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OPTICAL AND EPR STUDIES OF VO^{2+} IONS DOPED ZnS-CdS COMPOSITE NANOPARTICLES

J. Madhavi[1], C. Subramanyam[2], G.S.C. Bose[3], M. Venkata Ramanaiah[4] and R.V.S.S.N. Ravikumar[1,*]

[1]Department of Physics, Acharya Nagarjuna University, Nagarjuna Nagar-522 510, (A.P.) India
[2]Department of Physics, S.V. Arts College, Tirupati-517502, (A.P.) India
[3]Department of Physics, J.K.C. College, Guntur-522006, (A.P.) India
[4]S.K.R & S.K.R., Govt. Degree College, Kadapa-516001, (A.P.) India
*E-mail: rvssn@yahoo.co.in

ABSTRACT

VO^{2+} ions doped ZnS-CdS composite nanoparticles have been synthesized by chemical precipitation method. The prepared sample was investigated by different spectroscopic techniques such as optical absorption (UV-Vis) and Electron Paramagnetic Resonance (EPR) studies. The results and analysis reveal that site the VO^{2+} ion occupied in octahedral symmetry with tetragonal compression having (C_{4v}) symmetry in the host lattice. Optical absorption spectrum showed characteristic bands corresponding to (d ↔ d) transitions and the corresponding band gap energies are calculated. The evaluated crystal field and parameters are Dq = 1757, Ds = -2652 and Dt = 1111 cm^{-1}, $g_{\parallel}$ = 1.90, $g_{\perp}$ = 1.98, $A_{\parallel}$ = 2.11 x 10^{-4}, $A_{\perp}$= 41.38 x 10^{-4} cm^{-1}.

Keywords: VO^{2+} ion, Optical absorption, EPR, characteristic bands and Crystal field parameters.

INTRODUCTION

Semiconducting Chalcogenide nanocomposites, especially sulfides have been investigated extensively owing to their interesting optoelectronic devices[1]. For II-VI semiconductors ZnS and CdS are most promising inorganic materials[2]. ZnS is a non-toxic semiconductor and is an important versatile and luminescent material with large band gap energy of 3.6 eV at 300K[3-5]. It has been extensively investigated for variety applications in different fields, for example, photovoltaic crystal devices operating in the region from UV to IR regions, for the semiconductors we discuss the third-order non-linear susceptibilities due to virtual transitions (e.g., bound electrons in intrinsic semiconductors and non-linear motion and energy relaxation of free carriers in doped semiconductors) and due to real transitions (e.g. valence-to-conduction-band transitions, free-carrier transitions, impurity transitions and transitions in excitons and excitonic complexes). Phototransistor, Photocell, Solar cell[6], Transient-voltage-suppression diode, Laser diode, sensors, infrared windows and lasers etc.[7-11] similarly CdS a direct band gap semiconductor with a gap energy of 2.4 eV[12], for a wide gap range of uses including chemical & biological gas sensors[13,14], Light emitting diodes[15], storage devices[16], corrosion inhibitors[17], shielding materials[18] and photovoltaic devices[19,20]. Among these the collection of dissimilar compounds of an II-VI semiconductors forming inflexible solutions and is a valuable way to manage the potential of conduction and valence bands by successive changes in the composition. Significant semiconductor materials to combine with CdS forming a continuous series of solid solutions, where the metal atoms are commonly replaced in the crystal structure[21-24]. ZnS-CdS composite nanopowder was the most promising II-IV semiconductor compound materials has been investigated by many researchers in present years and the result have shown that the materials used in various applications like sensors, optoelectronic devices and in solar cells[25-28].

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For the synthesis of ZnS-CdS composite nanopowder materials are used in many experimental processes have been developed which can be broadly classified into colloidal chemical synthesis[29], electrochemical deposition[30], chemical bath deposition technique[31], facile chemical route[32], chemical precipitation method[33-35], Sonochemical synthesis[36] etc., have been widely used in the synthesis of semiconductor nanostructures. Among all these syntheses, chemical precipitation is one of the processes which permit the manipulation of matter at the molecular level. Various chemical methods are shows potential terms of cost reduction and ability to produce a large number of particles. It is a simple method of stabilizing and to avoid agglomeration to utilize semiconductor composite nanostructures as building blocks of different functional nano devices, it is essential to synthesize and having assorted physical properties this can be achieved by suitable doping of a transition metal ions doped ZnS-CdS composite nanopowder were the most popular materials for research in semiconducting nanocomposites. Doped nanocomposites of the semiconductor can yield elevated and is a collective term for different phenomena where a substance emits light without being strongly heated, i.e. the emission is not simply thermal radiation, a device that responds to a physical stimulus (such as heat, light, sound, and act as a laser material)[37]. The most important industrial vanadium compound, vanadium pentoxide is used as a catalyst for the production of sulfuric acid. Large amounts of vanadyl ions are found in a few organisms, possibly as a toxin. The oxide and some other salts of vanadium have moderate toxicity. Vanadyl ($VO^{2+)}$ ion is one of the most stable diatomic ions known and forms a wide range of complexes[38], it is an exceptional transition metal ion which acts as a self-activated luminescence center and also gives the information about coloring agent, reflects various regions from UV to IR[39]. Recently Madhavi et al. have reported spectroscopic investigations on Mn^{2+} doped ZnS/CdS nanocomposite powder through chemical precipitation method at room temperature[40]. In this work, for the first time, we successfully prepared nano-sized VO^{2+} doped ZnS-CdS composite nanoparticles well dispersed in a chemical precipitation method. This method is a contemporary technique for wastewater purification when processing mineral products, including for the removal of metals and sulfides. Chemical precipitation is a proven, energy-efficient and eco-friendly route, relatively simple quick mild and effective technique, it and can be used to obtain good results with a number of substances that are difficult to remove with other techniques. The prepared material is characterized by spectroscopic techniques used to obtain the information about the nature of site symmetry, find its energy level structure, distortion in the lattice and crystal structure of the prepared nano sized powder.

EXPERIMENTAL

Materials

All chemicals reagents are analytical grade and were purchased from Merck Chemicals, India. The new synthesized route of a VO^{2+} ions doped ZnS-CdS composite nanoparticles has the following reagents were used namely Zinc acetate $Zn(CH_3COO)_2$, Cadmium acetate $Cd(CH_3COO)_2$, Sodium sulphide (Na_2S), De-ionised water, Vanadium pentoxide (V_2O_5) and Ethanol.

Synthesis of ZnS-CdS Composite Nanoparticles

VO^{2+} ions doped ZnS-CdS composite nanoparticles were prepared by using 0.2 mol% of zinc acetate in 50 mL equal volumes of the water-ethanol mixture and same molar amount of Na_2S aqueous solution was mixed drop by drop. Then this mixture was stirred magnetically at 80ºC until a homogeneous solution was obtained, maintained at room temperature to form a milky white precipitate which indicates the formation of ZnS nanoparticles. After 0.09 mol% of cadmium acetate 50 mL equal volumes of the water-ethanol matrix which is added to the above colloidal solution then continuous stirring. After 10 min, 0.1 mol% Na_2S 50 mL (prepared in a deionized water-ethanol matrix) solution was added to dropwise in the above solution. After 4h of continuous stirring, the white solution turned to yellow colored voluminous precipitate appeared which indicates the formation of ZnS-CdS composite nanoparticles. Finally, 0.1 mol% of V_2O_5 dissolved in 50 mL equal volumes of water-ethanol matrix added to the above colloidal solution and stirred for 3h. The obtained mixture of nanocomposite solution was washed several times with deionized water to separate unwanted impurities. The obtained solution was kept in an ultracentrifuged at 10000 rpm about 30 min. The fine powder was collected and dried in a hot air oven at

120 °C for 2h and grind with agate motor by hand milling. The synthesized VO^{2+} ions doped ZnS-CdS composite nanoparticles were obtained and is characterized by various techniques.

Characterization Methods

Optical absorption (UV–VIS) spectrum was taken from Jasco V-670 Spectrophotometer in the wavelength region of 200–900 nm. The EPR spectrum was obtained from Jeol JES-TE 100 EPR spectrometer operating at X-band frequencies and having a100Hz frequency modulation.

RESULTS AND DISCUSSION

UV-Vis Study

The optical absorption research is beneficial to gain numerous optical and physical parameters with a view to being beneficial for better knowledge of the optical behavior of the nano substances.

In an octahedral crystal field, the single d-electron configuration of the vanadium ions occupies the T_{2g} orbital and it enables to ground state of $^2T_{2g}$ when the electron is in an excited state it occupies the state E_g orbit and gives rise to energy term ^2E_g. From the octahedral crystal field symmetry, only one band expected from the transition is to be expected $^2T_{2g} \rightarrow {}^2Eg$. However, vanadium ions are not arising octahedral crystal field symmetry with less value of tetragonal distortion (C_{4V}). In C_{4V} symmetry, the electron in the ground state is an orbital singlet and the d-electron is in the non-bonding ($^2B_{2g}$) type d_{xy} orbital. The $^2T_{2g}$ splits into two energy states $^2B_{2g}$ and ^2Eg, moreover, the state ^2Eg splits into $^2B_{1g}$ and $^2A_{1g}$. The energy bands are observed the distortion is observed only to tetragonal but not any other lower symmetry. This supports the EPR data also $^2B_{2g} \rightarrow {}^2E_g$, $^2B_{2g} \rightarrow {}^2B_{1g}$, $^2B_{2g} \rightarrow {}^2A_{1g}$ respectively. These bands are assigned as $^2B_{2g} \rightarrow {}^2Eg$, $^2B_{2g} \rightarrow {}^2B_{1g}$ and $^2B_{2g} \rightarrow 2A_{1g}$, respectively. In general, $^2B_{2g} \rightarrow {}^2A_{1g}$ transition is observed in the wavelength range 380 – 480 nm, $^2B_{2g} \rightarrow {}^2B_{1g}$ transition around 520 – 620 nm and $^2B_{2g} \rightarrow {}^2E_g$ transition in the range 700 – 820 nm. The order of energy levels is as follows: $^2B_{2g} < {}^2E_g < {}^2B_{1g} < {}^2A_{1g}$[41]. In the present investigation, the optical absorption spectrum of vanadyl ions doped ZnS-CdS composite nanoparticles is shown in Fig.-1.

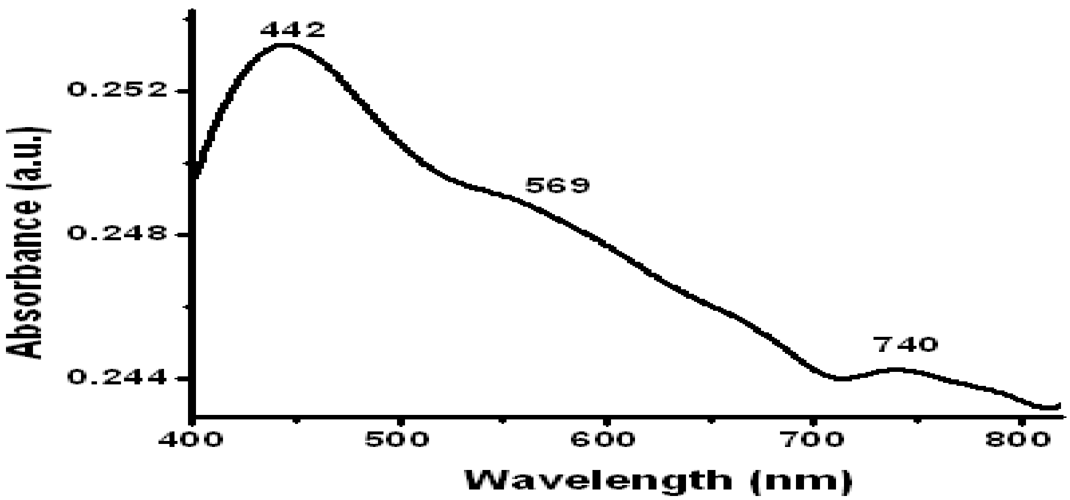

Fig.-1: Optical Spectrum of VO^{2+} Ions Doped ZnS-CdS Composite Nanoparticles

The spectrum exhibits three bands in UV-Vis region, the first band centered at 13513 cm^{-1}, second band at 17574 cm^{-1} and third band absorbed at 22624 cm^{-1} respectively. Accordingly, Balhausen and Gray the ordering of d-energy levels are in the Vanadium complex in terms of molecular orbital's[42]. The observed bands are assigned to d-d transitions and given are as follows[43]:

$^2B_{2g} \rightarrow E_g\,(d_{xy}, d_{xz}, d_{yz})$, $^2B_{2g} \rightarrow {}^2B_{1g}\,(d_{xy} \rightarrow d_{x^2-y^2})$ and $^2B_{2g} \rightarrow {}^2A_{lg}\,(d_{xy} \rightarrow d_{z^2})$

The cubic field parameter Dq and tetragonal field parameters Ds and Dt are evaluated form the following expressions:

$$^2B_{2g} \rightarrow {}^2E_g = -3Ds+5Dt \quad (1)$$
$$^2B_{2g} \rightarrow {}^2B_{1g} = 10Dq \quad (2)$$
$$^2B_{2g} \rightarrow {}^2A_{1g} = 10Dq-4Ds-5Dt \quad (3)$$

In present article the crystal field parameters are evaluated and is given by Dq = 1757 cm^{-1}, Ds = -2652 cm^{-1} and Dt = 1111 cm^{-1}. These results are good consistent with theoretical results[44]. Generally, Dq, Dt will have equal sign value in case of axial elongation and opposite in case of axial contraction, hence our present study indicates Dq, Dt are tetragonally elongated distorted octahedral site symmetry.

EPR Study

EPR is an actual experimental spectroscopic method to explore molecules, ions, radicals containing unpaired electrons by varying the magnetic field at which they attain into resonance with the consistent frequency. EPR studies have been carried out on VO^{2+} ions doped ZnS-CdS composite nanoparticles at room temperature. Generally, when the applied magnetic field parallel to the crystallographic axis, an eight-line pattern is expected for a vanadyl impurity, in most cases, the EPR spectrum of vanadyl complexes can be adequately explained in terms of a single unpaired electron (S = 1/2) interacting with the nuclear spin of a vanadium nucleus, i.e., I = 7/2, so the states are split into (2I+1) = 8 different energy states each, separated by the hyperfine coupling constant[45]. The single electron in the 3d shell is accountable for the paramagnetism. Among the isotopes of vanadium, ^{51}V isotope has an abundance of 99.76% with a nuclear spin. In all-out of the nanomaterials, the paramagnetic V^{4+} ion appears as VO^{2+} in a tetragonally distorted octahedral coordination. The EPR spectrum consists of a hyperfine construction owed to amongst the ^{51}V nucleus magnetic moment and the magnetic moment of d^1 electron. The hyperfine structure of eight lines resemble the eight values of the magnetic quantum numbers m = ±7/2, ±5/2, ±3/2 and ±1/2. In our present studies, a vanadyl ion consists of octahedral sites with tetragonal distortion from the spectrum consists of eight lines hyperfine with eight parallel and eight perpendicular lines of the spectrum are clearly observed. The transitions belong to the orientation of the V=O bond parallel to the applied magnetic field exhibit hyperfine coupling constants, that are larger than those for the perpendicular orientations as shown in Fig.-2.

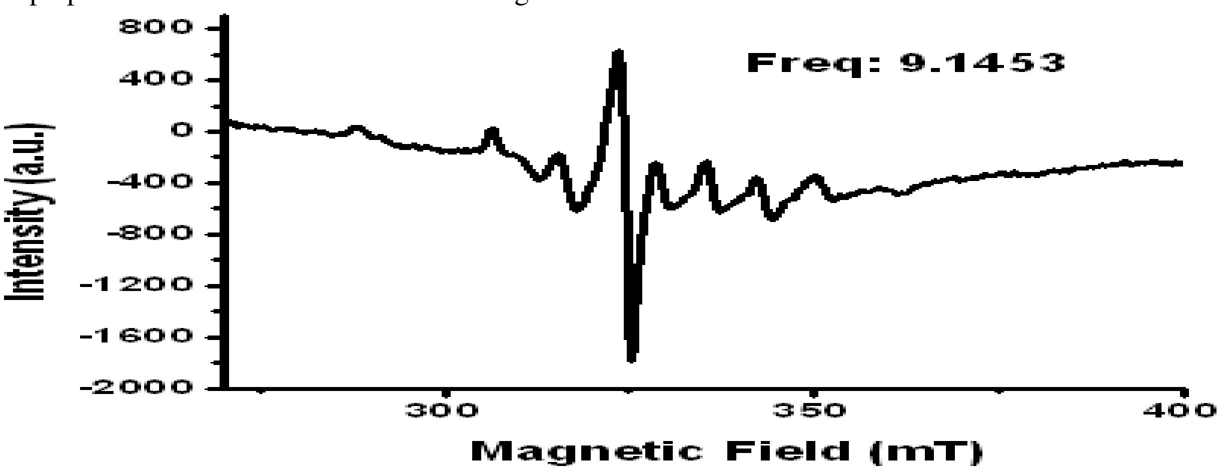

Fig.-2: EPR Spectrum of VO^{2+} Ions Doped ZnS-CdS Composite Nanoparticles

The spin Hamiltonian parameters have been evaluated, which indicate that the paramagnetic impurity has entered the lattice both interstitially and substitutionally. The spin Hamiltonian parameters are calculated as $g_{\parallel} = 1.90$, $g_{\perp} = 1.98$ and $A_{\parallel} = 211.86 \times 10^{-4}$, $A_{\perp} = 41.38 \times 10^{-4}$ cm^{-1} the g-values are held good and compared with earlier and all present values hold good with calculated and experimental results are listed in Table-1. An octahedral site with a tetragonal compression would give *g* values in the order $g_{\parallel} < g_{\perp} < g_e$. The present evaluated values of the spin-Hamiltonian parameters agree with the above order. Furthermore $A_{11} > A_{\perp}$[46,47] from these observations, it is suggested that the paramagnetic ion. The ratio of $\frac{\Delta_{||}}{\Delta_{\perp}} = (g_e - g_{||})/(g_e - g_{\perp})$ is greater than unity (>1) which measures the tetragonality of the vanadyl site. By inter connection with EPR and optical parameters, the Fermi contact term 'κ' and also the molecular bonding coefficients β_1^2, β_2^2 and γ^2, the dipolar hyperfine coupling constant 'P' can be resolved from the below expressions. The parameters $\Delta_\perp$ and $\Delta_{||}$ are the separation of energies from the ground state to the nearest higher states $\Delta_\perp$ = $^2B_{2g} \rightarrow {}^2Eg$ and $\Delta_{||}$ = $^2B_{2g} \rightarrow {}^2B_{1g}$ transitions respectively[48,49], coefficients β_1^2, β_2^2 and γ^2 are characterized by in-plane σ bonding, in-plane *π* bonding and out of plane *π* bonding, respectively, given in the below expressions[50]:

$$g_\perp = g_e\left[1-\left(\frac{\lambda\gamma^2\beta_2^2}{\Delta_\perp}\right)\right] \quad (4)$$

$$g_{||} = g_e\left[1-\left(\frac{4\lambda\beta_1^2\beta_2^2}{\Delta_{||}}\right)\right] \quad (5)$$

and

$$A_\perp = P\left[\frac{2}{7}-\kappa+\left(\frac{11}{14}\right)(g_\perp - g_e)\right] \quad (6)$$

$$A_{||} = -P\left[\kappa+\left(\frac{4}{7}\right)\beta_2^2+(g_e - g_{||})+\frac{3}{7(g_e-g_\perp)}\right] \quad (7)$$

The free ion value of spin-orbit coupling constant for vanadyl is λ (= 170 cm^{-1})[51] from the above equation $g_\perp$ and $g_{||}$[52] are associated with the bonding parameters and the free electron 'g_e' value (2.0023). Where the Fermi-contact interaction parameter (κ) representing the amount of unpaired electron density at the vanadium nucleus which is held with the degree of distortion is approximated. Moreover, in the d orbital the unpaired electron causes a zero Fermi contact interaction. A non-zero value of κ due to the Spin polarization of inner-electrons. The dipolar coupling parameter, the radial distribution parameter P of the wave function of the ions $P = g_e g_N \beta_1^2 \beta_N \langle r^{-3} \rangle$. $A_{||}$ and $A_\perp$ are related to the molecular orbital bonding coefficient (β_2^2)[53]. Where P is the direct dipole interaction of electron and g_n is the nuclear moments with a factor g, β_e and β_N are the Bohr and nuclear magnetons and 'r' is the effective radius of 3-d shell[54]. The isotropic hyperfine coupling and Fermi contact terms are directly related to the amount of unpaired electron density at the nucleus by neglecting the second order effects and considering negative values for all and $A_\perp$ and $A_{||}$[55] were calculated from equation (8) and are listed in given Table-1.

$$P = 7(A_{||} - A_\perp) / (6 + 3\lambda/2\Delta_{||}) \quad (8)$$

The isotropic and anisotropic parameters (g_{iso} and A_{iso}) are estimated using the formulae:

$$g_{iso} = (2g_{||}+g_\perp)/3 \quad (9)$$

$$A_{iso} = (2A_{||}+A_\perp)/3 \quad (10)$$

Using the above expressions with equations (5) and (6)

One gets $\kappa = -(A_{iso}/P) - (g_e - g_{iso})$ (11)

The parameter 'κ' indicates extreme sensitivity to the deformation of the electron orbitals of the central vanadium ion and the P value decreases as covalency increases and should be reported in units of 10^{-4} cm^{-1}. The theoretical value of P ranges from 100 to 160 (x 10^{-4}) cm^{-1} [56]. The obtained values of P and κ are consistent with the vanadyl complexes having tetragonal symmetry[57,58]. The free-ion value P is reduced which is indicating that the complex is fairly covalent. Using P and κ in expressions, β_2^2 the covalency of V=O ratio is evaluated. β_1^2 and γ^2 are calculated. The evaluated values of P, κ are 104 x 10^{-4} cm^{-1}, 0.44 and β_1^2, β_2^2, γ^2 are 0.2, 1.0, 0.83 and the deviation of β_2^2 is unity represents the admixture of the degree of the ligand orbitals and increase in the degree of the covalency. In the present investigations, β_2^2 is clearly indicated that the bonding is nearly ionic and represents poor π bonding of the ligands. It seems that 'κ' value is very less than β_2^2 and equal to unity. However, by comparing the all parameters generally, 'κ' value indicates the combinations of the 4s orbital into the d_{xy} orbital due to low symmetry ligand field[59]. The values of (1- β_1^2) and (1-γ^2) are measures the covalency. If the bonding coefficients β_1^2 = 1, the bond would be purely ionic and if β_2^2 = 0.5, the bond would be purely covalent.

The bonding coefficients parameter gives an indication of the strength of σ bonding between the vanadium atom and equatorial ligands, while the other indicates the influence of π bonding between the vanadium ion and the vanadyl oxygen. In the present results, these values are clearly mentioned. The bonding coefficients β_1^2, β_2^2 and γ^2 characterize in-plane σ bonding, in-plane π bonding and out of plane π bonding. The value β_2^2 is greater than β_1^2, γ^2 which indicating that in the plane σ bonding, out of plane π bonding are more covalent than in the plane π bonding confirms that in the paramagnetic ionV^{4+} in the complex exists as vanadium has tetragonal distortion with octahedral site symmetry (C_{4v})[60]. In the present article very less value of bonding coefficient ($1–\beta^2 =1$) indicates the strongly recommended in the ionic nature with σ bonding in-plane, similarly, $1-\gamma^2$ suggests moderately ionic out-of-plane π bonding are listed in the given Table-1.

Table-1: Principal g, Hyperfine (A) and Molecular Orbital Coefficients for VO^{2+} Ions Doped ZnS-CdS Composite Nanoparticles.

$g_{\|\|}$	1.90
$g_{\perp}$	1.98
$A_{\|\|}$	211.86 x10^{-4} cm^{-1}
$A_{\perp}$	41.38 x10^{-4} cm^{-1}
β_1^2	0.28
β_2^2	1.0
γ^2	0.8
$(1-\beta_1^2)$	0.71
$(1-\gamma^2)$	0.10
κ	0.44
P	104 x10^{-4} cm^{-1}
$\frac{\Delta_{\|\|}}{\Delta_{\perp}}$	1.30 x10^{-4} cm^{-1}

CONCLUSION

VO^{2+} ions doped ZnS-CdS composite nanoparticles were synthesized by a chemical precipitation method and are characterized by EPR and UV-Visible studies. From EPR studies, VO^{2+} ions are in an octahedral coordination with a tetragonal compression and have a C_{4v} symmetry. The optical spectrum exhibits three characteristic bands and also evaluated the crystal field parameters Dq, Ds, Dt. This supports the conclusion drawn from the EPR data that the tetragonal distortion is higher in the host lattice.

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