\eta\rangle; \quad {}^5\hat{B}_2 : |t_2\zeta\rangle. \quad (7)$$

The " $\hat{}$ " characterize the irreducible representations of the tetragonal group D_{2d} . The degeneracy of these states is lifted by the spin-orbit, spin-spin, and the Tress interactions as follows:

$${}^5\hat{A}_1 : \hat{\Gamma}_1 + \hat{\Gamma}_3 + \hat{\Gamma}_4 + \hat{\Gamma}_5,$$

$${}^5\hat{B}_1 : \hat{\Gamma}_1 + \hat{\Gamma}_2 + \hat{\Gamma}_3 + \hat{\Gamma}_5,$$

$${}^5\hat{B}_2 : \hat{\Gamma}_1 + \hat{\Gamma}_2 + \hat{\Gamma}_4 + \hat{\Gamma}_5,$$

$${}^5\hat{E} : \hat{\Gamma}_1 + \hat{\Gamma}_2 + \hat{\Gamma}_3 + \hat{\Gamma}_4 + 3\hat{\Gamma}_5,$$

where $\hat{\Gamma}_1, \hat{\Gamma}_2, \hat{\Gamma}_3, \hat{\Gamma}_4$ are one-dimensional representations and $\hat{\Gamma}_5$ is a two-dimensional representation of the D_{2d} group. The set of the energy levels associated with the irreducible representations $\hat{\Gamma}_i$ will be named fine structure. Note that the energy distances of the fine components in the ground state ${}^5\hat{B}_2$ are $3|D|$ between the lowest $\hat{\Gamma}_1, \hat{\Gamma}_2$ ground state and $\hat{\Gamma}_5$, and $4|D|$, between the lowest $\hat{\Gamma}_1, \hat{\Gamma}_2$ ground state and $\hat{\Gamma}_4$ (see Fig. 1a in [10]).

The main optical no-phonon transition ${}^5E(D) \leftrightarrow {}^5T_2(D)$, observed experimentally, appears as a doublet at 5218 and 5212 cm^{-1} , coinciding for emission and absorption spectra. This doublet is determined by transitions from the ${}^5E(D)$ excited state into the fine components $\hat{\Gamma}_1, \hat{\Gamma}_2$, and $\hat{\Gamma}_5$ of the ${}^5T_2(D)$ ground state. From these results we obtain $3|D| = 6 \text{ cm}^{-1}$, in agreement with those of [2, 10, 19].

The transition $\hat{\Gamma}_5 (^5\hat{B}_2) \leftarrow \hat{\Gamma}_1, \hat{\Gamma}_2 (^5\hat{B}_2)$ may be described as a magnetic-dipole transition, similar to the Cr^{2+} in ZnSe crystal [20]. $^5\hat{E}(T_2) \leftarrow ^5\hat{B}_2(T_2)$, which takes place between the "Jahn–Teller" components of the $^5T_2(D)$ ground state, has been investigated experimentally by Goetz et al. [10]. They have detected an absorption band with the maximum near 1300 cm^{-1} , which indicates a Jahn–Teller energy $E_{JT} \sim 430 \text{ cm}^{-1}$.

This band could consist of two or three bands ascribed to the transitions from the fine energy levels $\hat{\Gamma}_1, \hat{\Gamma}_2$, and $\hat{\Gamma}_5$ or/and $\hat{\Gamma}_4$ of the Jahn–Teller ground state $^5\hat{B}_2$.

3. CONCLUSION

The fine structure of the energy levels of the Cr^{2+} centre in ZnS crystal plays a major role in the interpreting of optical spectra of this system. The experimental results [10] allow one to determine the $3|D|$ energy between $\hat{\Gamma}_1, \hat{\Gamma}_2$ ground states and the first excited $\hat{\Gamma}_5$ state of $^5\hat{B}_2(T_2)$ Jahn–Teller energy level.

The observed experimental band [10] with the maximum near 1300 cm^{-1} can consist of two or three bands ascribed to the transitions between the fine energy levels of $^5\hat{B}_2(T_2)$ ground state and the first excited $^5\hat{E}_2(T_2)$ Jahn–Teller energy level. Thus we suggest that the static Jahn–Teller effect gives a good description of the tetrahedral symmetry of Cr^{2+} ions in ZnS hosts.

REFERENCES

1. Vallin, J. T., Slack, G. A., Roberts, S., Hughes, A. E. Phys. Rev., 1970, **B2**, 4313–4333.
2. Vallin, J. T., Watkins, G. D. Phys. Rev., 1974, **B9**, 2051–2072.
3. Grebe, G., Roussos, G., Schulz, H.-J. J. Phys., 1976, **C9**, 4511–4516.
4. Kaminska, M., Baranowski, J. M., Uba, S. M., Vallin, J. T. J. Phys., 1979, **C12**, 2197–2203.
5. Biernacki, S. W., Schulz, H.-J. Phys. stat. sol.(b), 1981, **103**, K163–K167.
6. Fazzio, A., Caldas, M. J., Zunger, A. Phys. Rev., 1984, **B30**, 3430–3455.
7. Abhvani, A. S., Bates, C. A., Clerjaud, B., Pooler, D. R. J. Phys., 1982, **C15**, 1345–1353.
8. Abhvani, A. S., Bates, C. A., Pooler, D. R. J. Phys., 1984, **C17**, 1713–1721.
9. Goetz, G., Schulz, H.-J. Solid State Commun., 1992, **84**, 523–525.
10. Goetz, G., Zimmermann, H., Schulz, H.-J. Z. Phys., 1993, **B91**, 429–436.
11. Griffith, J. S. The Theory of Transition Metal Ions. Cambridge University Press, Cambridge, 1961.
12. Hutchins, M. T. – In: Seitz, F. and Turnbull, D. (eds.) Solid State Physics. Academic Press, New York, 1965, **16**, 227.
13. Ham, F. S. Phys. Rev., 1965, **138**, A1727–1740; 1968, **166**, 307–321.
14. Sturge, M. D. – In: Seitz, F. and Turnbull, D. (eds.) Solid State Physics. Academic Press, New York, 1967, **20**, 91.
15. Tress, R. E. Phys. Rev., 1951, **82**, 683–696.
16. Bersuker, I. B., Polinger, V. Z. Vibronic Interactions in Molecules and Crystals. Springer, Berlin, 1989.
17. Geroch, M., Slade, R. C. Ligand Field Parameters. Cambridge University Press, London, 1973.
18. Yeung, Y. Y., Rudowicz, C. Computers Chem., 1992, **16**, 207–216.
19. Grebe, G., Schulz, H.-J. Z. Naturforsch., 1974, **A29**, 1813–1817.
20. Vallin, J. T., Slack, G. A., Roberts, S., Hughes, A. E. Solid State Commun., 1969, **7**, 1211–1215.

STAATILINE JAHNI-TELLERI MUDEL TETRAEEDRILISE SÜMMEETRIAGA $\text{Cr}^{2+}(d^4)$ TSENTRI TARVIS ZnS KRISTALLIS

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Asendusliku $\text{Cr}^{2+}(3d^4)$ optilised spektrid ZnS kristallis on interpreteeritavad kristallivälja teooria abil, mida on vaja modifitseerida Jahni-Telleri efekti lisamisega. ZnS (Cr^{2+}) optiliste spektrite struktuur on interpreteeritud staatilise Jahni-Telleri mudeli, spinn-orbitaalse, spinn-spinn- ja Tressi interaktsiooni abil. On määratud põhiseisundi Jahni-Telleri energianivoode peenstruktuuri konstant $|D|$ ja osutatud kahele uuele siirdele.

СТАТИЧЕСКАЯ ЯН-ТЕЛЛЕРОВСКАЯ МОДЕЛЬ ДЛЯ ЦЕНТРА $\text{Cr}^{2+}(d^4)$ ТЕТРАЭДРИЧЕСКОЙ СИММЕТРИИ В КРИСТАЛЛЕ ZnS

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Оптические спектры центра замещения $\text{Cr}^{2+}(3d^4)$ в кристалле ZnS интерпретируемы с использованием теории кристаллического поля, модифицированного эффектом Яна-Теллера. Структура оптических спектров ZnS (Cr^{2+}) интерпретирована с помощью статической ян-теллеровской модели, спин-орбитального и спин-спинового взаимодействий и взаимодействия Тресса. Определена постоянная $|D|$ тонкой структуры ян-теллеровских энергетических уровней основного состояния и показано наличие двух новых переходов.