

Electronic Structure of CaF_2 CrystalKun Wu¹, Changxin Guo¹, Ru Dong², Chaoxi Shi^{1,2}

1. Phys. Dept., University of Science and Technology of China, Hefei 230026, China

2. National Synchrotron Radiation Laboratory, USTC, Hefei 230026, China

CaF_2 crystal is a fast, high collection efficiency scintillator. Since it was proposed as position sensitive read by calorimeter of LSP, much work has been made on this material. But almost no theoretical work has been done on this field. In this paper, we use different cluster model and try to complete the electronic structure of this crystal, including LaF_3 doped by Ce^{3+} and CaF_2 crystal. Results are compared with the experiment. It is found that Ce^{3+} ions play an important role in the optical property of CaF_2 crystal.

1. Introduction

With the development of high energy physics and astrophysics physics, the search for fast, hard emission crystal is very active in recent years. It is pointed out^[1] this heavy inorganic scintillator CaF_2 seems rather promising for application in electromagnetic calorimetry due to its short decay time and high light yield. Nevertheless, as we know, the energy structure of this scintillator has not been reported yet. Recently, we have used a cluster model to calculate the energy structure of this material to obtain better understanding of the luminescence properties of CaF_2 .

2. Theoretical method

In this work, we employ the Hartree-Fock-Slater model for determining the occupied levels and lowest excitation level of CaF_2 , adopting the simplest one-electron direct-transition to interpret the excitation spectra. Thus, the effective Hamiltonian is

$$H = T + V_c + V_x \quad (1)$$

where the first two terms are the kinetic energy and nucleus potential, respectively, and the exchange potential operator V_x is approximately expressed by the local potential

$$V_x = -3\alpha(3\rho/\pi)^{1/3} \quad (2)$$

where ρ is the electronic charge density, and the

exchange coefficient α is treated as an adjustable parameter, which in our work is set as 0.7.

A single-particle excitation energy can be generally written as

$$\Delta E_{r \rightarrow s} = \epsilon_s - \epsilon_r + U_{rs} \quad (3)$$

where ϵ_r and ϵ_s are one-electron eigenvalues of H , and U_{rs} denotes self-energy and correlation terms derived from many-electron theory. In the Hartree-Fock model U_{rs} takes a simple well-known form^[2], but it is difficult in calculation. If it were complicated, ϵ_r and ϵ_s around all eigenvalues of the many-electron system (ground state). The "transition state" method has been suggested as a simple alternative, but it requires a separate calculation for each transition.^[3] For the present, we investigated the simple method generally used in band theory, of determining all ϵ_r from a single potential and neglecting all U_{rs} correlation.

3. Cluster model selection

CaF_2 adopts the same structure as LaF_3 , the space group of these two crystals is $Fm\bar{3}C$.^[4] The highest point group of this structure is D_{2h} . In a each molecule, the point group number is 8, i.e. each orbital is characterized by 8 orbitals. We used $(\text{CaF}_2)_n^+$ cluster to calculate the electronic structure for the first time. The symmetry of $(\text{CaF}_2)_n^+$ is C_{2v} . The choice of this model is reasonable verified in the view that as each molecule or complex units separately from the crystal. This model does not represent the structure of CaF_2 crystal itself, but it

can better represent the structure of LaF_3 doped with Ce^{3+} . As to LaF_3 doped with Ce^{3+} , Ce^{3+} replaces the La^{3+} and forms localized structure of LaF_3 crystal [2]. Basically, we use the $(\text{Ce}_2\text{F}_7)^{3+}$ cluster, which gives better representation of the crystal structure, to calculate the energy structure of the crystal. The Double Variational X α method has been used for the calculation. Details of the DV-X α formulation has been given elsewhere [3-6]. The variational method is based on the SCF (single-charge-orbital) basis. The sampling points are 300 for each step.

4. Results and discussion

(1). $(\text{Ce}_2\text{F}_7)^{3+}$ cluster: The structure of the cluster adopts C_2 symmetry. In such structure, the environmental crystal field is composed of 9 F ions. The Ce^{3+} center possesses a single active electron, in which 4f orbit is split weakly by crystal field. On the other side, the unoccupied 5d orbital is largely influenced by the environmental field. Thus the 4f-5d transition is split into 7 components. Fig.1 shows absorption spectrum of $\text{LaF}_3:\text{Ce}$ 0.05% [7]. The 7 peaks on the right correspond to them 5 energies. Using one-electron direct transition approximation, mentioned above, Table 1 gives them calculated results. The absorption peaks presented in Fig.1 are also listed in Table 1. As discussed in section 3, the two results agree with each other. The remaining peak in Fig.1 (157nm, 7.86eV) can be identified from our calculation as 4f-4f transition.

Table 1: Comparing calculation values with experimental results of absorption peaks obtained in $\text{LaF}_3:\text{Ce}$ in eV.

Experiment	6.5	6.0	5.6	5.9	6.9
Calculation	6.48	6.5	5.9	5.2	6.1

(2). $(\text{Ce}_2\text{F}_7)^{3+}$ cluster: The space group of CeF_3 is $R\bar{3}c$. This is a two-point space group. In this structure, each unit cell contains 4 Ce^{3+} and 14 F ions. To avoid complex calculation, we chose $(\text{Ce}_2\text{F}_7)^{3+}$ cluster, which is just a half of the total number of water in a unit cell. The other water in unit cell can be rebuilt by displacing the cluster along z-axis. Compared to the above cluster model, this model gives better representation of crystal field.

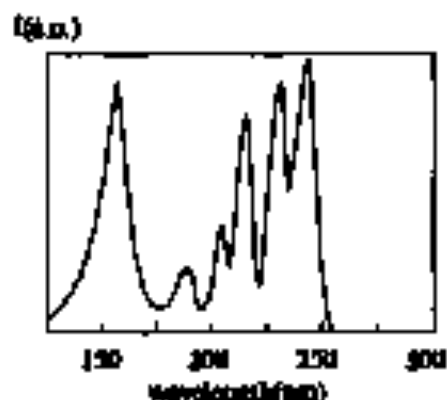


Fig.1 Absorption spectrum of $\text{LaF}_3:\text{Ce}$ (0.05%)

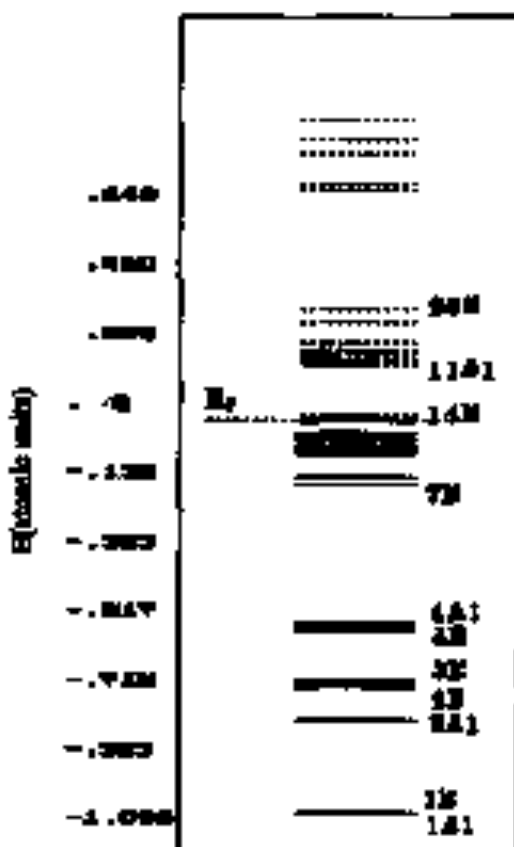


Fig.2 The energy level diagram of $(\text{Ce}_2\text{F}_7)^{3+}$ cluster in our calculation. (partic representation).

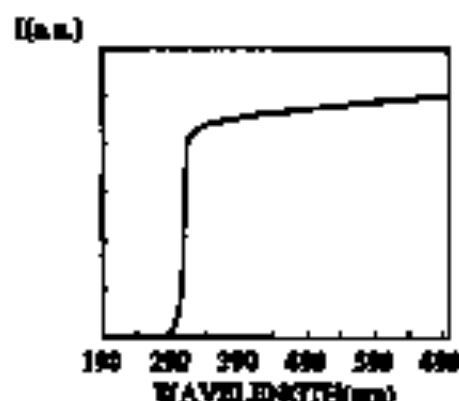


Fig.3 The transmission spectrum of a CoF_2 crystal.

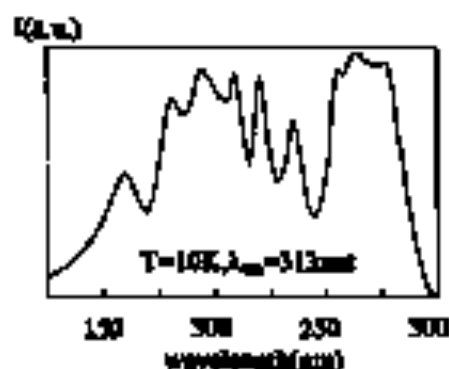


Fig.4 The Excitation spectrum of a CoF_2

To simulate the environment, the Wigner Sphere is also applied in the calculation. Fig.2 gives the energy level of this cluster, it can be seen that the cluster orbitals are splitted into several groups corresponding to different bands of band theory. Using the Mulliken method as Puthoff¹⁰ the orbital

population, it can be pointed out that the highest occupied molecular orbitals (HOMO) consists mainly of Co^{2+} 4f orbit, and the lowest unoccupied molecular orbitals (LUMO), of Co^{2+} 5d orbit. The gap between the Co^{2+} 4f band and Co^{2+} 5d band is 3.96 eV in our calculation. Fig.3 shows the absorption of CoF_2 crystal obtained in our experiments. There is a strong absorption near 300 nm (4.13eV) which is in better agreement with the results of our calculations. Besides, from our calculations, the 4f band is a narrow band the electric dipole transitions from 4f-5d, 6s are in the range of 3.96-8.29 eV. This result is also justified by experiments. Fig.4 gives excitation spectra of Co^{2+} ions in CoF_2 crystal¹⁰. It can be seen that the excitation peaks are in the 286nm (4.35eV)-310nm (3.99eV) range. This shows that Co^{2+} is essential for the optical property of CoF_2 crystal. This result agrees with the discussion of A.J. Wozniak¹⁰.

References

1. W.W. Wilson et al., IEEE Trans. Nucl. Sci. NS-34, 157 (1987)
2. I.C. Slater, Quantum Theory of Molecules and Solids (McGraw-Hill, New York, 1961, vol.1)
3. I.C. Slater et al., Phys. Rev. B 3, 944 (1972) and references therein.
4. Zolita A. et al., Inorg. Chem. 3, 1660 (1965)
5. L.R. Allen et al., Phys. Rev. B 8, 4289 (1973)
6. D.E. Ellis et al., Phys. Rev. B 3, 2837 (1970)
7. E.J. Hechtel et al., Chem. Phys. 3, 41 (1973)
8. D.E. Ellis et al., Phys. Rev. B 28, 3897 (1983)
9. B.A. Antognon et al., Nucl. Instr. Meth. in Phys. Res. A332, 371 (1993)
10. A.J. Wozniak et al., IEEE Trans. Nucl. Sci. NS-39, 494 (1992)

* The work is supported by National Nature Science Fund Commission of China.