DIPOLE POLARISABILITY, OSCILLATOR STRENGTH AND MAGNETIC SUSCEPTIBILITY OF FLUORIDE ION IN FLUORIDE STRUCTURE CRYSTALS

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Abstract

A variational-perturbation approach is invoked to study the effect of the environment potential around Fluoride ion on some important electronic properties. The dipole polarisability α, oscillator strength S(-٢) and S (-١) and magnetic susceptibility χ are theoretically estimated for Fluoride ion in different potentials. Also we calculate these electronic properties in many Fluoride structure crystals such as $CdF_{٢}$, $CaF_{٢}$, $PbF_{٢}$, $SrF_{٢}$ $BaF_{٢}$, and LiF.

الاستقطابية الثناقطبية والعزم الثنائي لشدة المتذبذب والتأثرية المغناطيسية لآيون الفلورايد في بلورات ذات تشكيل الفلورايد

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الخلاصة

لقد تم تطبيق نظرية الاضطراب مع طريقة التغاير لدراسة تأثير الجهد المحيط حول ايون الفلورايت على بعض الخواص الالكترونية المهمة. ولقد تم حساب الاستقطابية الثناقطبية S(-١) وS(-٢) والعزم الثنائي لشدة المتذبذب والتأثرية المغناطيسية لآيون الفلورايد في جهود مختلفة. وكذالك تم حساب الخواص الالكترونية في بعض مركبات من بلورات ذات تشكيل الفلورايت $CdF_{٢}$, $CaF_{٢}$, $PbF_{٢}$, $SrF_{٢}$ $BaF_{٢}$, و LiF.

١. Introduction

Many important atomic properties such as a dipole polarisability, total inelastic scattering cross section and stopping power are depend on moments of dipole oscillator strength distribution. It is useful in determination of optical and dispersion of atoms as well as assessing the quality of ab initio wave function [١-٣]. Also, the relationship between the dipole polarisability and dielectric constant or refractive index which they hold by Clausius-Mosotti relation [٤] makes these properties very important. Many studies are found of electrical polarisability for fluoride ion in alkali halides crystals [٥,٦] and moment of oscillator strength distribution of atoms [٧].

Crystal with Fluoride structure such as $BaF_{٢}$, $CaF_{٢}$ and LiF are used to manufacture windows, prisms and lenses to be operated over the whole spectral range from UV and visible to the near and middle IR. Barium Fluoride ($BaF_{٢}$) is relatively hard but it is extremely sensitive to thermal shock. For its transmittance ١- ١١ μm, the material is used for optical windows, lenses and prisms in UV-IR range. It is commonly used as a scintillated material for Gamma ray and fastest scintillating crystals [٨]. Also it is used in the correction paret of lens system, radiation resistant and it is susceptible to laser damage threshold [٨]. Calcium Fluoride (CaF$_٢$) is an ionic crystals insulator. The usefulness of its application is in UV as Eximer laser windows. Many basic growths and analysis techniques such as Molecular Beam Epitax (MBE and X-ray Photo Spectroscopy (XPS) are used to grow CaF$_٢$ films on Si (١١١).

Pure CaF$_٢$ crystal has excellent transmission properties without absorption bands over wide wave length range from UV to IR [٩]. Selective absorption band exist in CaF$_٢$ if the crystal contains impurities. Lithium Fluoride (LiF) shows excellent transmit-ance in the VUV region. It is used for windows, prisms in the visible and infrared in ٠.١٠٤-٧ µm region and also it is sensitive to thermal shock. There are measurements of the intrinsic birefringence in CaF$_٢$ and BaF$_٢$ for wave length in the range ٣٦٥ to ١٥٦ nm[١٠].

٢. Theory

I. A Variation-perturbation approach.

Assume an external static electric field **F** along the normal to a given system (z-direction) acting on the atom or ion; the resulted energy shifts in second order due to **F** is given by **–αF,** where **α** the dipole polarisability of a given atom or ion. The energy shift can be estimated variationally. The trial function **Φ** taken in the following form:

$$\Phi = \Phi_o(1+\omega) \qquad ...(1)$$

Where **Φ$_o$** unperturbed wave function and w is a symmetric function:

$$\omega = U(r_i) \qquad ...(2)$$

The trial function U(**r**$_i$) should contain the necessary parameters β$_i$ and one of its appropriate form is the following[١٥]:

$$U(r) = F_z(\beta_i, r)H,' \qquad ...(3)$$

Where **β$_i$** are two variational parameters and **H'** is the perturbed field which takes the Legender polynomial of order **L**. For dipole **L=١** and the values of **β$_i$** can be derived to give minimum energy. From our previous work [١١] for multipole polarisability and for dipole polarisability (**L=١**):

$$\alpha = -\sum_{i=1}^{2}\left(\frac{3}{4}\left(A_i\sum_{j=1,\,j\neq i}^{2}\beta_i\beta_j + B_i\beta_i + iA_{2i}\beta_i^2\right)\right) \qquad ..(4)$$

Where $A_k = \left\langle \phi_o \middle| r_i^{k-2} \middle| \phi_o \right\rangle$ and $B_k = \left\langle \phi_o \middle| r_i^{k-1}(r_i \cdot r_j) \middle| \phi_o \right\rangle$ and **Φ$_o$** is approximated by a single Slater determinate.

A$_k$ contributions involve the sum of terms each of which is associated with a single one-electron orbital (**i=j**) while **B$_k$** contains both diagonal and non diagonal terms **(i≠j)** expressing the coupling between two one-electron states of different angular momentum.

II.Crystalline Environment

The variation-perturbation approach was extended to consider **F$^-$** ion in various spherical hollow shepherd potential **V$_o$** to corresponding bulk configuration using a available orbitals [١٢]. This potential has been varied from ٠.٥٢٣ to ٠.٦٧٥ a.u. to demonstrate the electrostatic properties dependence on the environment binding. The actual Madelung potential for these compounds Fluoride structure crystals in this study lies approximately within the range of **V$_o$**. In a given potential **V$_o$**, any of those electronic properties can be approximately expresses as:

$$\eta = \sum_{i=1}^{3} D_i V_o^i . \qquad ...(5)$$

A third order polynomial has been obtained with the parameters **D$_i$** are calculated from the values of **V$_o$**. The Madelung potential for any crystal **V$_m$** is given by:

$$V_m = \frac{Ze^2 M}{4\pi\varepsilon_o d}, \qquad ...(6)$$

Where **d** is the nearest neighbor distance and **M** is the Madelung constant for these fluoride structure crystals.

III. Oscillator Strength

Oscillator strength sum **S (k)** is defined in terms of spherical average oscillator strength **f$_{no}$** and corresponding transition energy **E** by the following relation:

$$S(k) = \sum_n f_{no} E_{no}^k , \qquad ...(7)$$

Where the summation above is run over all the discrete and continuous states. By substituting **(H-E$_o$)** for E and the commutation relationship **[H,X$_i$]=-I P$_{xi}$(X$_i$=z,y,z),** the well known sum rules are obtained[١٣, ١٤]:

$$S(-1)=\frac{2}{3}\left[\,\langle\phi_o|\sum r_i^2|\phi_o\rangle+\langle\phi_o|\sum r_i\cdot r_j|\phi_o\rangle\,\right] \qquad ...(8)$$

Equation (٨) involves one and two electron parts.

The first term is directly related to the diamagnetic susceptibility **χ** as:

$$\chi=-\left(\frac{e^2}{6mc^2}\right)\langle\phi_o|\sum r_i^2|\phi_o\rangle, \qquad ...(9)$$

Where **e** is the electron charge, **m** is the mass of electron and **c** is the light velocity. In terms of the second order distortion; the sum [١٣, ١٤]:

$$S(-2)=\frac{1}{8}\Bigg[\sum_{k=1}^{3} g\langle\phi_o|\sum r_i^{k-1}|\phi_o\rangle\beta_1^{3-k}\beta_2^{k-1} + 2.333\langle\phi_o|\sum r_i^n|\phi_o\rangle\beta_1^n\beta_2^n\,\Bigg] \qquad ...(10)$$

Where **g=k+١** and **n=١.**

٣. Results and Discussion

Table ١ shows the different potentials created by a hollow sphere around **F**$^-$ ion, the **F**$^-$ ion embedded in the sphere with opposite charge. We can see from this table that in the free state the **S(-٢), S(-١)** and **α** for **F**$^-$ ion have values higher than the other values when the potential increases. These properties are varying when the environment around the ion is change, such as a crystal environment. By using the data in this table with equation ٦, we can estimate the three parameters **D$_i$(i=١,٢,٣.)** for the third polynomial. **The** values of **D$_i$** can be used with Madelung potential (Eq.٧) to calculate the dipole polarisability **α** and moment of dipole oscillator strength **S(-٢)** for **F**$^-$ ion in crystalline environment.

Table ١: Moment of oscillator strength S(-٢),S(-١) and S(٠), dipole polarisability α and magnetic susceptibility χ(-١٠$^{-٦}$ cm/mol) of F$^-$ ion in different hollow sphere potential V(a.u.).

Ion	V	S(-٢)	S(-١)	S(٠)	α	χ
F$^-$	free	٢.٨٧	٧.٤٥	٩.٩٩	١.٧٠٢	١٢.٦٢
	٠.٥٢	١.٥٤	٦.١٣	٩.٩٩	٠.٨٩٥	١٠.٩٩
	٠.٥٧	١.٤٦	٦.٠٩	١٠.٠	٠.٨٦٨	١٠.٨٩
	٠.٦٧	١.٤٣	٦.٠٠	٩.٩٩	٠.٨٤٨	١٠.٨٢

We have presented these calculations in Table ٢. For Mdelung potential **V$_m$** represents the effective potential in crystal, we observe that it is affected by the crystal environment. So the dipole polarisability **α** and moment of oscillator strength **S(-٢)** of **F**$^-$ ion are also affected. We can see that they vary with Madelung potential. As the the Madelung potential increases the dipole polarisability **α** and **S(-٢)** of F$^-$ ion decrease. From Equation (٥), there are four terms: the first term is constant so the dipole polarisability proportional with the inverse of lattice constant. This means that it is the dominant for the dipole polarisability. We have plotted the variation of dipole polarisability and oscillator strength as a function of lattice constant in Figure ١. for CdF$_٢$, CaF$_٢$, PbF$_٢$, BaF$_٢$ and SrF$_٢$ crystals what have Fluoride structure. We observe that the linearity of these variable with lattice constant. This means that the first term in Eq.٥ is the dominant term. The estimating of S(٠) which represents the number of electrons in the Fluoride ion was done to check our calculations.

٤. Conclusion

It is very clear from the results of our study that the dipole polarisability, oscillator strength sum and magnetic susceptibility of ions are very sensitive to their environment. They vary with lattice constant. Also our ionic model which it is used in this study is very simple and gives reasonably good results.

Table ٢: Lattice constant a (a.u.), Madelung potential V$_m$(a.u.), dipole polarisability α and moment of oscillator strength S(-٢) of F$^-$ ion in some compounds of Fluoride structure crystals

Crystal	a	V$_m$	α	S(-٢)
CdF$_٢$	٥.٣٨	٠.٣٤٢	٠.٩٩	١.٦٧٦
CaF$_٢$	٥.٤٦	٠.٣٣٨	١.٠٠	١.٦٩٣
pbF$_٢$	٥.٩٢	٠.٣١١	١.٠٨	١.٨٢٩
BaF$_٢$	٦.١٩	٠.٢٩٧	١.١٢	١.٩٠٣
SrF$_٢$	٦.٧٩	٠.٢٧١	١.٢١	٢.٠٤٦
LiF	٤.٠٢	٠.٤٥٨	١.٣٤	١.٤٣١

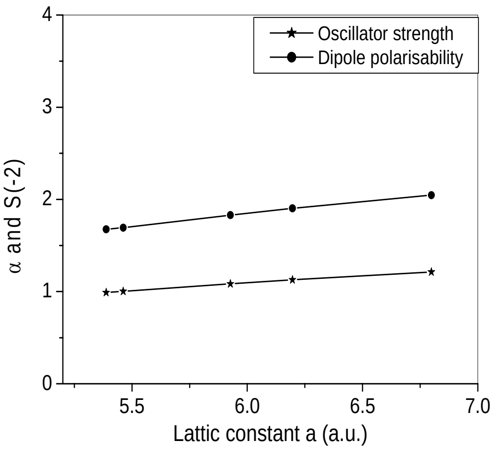

Figure ١: Dipole Polarisability α(Å^{٣}) and oscillator strength S(-٢) versus lattice constant a (a.u.) for CdF$_{٢}$, CaF$_{٢}$, pbF$_{٢}$, BaF$_{٢}$ and SrF$_{٢}$.

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