



Ab initio calculation of BaF₂ cross-luminescence spectrum

A. Myasnikova*, E. Radzhabov, A. Mysovsky

Vinogradov Institute of Geochemistry, Russian Academy of Sciences, Siberian Branch, Favorsky Street 1A, 664033 Irkutsk, P.O. Box 4019, Russia

ARTICLE INFO

Available online 7 May 2009

PACS:
71.20.Dg
78.20.Bh

Keywords:
Cross-luminescence
BaF₂
Embedded-cluster method

ABSTRACT

We present the theoretical calculations of the core hole electronic and spatial structure and cross-luminescence spectrum in [Ba₁₃F₃₂]⁻⁶ cluster. The *ab initio* Hartree–Fock calculation of cross-luminescence has been performed in embedded-cluster approach. The theoretical spectrum reproduces well the characteristics of the experimental one. The valence states corresponding to the 5.6, 6.3 and 7.1 eV emissions is found to be localized. The low-energy tail is shown to be due to transitions between 5p core states of Ba²⁺ ion and 2p valence states of next-nearest F⁻ ions.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Cross-luminescence (CL) of barium fluoride crystal have been studied for more than 20 years (see, for example, review in Ref. [1]). Despite these extensive studies, certain aspects of the emission is not clear. Cross-luminescence is well known to be related to radiative transition between valence (F, 2p) and core (Ba, 5p) bands of the crystal. Therefore the luminescence photon energy $h\nu$ have to be located in the region of $E_{vc} - \Delta E_v \leq h\nu \leq E_{vc}$, where ΔE_v is the valence band width and E_{vc} is the width between top of outermost core band and that of valence band. Recent photoelectron [2] and time-resolved investigations [3,4] of BaF₂ CL emission indicated the low-energy tail with photon energy $h\nu \leq E_{vc} - \Delta E_v$. It was supposed that the low-energy emission is due to the lattice relaxation effect.

The first theoretical calculation of the barium fluoride cross-luminescence spectrum had been performed by Andriessen et al. [5] with molecular cluster approach using [Ba³⁺F₈]⁵⁻ cluster. These calculations were reexamine by Ikeda et al. [6] using larger cluster [Ba₁₉F₃₂]⁶⁺ with DV – X_α method. The predicted spectra of both works agreed well with experiment, but transition energies were calculated only from one-electron states spectrum. It is well known that using one-electron energies for calculation of optical transition can lead to not only quantitatively, but also qualitatively wrong results. Also the results of Refs. [5,6] were obtained without taking into account the lattice relaxation in the presence of core hole. Therefore these results have to be refined, since the data of ultraviolet photoelectron spectroscopy clearly indicate that the core hole induces lattice distortion around itself [7].

Besides cluster calculations there exists two-band model approach in using schematic configuration diagram for analyzing cross-luminescence emission spectra [8,9]. In this case the core hole relaxation is taken into account, but there is no possibility to estimate the influence of surrounding ions to cross-luminescence process.

In this paper we present the results of the theoretical calculations of the core hole electronic and spatial structure and cross-luminescence spectrum in [Ba₁₃F₃₂]⁻⁶ cluster, with lattice distortion in the presence of core hole taking into account.

2. Calculation details

The *ab initio* Hartree–Fock (HF) calculations of cross-luminescence have been performed in embedded-cluster approach implemented in the GUESS computer code [10]. In this approach a quantum-mechanical (QM) cluster with the defect and its nearest neighbors is surrounded by interface ions and by several hundreds of ions, which treated classically in the shell model. Between QM and classical regions one needs to place an interface area in order to avoid the distortion of geometric and electronic structure at the edge of QM cluster. In the case of purely ionic crystals like BaF₂ a quite simple interface is sufficient. All quantum-mechanical, interface and classical ions are allowed to relax during the geometry optimization run. This region is surrounded by several thousands of fixed atoms, which are represented as point charges and provide accurate electrostatic potential inside classical and QM regions. GUESS does not itself calculate electronic structure of QM cluster. But calls another quantum-chemical programme (Gaussian 03 [11]) for this purpose and then adds classical terms to the obtained total energy.

* Corresponding author.

E-mail address: sasham@igc.irk.ru (A. Myasnikova).

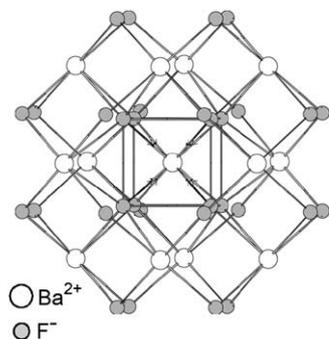


Fig. 1. $[\text{Ba}_{13}\text{F}_{32}]^{-6}$ cluster with the optimized geometry.

We used standard Huzinaga D95 basis set on fluorine ions and LANL2DZ basis with LANL2 pseudopotential on barium ions. To avoid the distortion of ground and excited states with the presence of positive point charges in some vicinity of QM cluster they were replaced by LANL1 pseudopotential (interface area). Configuration interaction singles (CIS) method was applied for calculation of transition energies.

We performed calculations for $[\text{Ba}_{13}\text{F}_{32}]^{-6}$ cluster with symmetry O_h . The core hole was modulated on central barium ion. The cluster contains 45 ions and includes nearest (NN—nearest-neighbor) and next-nearest (NNN—next-nearest-neighbor) fluorine ions relative to central Ba^{2+} ion (Fig. 1).

3. Results and discussion

As a first step we calculated the equilibrium geometry of the cluster $[\text{Ba}_{13}\text{F}_{32}]^{-6}$ which contains core hole. The core hole is a highly excited state, which is impossible to simulate using HF method. In order to optimize its geometry the following approach has been used. It was assumed that core hole is strongly localized on the barium ion and the nearest surrounding fluorine ions feel it mainly as additional positive charge positioned on cation, which becomes Ba^{3+} . Thus we placed additional +1 charge on the barium ion and then allowed the cluster and lattice to relax. The maximum displacement of nearest fluorine ions was 0.24 Å (8.7% from initial $\text{Ba}^{2+}-\text{F}^-$ displacement) in the direction to the barium ion with core hole. The displacements of others ions was less than 0.05 Å. The relaxation energy was 2.97 eV.

The lattice distortion resulted in deformation of BaF_2 energy-band structure (Fig. 2). After lattice relaxation 24 states of nearest fluorines were splitted from valence states of cluster. These F_{NN} valence states segregated into two group. Therefore one can expect the appearance of two main maxima in cross-luminescence spectrum.

Core hole states localized mainly on central barium ion. This hole states correspond to t_{1u} irreducible representations of O_h group. In dipole approximation $a_{1g} \rightarrow t_{1u}$, $e_g \rightarrow t_{1u}$, $t_{1g} \rightarrow t_{1u}$, $t_{2g} \rightarrow t_{1u}$ transitions is allowed. Thus there are only 12 allowed transitions in cross-luminescence process (Fig. 3).

For the calculation of the energies and intensities of core–valence transitions the following approach has been used. Since the core hole on $5p \text{Ba}^{2+}$ level is in highly excited state it is impossible to converge the electronic density of such state in SCF (self-consistent field) procedure. Therefore the densities corresponding to the hole on 24 different states splitted from valence band were obtained first with SCF calculations, and after that the transitions of these holes to $5p \text{Ba}^{2+}$ core level were calculated with CIS. In other words we calculated $5p \text{Ba}^{2+} \rightarrow 2p \text{F}^-$ transition energies and oscillator strengths. The spectrum shape in this approach is

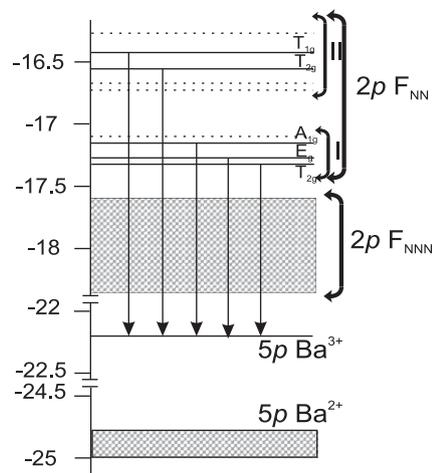


Fig. 2. One-electron energy diagram of BaF_2 crystal after geometry optimization.

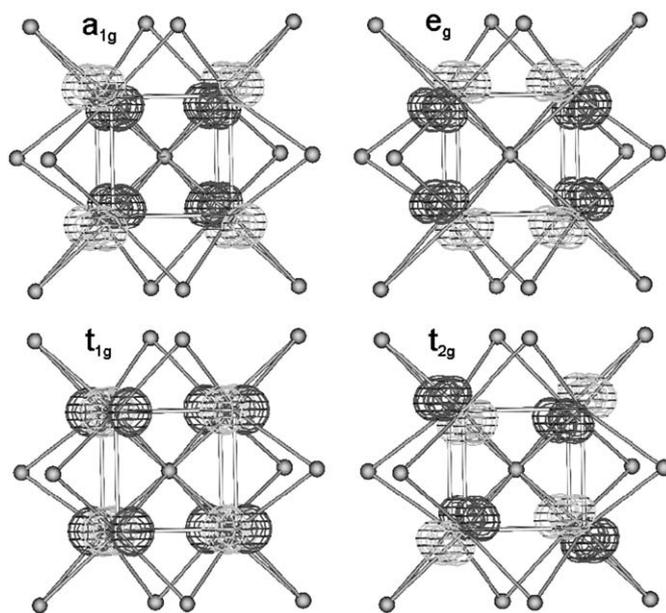


Fig. 3. Examples of calculated nearest fluorines density plot.

defined by transitions probability from core states to local valence states of the crystal. Calculated energies and oscillator strengths are presented in Table 1.

The transition energies from F_{NNN} ions valence states were estimated. We performed calculations of matrix elements of dipole transitions on the basis of output Gaussian 03 file. In accordance of this assessment we concluded that low-energy tail is due to transitions from next-nearest fluorine ions to the outermost core band.

Fig. 4 shows the calculated spectrum in accordance with experimental data, measured after 7 keV electron excitation at 80 K. Both spectra was normalized by 5.7 eV luminescence intensity. We used the following approach of converting the discrete data into spectral one. It is known that the frequency of mode, which influence the band widening, is close to transverse crystal mode under room temperature. Therefore we compare the calculated width with value estimated from this approximation. The calculated spectrum demonstrates three peaks at 5.2, 6.1, 7.1 eV and low-energy tail and agrees well with experimental data.

Table 1
Results of calculated cross-luminescence transitions in $[\text{Ba}_{13}\text{F}_{32}]^{-6}$ cluster.

Group of states	Transition	Energy of transition, eV	Oscillator strength
I	$t_{2g} \rightarrow t_{1u}$	5.38	0.2976
	$e_g \rightarrow t_{1u}$	5.43	0.0151
	$a_g \rightarrow t_{1u}$	5.47	0.4977
II	$t_{2g} \rightarrow t_{1u}$	6.28	0.1027
	$t_{1g} \rightarrow t_{1u}$	6.98	0.0445
F_{NNN}		4.35	0.0139

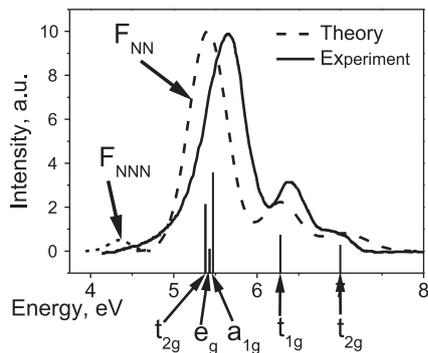


Fig. 4. Calculated spectrum obtained by using $[\text{Ba}_{13}\text{F}_{32}]^{-6}$ cluster. Experimental spectra measured under excitation by 7 keV electrons [12]. The intensity was normalized on 5.7 eV emission.

4. Conclusion

In this paper the cross-luminescence spectrum have been calculated for localized core hole. The theoretical spectrum reproduces well three maxima and low-energy tail of experi-

mental one, with the low-energy tail being due to electron transitions between next-nearest fluorines and outermost core band. The 5.7, 6.3 and 7.1 emission is due to transitions from nearest fluorine states.

Acknowledgment

This work was partially supported by Grant 07-02-01057 from Russian Foundation for Basic Research (RFBR).

References

- [1] P.A. Rodnyi, Radiation Measurements 38 (2004) 343.
- [2] A. Ejiri, S. Kubota, A. Hatano, K. Yahagi, Journal of Physical Society of Japan 64 (1995) 1484.
- [3] T. Matsumoto, K. Kan'no, M. Itoh, N. Ohno, Journal of Physical Society of Japan 65 (1996) 1195.
- [4] M. Itoh, M. Kamada, N. Ohno, Journal of the Physical Society of Japan 66 (1997) 2502.
- [5] J. Andriessen, P. Dorenbos, C.W.E. van Eijk, Molecular Physics 74 (1991) 535.
- [6] T. Ikeda, H. Kobayashi, Y. Ohmura, H. Nakamatsu, T. Mukoyama, Journal of Physical Society of Japan 66 (1997) 1079.
- [7] M. Itoh, M. Kamada, Journal of Physical Society of Japan 70 (2001) 3446.
- [8] Y. Kayanuma, A. Kotani, Journal of Electron Spectroscopy and Related Phenomena 79 (1996) 219.
- [9] M. Fukaya, Y. Kayanuma, M. Itoh, Journal of Physical Society of Japan 71 (2002) 2557.
- [10] P.V. Sushko, A.L. Shluger, C.R.A. Catlow, Surface Science 450 (2000) 153.
- [11] M.J. Frisch, G.W. Trucks, H.B. Schlegel, et al., Gaussian 03 (Revision E.1), Gaussian Inc., Pittsburgh, PA, 2007.
- [12] J.J.L. Jansons, V.J. Krumins, Z.A. Rachko, J.A. Valbis, Physica Status Solidi B 144 (1987) 835.