The electronic structures of V²⁺-doped fluoride crystals

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Abstract. This paper reports the spin-polarized discrete-variation X_α calculations for the V²⁺-doped fluoride crystals $CsCaF_3$, $RbMnF_3$, $KMnF_3$ and $KMgF_3$. The calculated values are in good agreement with the experimental results.

1. Introduction

In vibronic laser crystals transition-metal ions are generally used as active ions and the laser transition is a d–d transition. Because in transition-metal ions d electrons are located in the outermost electronic shell of the ion, these ions are strongly coupled with the crystal lattice. Therefore laser properties of the crystal are directly related to the crystal field strength. Studies of the electronic structures of laser crystals are helpful to the further understanding of the laser behaviour of the crystal and provide grounds for searching for new laser crystals.

In recent years much progress has been achieved in the researches of vibronic laser crystals. Successful pulsed and continuous-wave (CW) laser operation has been demonstrated for a series of transition-metal-doped oxides and fluorides. Interest has focused on Cr³⁺-doped crystals, because many of them can be operated at room temperature with the potential of broadband single mode tunability. V²⁺ is isoelectronic to Cr³⁺ but few laser oscillations have been realized with that transition-metal ion. One reason might be that charge compensation is necessary for the oxides that are successful with Cr³⁺ doping. On the other hand, in many fluorides, V²⁺ may substitute doubly charged metal ions without charge compensation, so laser oscillations may be realized in those crystals. The first pulsed operating vibronic laser on the basis of such materials was MgF_2: V²⁺ [1]. Recently CW laser oscillation has been achieved with the vibronic solid-state material $CsCaF_3$: V²⁺ [2].

We calculated the electronic structures of the crystal MgF_2: V²⁺ with the X_α method [3]. In this paper we systematically calculate the electronic structures of the V²⁺-doped fluoride crystals $CsCaF_3$, $RbMnF_3$, $KMnF_3$ and $KMgF_3$ to explain the relations between the electronic structures and the optical properties of the crystals.

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Table 1. Distances between the central ion and the ligand ions.

	$CsCaF_3$	$RbMnF_3$	$KMnF_3$	$KMgF_3$
R (Å)	2.23	2.12	2.09	1.99

2. Method of calculation

The formula of cubic fluorides with perovskite structure can be expressed as ABF_3, where A and B are cations. The sum of the valences of the cations must equal three to neutralize the three F^- ions. The space group of an ideal perovskite structure is $Pm3m$-O_h^1. The A, B and F ions all locate at the special positions $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$, $(0,0,0)$ and $(\frac{1}{2},0,0;0,\frac{1}{2},0;0,0,\frac{1}{2})$, respectively. The F ions form a series of three-dimensional connected octahedra. The B ions locate at the centres of these octahedra while the A ions locate at the large interstices, and each one is surrounded by twelve F ions. In the vanadium-doped fluoride with perovskite structure the V^{2+} ion substitutes the cation at site B. Therefore its point group is O_h. The optical properties of the crystal can be obtained by calculations of the ion cluster $(VF_6)^{4-}$ formed by the luminescent centre V^{2+} and the six nearest oxygen ions, F^-. The distances, R, between the central ions and the ligand ions of the crystals $CsCaF_3$, $RbMnF_3$, $KMnF_3$ and $KMgF_3$ are listed in table 1 [4]. Calculations were performed for the cluster $(VF_6)^{4-}$ by the spin-polarized SCC-DV-X_α method. 1s–4s were taken as the numerical basis sets for V^{2+} and 1s–2p as those for F^-. The effect of the ions in the 64 surrounding unit cells was considered. All calculations were performed on the Siemens 7.570-C computer in Tongji University.

3. Results and discussion

3.1. One-electron energy levels

The calculated results of the one-electron energy levels of the cluster $(VF_6)^{4-}$ for the crystals $CsCaF_3$, $RbMnF_3$, $KMnF_3$ and $KMgF_3$ are shown in figure 1. These energy levels can be roughly divided into five regions: (i) F_{2s}^- non-bonding levels with energy values around -16 eV; (ii) bonding levels formed by V_{3d}^{2+} and F_{2p}^- with energy values around 0 eV; (iii) F_{2p}^- non-bonding levels with energy values around 1 eV; (iv) V_{3d}^{2+} crystal field levels with energy values between 9 eV and 15 eV; (v) anti-bonding levels formed by V_{4s}^{2+} and F_{2p}^- with energy values between 15 eV to 19 eV (not shown in figure 1). It is shown that in all the crystals, V^{2+} have a similar one-electron electronic structure, but the energies of the 3d levels and the intervals between the 3d levels and the F_{2p}^- non-bonding levels increase with decreasing distances, R, between the central ions and the ligand ions. The reason is that as R decreases, the interaction between the 3d levels with the ligand levels increases. Thus the 3d levels are pushed up further. The one-electron eigenvalues of the 3d levels are listed in table 2.

3.2. Spin polarization splittings

The splittings of spin-up levels and spin-down levels characterize the effect of spin polarization. The empirical expression for estimating the spin polarization splitting ΔE
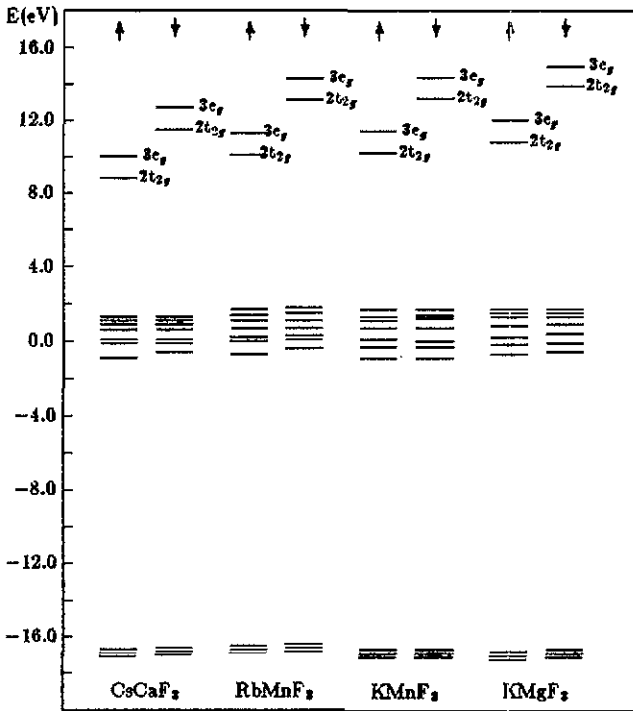
Figure 1. Energy levels of the cluster $(VF_6)^{4-}$.

Table 2. One-electron eigenvalues of the 3d energy levels (eV).

	$CsCaF_3$	$RbMnF_3$	$KMnF_3$	$KMgF_3$
$3e_g\downarrow$	12.4579	14.0572	14.2462	15.0737
$2t_{2g}\downarrow$	11.5884	12.9726	13.1229	13.8370
$3e_g\uparrow$	9.8934	11.1813	11.2459	11.5317
$2t_{2g}\uparrow$	8.8781	10.0104	10.0344	10.1867

Table 3. Spin polarization splittings of the one-electron energy levels (eV).

	$CsCaF_3$	$RbMnF_3$	$KMnF_3$	$KMgF_3$	Empirical
$3e_g\uparrow-3e_g\downarrow$	2.5645	2.8759	3.0003	3.5420	2.48
$2t_{2g}\uparrow-2t_{2g}\downarrow$	2.7103	2.9622	3.0885	3.6503	—

is $\Delta E = n(3.5\,B + 1.4\,C)$ [5], where n is the number of unpaired electrons, and B and C are the Racah parameters of the central ion. The calculated and empirical values ($B = 766\ cm^{-1}$ and $C = 2855\ cm^{-1}$ [6] were used for calculating the empirical values) of the spin polarization splittings for the one-electron energy levels of $(VF_6)^{4-}$ are listed in table 3. It is seen that the calculated values are in good agreement with the empirical

Table 4. The value of $10\,Dq$ (cm^{-1}).

	$CsCaF_3$	$RbMnF_3$	$KMnF_3$	$KMgF_3$
Calculated	8276	9467	9792	10868
Experimental [4]	8660	9470	9801	10914

ones. It is reasonable that the value of ΔE for an e_g level is smaller than that for a t_{2g} level. An e_g level is a σ level, while a t_{2g} level is a π level. The interaction of a σ level with a p level of the ligands is stronger than that of a π level, so the energy level of an e_g level is pushed higher. However, because the $e_{g\uparrow}$ level is closer to the p level of the ligands than the $e_{g\downarrow}$ level, the upward shift of an $e_{g\uparrow}$ level is the largest. This is the reason why the spin polarization splitting of an e_g level is smaller.

3.3. Effect of the crystal field strength

The electronic configuration of the free ion V^{2+} is d^3, and is t_{2g}^3 under O_h site symmetry. $^4A_{2g}(t_{2g}^3)$ is the ground state, and $^4T_{2g}(t_{2g}^2 e_g)$ is the lowest quartet excited state. Experimentally, the value of $10\,Dq$ can be considerd as the energy interval between $^4T_{2g}$ and $^4A_{2g}$. We calculated, with Slater's transition theory, the transition energies of $2t_{3g\uparrow}-3e_{g\uparrow}$ to obtain the values of $10\,Dq$. The calculated and experimental values are listed in table 4. It is seen that the agreement is very good. They are the first calculated values of $10\,Dq$ for these crystals. In table 4 it is shown that the $10\,Dq$ values increase with decreasing distance, R, between the central ions and the ligand ions. This implies that the value of $10\,Dq$ reflects the magnitude of the crystal field strength.

4. Summary

The electronic structures of V^{2+}-doped fluoride crystals $CsCaF_3$, $RbMnF_3$, $KMnF_3$ and $KMgF_3$ were calculated with the DV-X_α method. The calculated values of $10\,Dq$ for these crystals were obtained for the first time and the effect of the crystal field strength was discussed. Further calculations of the vibrational structures and transition probabilities should be complemented with respect to their potential as laser materials.

References

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