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Electron paramagnetic resonance parameters of substitutional Cr^{2+} impurity in GaAs by a cluster approach

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A cluster treatment incorporating Jahn-Teller distortion and covalency effects has been given for a substitutional Cr^{2+} impurity in GaAs to interpret the g factors and zero-field splitting parameters. Significant charge-transfer effects have been found to be present in this system. The g factors and the zero-field splitting parameter have been explained by the present treatment but the calculated cubic field parameter is an order of magnitude too low in comparison with the EPR experimental data. The results have been discussed in terms of the approximations used and compared with the previous available calculations in this system. Suggestions for future improvements have been indicated.

I. INTRODUCTION

There has been an increasing interest in the III-V semiconductor materials containing transition-metal impurities because of their important applications, as in photoconductors, microwave detectors, and other optoelectronic devices. In particular, GaAs:Cr^{2+} has been the subject of a considerable number of experimental as well as theoretical investigations and much progress has been made, although mainly in understanding the electronic structure of the ground state of the impurity. Many theoretical questions, however, have remained unanswered for the excited states of the impurity ion, particularly Cr which is essential for semiinsulating substrates in device applications.

The experimental evidences from the electron paramagnetic resonance[1,2] (EPR) and ultrasonic attenuation[3] have established that the GaAs:Cr^{2+} system undergoes a Jahn-Teller distortion, effecting the change in symmetry from tetrahedral to tetragonal at the Cr^{2+} site. The photoluminescence experiments[4] have indicated that the 0.84-eV line observed for GaAs in a number of experiments corresponds to the Cr^{2+} impurity transition between the relaxed Jahn-Teller distorted states derived from ^5E and $^5T_2$. The ground state $^5T_2$ splits[2] into $^5B_2$ and ^5E states corresponding to D_{2d} symmetry due to Jahn-Teller effect, whereas ^5E splits into $^5A_1$ and $^5B_1$ of D_{2d} symmetry. These results are consistent with photoconductivity measurements.[5,6] Similar results were also found for Cr^{2+} in II-VI compounds form EPR and infrared absorption experiments.[7–9]

On the theoretical side, very few detailed attempts have been made to characterize the electronic properties of GaAs:Cr^{2+}. Recently Hemstreet and Dimmock[10] and also Sharma, Viccaro, and Sundaram[11,12] have performed electronic structure calculations on GaAs:Cr^{2+} (and on GaAs:Cr^{3+}) by modifying the free-ion one-electron orbitals. Explicitly, they altered the normalization constants of the orbitals by including three parameters (R_{ee}, R_{tt}, and R_{et}) which were deduced from the $X\alpha$-scattered wave calculations. This method has predicted correctly the ground state of Cr^{2+} in GaAs and obtained 0.6 eV as the energy separation between the states $^5T_2$ and ^5E of Cr^{2+}, compared to the corresponding experimental value of 0.68 eV for the cubic field splitting. The effects of the Jahn-Teller distortion, however, were not considered in these calculations. Also, the magnetic properties of this system were not analyzed. For Cr^{2+} in II-VI compounds, Vallin and Watkins[9] have adopted a molecular-orbital treatment in the framework of the ligand field theory. Their approach has been based on the one-parameter theory and has revealed the importance of the charge-transfer effects on the magnetic properties of the impurities in such systems.

The aim of the present article is to report our theoretical analysis of the g factors, the zero-field splitting parameter D, and the cubic field parameter a in GaAs:Cr^{2+}. The Cr^{2+} impurity occurs substitutionally at Ga site in the crystal. Krebs and Stauss[1] have identified by means of the EPR experiments the Cr^{2+} $3d^4$ center in Cr-doped GaAs and have experimentally determined the g factors, the zero-field splitting parameter D, and the parameter a associated with the Cr^{2+} center.

To the knowledge of the authors no theoretical evaluations of the *g* factors and the *D* and *a* parameters have yet been given in the literature for this system although a pertinent preliminary report has been given by the authors previously.[12]

In Sec. II we describe briefly the relevant theory which includes the construction of the wave functions of a cluster containing the central magnetic ion and the nearest neighbors and gives the derived expressions for the spin-Hamiltonian parameters $g_{||}$, $g_{\perp}$, D and a. The effect of the crystal environment has been accounted for in two steps, first by subjecting the cluster to the cubic crystal field and second, by incorporating directly in calculations the experimental Jahn-Teller splittings of the energy levels observed in crystals. In Sec. III we discuss our calculated results. Concluding remarks have been made in Sec. IV.

II. THEORY

As mentioned earlier, the theory of the electronic structure of the transition-metal ion impurities in semiconductors has not been well developed. In our theoretical analysis, we have employed a molecular-orbital theory which considers a molecular cluster Cr^{2+}-As_4 subjected to the cubic crystal field and Jahn-Teller distortion. Because of the Jahn-Teller effect[13] the Cr^{2+} experiences the tetragonal symmetry instead of the tetrahedral symmetry which is present at the Ga site in the pure crystal. In the present treatment the molecular orbitals have been constructed as linear combinations of the *d* orbitals of Cr^{2+} and the outermost *s* and *p* orbitals of the As atoms. The molecular orbitals are given by

$$\Psi_\alpha = N_\alpha(\phi_{d\alpha} - \sqrt{3}\lambda_{dp_\pi}\chi_{p_\pi\alpha}) , \qquad (1)$$

$$\Psi_\beta = N_\beta(\phi_{d\beta} - \lambda_{dp_\sigma}\chi_{p_\sigma\beta} - \lambda_{ds}\chi_{s\beta} - \lambda_{dp_\pi}\chi_{p_\pi\beta}) , \qquad (2)$$

where (in terms of the cubic field representations $\theta,\epsilon,\xi,\eta,\zeta$) α stands for the symbols θ and ϵ, and β for ξ, η, and ζ. The wave functions $\phi_{d\alpha}$ and $\phi_{d\beta}$ represent the *d* orbitals of the transition-metal ion (Cr^{2+}) whereas $\chi_{s\beta}$, $\chi_{p_\sigma\beta}$, $\chi_{p_\pi\alpha}$, and $\chi_{p_\pi\beta}$ are the appropriate symmetry combinations of the outermost *s*, p_σ, and p_π orbitals of the ligands (As). As, for example, $\chi_{s\xi}$ is $\frac{1}{2}(\chi_{s_1} - \chi_{s_2} + \chi_{s_3} - \chi_{s_4})$, where χ_{s_i} are the outermost *s* orbital wave functions of the *i*th ligand (see Fig. 1). For convenience of consultation, particularly, concerning our choice of phase conventions, the wave functions $\phi_{d\alpha}$, $\phi_{d\beta}$, $\chi_{s\beta}$, $\chi_{p_\sigma\beta}$, $\chi_{p_\pi\alpha}$, and $\chi_{p_\pi\beta}$ have been listed in Table I. The central-ion wave functions ϕ_{dj} ($j \equiv \theta$, ϵ, ξ, η, and ζ) correspond to the *xyz* axis system located at the central ion, whereas the ligand s_i and the p_{x_i}, p_{y_i}, and p_{z_i} orbitals correspond to the local x_i, y_i, z_i axis system situated at the *i*th ligand site (see Fig. 1). In Eqs. (1) and (2) N_α and N_β are the normalization constants and λ_{ds}, λ_{dp_σ}, and λ_{dp_π} are the admixture coefficients.

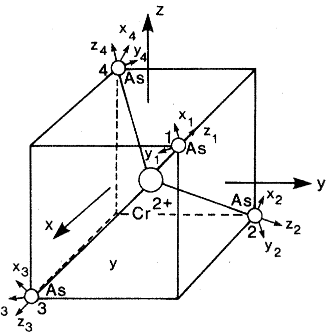

FIG. 1. Depicts the locations of Cr^{2+} and As in Cr^{2+}-As_4 cluster showing the numbering of the As atoms and the axis system.

In a cubic crystal field the cluster wave functions Ψ_ξ, Ψ_η, and Ψ_ζ are the degenerate one-electron orbitals representing the ground state $^5T_2$ (in cubic field representation) and the cluster one-electron orbitals $\Psi_\theta, \Psi_\epsilon$ representing the degenerate excited state ^5E (see Fig. 2). Because these states are orbitally degenerate,[13] they undergo Jahn-Teller distortion. Consequently, the ground state $^5T_2$ (in cubic field representation) splits into $^5B_2$ and ^5E (in tetragonal crystal field representation), whereas the cubic field excited state ^5E splits into the tetragonal crystal field levels $^5A_1$ and $^5B_1$ (see Fig. 2). The information as to the new ground state (which is $^5B_2$) and the separation between these levels has recently been available from the EPR experiments.[1,2]

In the present treatment we have assumed as a first approximation that the wave functions of the cluster are not altered significantly in going from tetrahedral symmetry to the tetragonal symmetry resulting from the Jahn-Teller distortion and that the main effect of the Jahn-Teller distortion is to split the energy levels of T_2 and E symmetry of the tetrahedron in the manner mentioned above. It is because of this reason that we have been restricted to take the same parameter λ_{dp_π} in both Eqs. (1)

TABLE I. Basis functions used for forming linear combinations to obtain cluster molecular orbitals. ϕ_{dj} are the $3d$ orbitals of the central magnetic ion and χ_{sj}, $\chi_{p_\pi j}$, and $\chi_{p_\sigma j}$ are tetrahedral symmetry combinations of s and p orbitals of the ligands. s_i, p_{x_i}, and p_{y_i} denote the s, p_x and p_y orbitals of the ligands at site i.

j	ϕ_{dj}	χ_{sj}	$\chi_{p_\pi j}$	$\chi_{p_\sigma j}$
θ	$\phi_{d(3z^2-r^2)}$		$\frac{1}{2}(p_{x_1}-p_{x_2}-p_{x_3}+p_{x_4})$	
ϵ	$\phi_{d(x^2-y^2)}$		$\frac{1}{2}(p_{y_1}-p_{y_2}-p_{y_3}+p_{y_4})$	
ξ	$\phi_{d(yz)}$	$\frac{1}{2}(s_1-s_2+s_3-s_4)$	$\frac{1}{4}[p_{x_1}+p_{x_2}-p_{x_3}-p_{x_4}$ $+\sqrt{3}(-p_{y_1}-p_{y_2}+p_{y_3}+p_{y_4})]$	$\frac{1}{2}(p_{z_1}-p_{z_2}+p_{z_3}-p_{z_4})$
η	$\phi_{d(xz)}$	$\frac{1}{2}(s_1+s_2-s_3-s_4)$	$\frac{1}{4}[p_{x_1}-p_{x_2}+p_{x_3}-p_{x_4}$ $+\sqrt{3}(p_{y_1}-p_{y_2}+p_{y_3}-p_{y_4})]$	$\frac{1}{2}(p_{z_1}+p_{z_2}-p_{z_3}-p_{z_4})$
ζ	$\phi_{d(xy)}$	$\frac{1}{2}(s_1-s_2-s_3+s_4)$	$-\frac{1}{2}(p_{x_1}+p_{x_2}+p_{x_3}+p_{x_4})$	$\frac{1}{2}(p_{z_1}-p_{z_2}-p_{z_3}+p_{z_4})$

and (2) [besides the factor $\sqrt{3}$ in Eq. (1)]. This point will be discussed further in Sec. III.

In order to obtain the g factors and the D and a parameters in the spin Hamiltonian[1]

$$H_s=\mu_B[g_{\parallel}S_zH_z+g_{\perp}(S_xH_x+S_yH_y)]+D[S_z^2-\tfrac{1}{3}S(S+1)]+a/6(S_x^4+S_y^4+S_z^4)\,, \tag{3}$$

one perturbs the ground state ${}^5B_2$ by the spin-orbit, Zeeman, and spin-spin interactions:

$$V_{\text{so}}=\sum_i \zeta_i \vec{\ell}_i\cdot\vec{s}_i\,, \tag{4}$$

$$V_z=\mu_B\left[\sum_i \vec{\ell}_i+g_0\sum_i \vec{s}_i\right]\cdot\vec{H}\,, \tag{5}$$

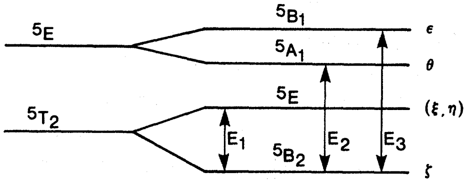

FIG. 2. Energy-level diagram with symmetry designations for Cr^{2+} $3d^4$ ion in a cubic crystal field and Jahn-Teller distortion. The left-hand-side levels correspond to the energies of d electrons in a cubic field. The right-hand-side levels show the splittings due to the Jahn-Teller distortion producing D_{2d} symmetry. The one-electron orbitals θ, ϵ, ξ, η, and ζ in the cubic field representation have been used to show the orbitals appropriate to the energy levels.

$$V_{\text{ss}}=4\mu_B^2\sum_{i>j}\left[\frac{\vec{s}_i\cdot\vec{s}_j}{r_{ij}^3}-\frac{3(\vec{s}_i\cdot\vec{r}_{ij})(\vec{s}_j\cdot\vec{r}_{ij})}{r_{ij}^5}\right]. \tag{6}$$

In the spin-orbit interaction V_{so}, ζ_i is the usual spin-orbit coupling parameter for the general ith electron; V_z is the usual Zeeman interaction and V_{ss} is the usual spin-spin interaction; $\vec{\ell}_i$ and $\vec{s}_i$ are the angular momentum and spin angular momentum for the ith electron, respectively; μ_B is the Bohr magneton; g_0 is the free-electron g factor; and $\vec{H}$ is applied magnetic field. Considering up to the second-order perturbations of the Zeeman and spin-orbit interactions and the first-order perturbation of the spin-spin interaction on the ground state and comparing with the spin-Hamiltonian in Eq. (3), one obtains the expressions for $g_{\parallel}$, $g_{\perp}$, and D. For obtaining the spin-Hamiltonian parameter a we consider the fourth-order effects of spin-orbit interaction and the second-order effects of the spin-spin interaction. Accordingly, the expressions for $g_{\parallel}$, $g_{\perp}$, D, and a parameters are obtained as

$$g_{\parallel}=g_0-\frac{8\zeta_2S_2}{E_3}\,, \tag{7}$$

$$g_{\perp}=g_0-\frac{2\zeta_1S_1}{E_1}\,, \tag{8}$$

$$D=\zeta_1^2\left[\frac{1}{E_1}-\frac{5}{3E}\right]-4\zeta_2^2\left[\frac{1}{E_3}-\frac{5}{3E}\right]-3\rho\,, \tag{9}$$

$$a=\frac{36}{E_1^2E_2}\left\{\zeta_2^2\zeta_1^2\left[1+\frac{5}{3}\left[\frac{2E_1+E_2}{E}\right]+\left[\frac{5E_1}{3E}\right]^2\right]+\rho^2E_1^2+2\zeta_2\zeta_1\rho E_1\left[1+\frac{5E_1}{3E}\right]+\zeta_1^2E_2\rho\right\}, \tag{10}$$

where

$$\zeta_2=\frac{N_EN_{T_2}}{4}\{\zeta_{d,d}-[4\lambda_{dp_\pi}\langle\phi_{d\zeta}|\zeta(r)|\chi_{p_\pi\zeta}\rangle+\lambda_{dp_\sigma}\langle\phi_{d\zeta}|\zeta(r)|\chi_{p_\sigma\zeta}\rangle+\lambda_{ds}\langle\phi_{d\zeta}|\zeta(r)|\chi_{s\zeta}\rangle]$$

$$+[(\lambda_{dp_\pi}\lambda_{dp_\sigma}/\sqrt{2}+\lambda_{dp_\pi}^2/2)]\zeta_{p,p}\}, \tag{11}$$

$$S_2=N_EN_{T_2}[1-(4\lambda_{dp_\pi}\langle\phi_{d\zeta}|\chi_{p_\pi\zeta}\rangle+\lambda_{dp_\sigma}\langle\phi_{d\zeta}|\chi_{p_\sigma\zeta}\rangle+\lambda_{ds}\langle\phi_{d\zeta}|\chi_{s\zeta}\rangle)$$

$$+(\lambda_{dp_\pi}\lambda_{dp_\sigma}/\sqrt{2}+\lambda_{dp_\pi}^2/2-AR\lambda_{dp_\pi}\lambda_{ds})], \tag{12}$$

$$\zeta_1=\frac{N_{T_2}^2}{4}\{\zeta_{d,d}-[2(\lambda_{dp_\pi}\langle\phi_{d\xi}|\zeta(r)|\chi_{p_\pi\xi}\rangle+\lambda_{dp_\sigma}\langle\phi_{d_\xi}|\zeta(r)|\chi_{p_\sigma\xi}\rangle+\lambda_{ds}\langle\phi_{d\xi}|\zeta(r)|\chi_{s\xi}\rangle)]$$

$$+(\sqrt{2}\lambda_{dp_\pi}\lambda_{dp_\sigma}-\lambda_{dp_\pi}^2/2-2AR\lambda_{dp_\pi}\lambda_{ds})\}, \tag{13}$$

$$S_1=N_{T_2}^2\{1-[2(\lambda_{dp_\pi}\langle\phi_{d\xi}|\chi_{p_\pi\xi}\rangle+\lambda_{dp_\sigma}\langle\phi_{d\xi}|\chi_{p_\sigma\xi}\rangle+\lambda_{ds}\langle\phi_{d\xi}|\chi_{s\xi}\rangle)]$$

$$+(\sqrt{2}\lambda_{dp_\pi}\lambda_{dp_\sigma}-\lambda_{dp_\pi}^2/2-2AR\lambda_{dp_\pi}\lambda_{ds})\}, \tag{14}$$

$$N_E^2=(1+3\lambda_{dp_\pi}^2-2\sqrt{3}\lambda_{dp_\pi}\langle\phi_{d\theta}|\chi_{p_\pi\theta}\rangle)^{-1}, \tag{15}$$

$$N_{T_2}^2=(1+\lambda_{dp_\sigma}^2+\lambda_{ds}^2+\lambda_{dp_\pi}^2-2\lambda_{dp_\sigma}\langle\phi_{d\zeta}|\chi_{p_\sigma\zeta}\rangle-2\lambda_{ds}\langle\phi_{d\zeta}|\chi_{s\zeta}\rangle-2\lambda_{dp_\pi}\langle\phi_{d\zeta}|\chi_{p_\pi\zeta}\rangle)^{-1}, \tag{16}$$

$$\rho=\mu_B^2\frac{2}{49}(7p_{1,2}-8p_{3,4}), \tag{17}$$

$$p_{n,m}=\int_0^\infty\frac{1}{r^n}\Psi_d^2(r)\int_0^r r'^m\Psi_d^2(r')\,dr'\,dr, \tag{18}$$

$$A=\frac{1}{\sqrt{2}}\left\langle\chi_s\left|\frac{d}{dy}\right|\chi_{p_y}\right\rangle, \tag{19}$$

with $\Psi_d(r)$ as the radial wave function of the magnetic ion and R as the distance of a ligand from the central ion; χ_s and χ_{p_y} are the s and p_y orbital wave functions of a ligand.

In arriving at the expressions (7)–(14) we have retained all the "local," "nonlocal," and "distant" terms[14] as far as the spin-orbit effects are concerned where the "local" terms are defined as those matrix elements which contain only the wave functions of the central ion, the "distant" terms which contain only the wave functions of the ligands, and the "nonlocal" terms which contain not only the wave functions of the central ion but also of the ligand ions. For the spin-spin interaction only the local terms have been retained. Also, in deriving the expression for $g_{\parallel}$, $g_{\perp}$, D, and a the ligand-ligand interaction terms arising from the spin-orbit and spin-spin effects and the ligand-ligand overlaps have been neglected. The subscripts 1 and 2 of the various parameters in Eqs. (7)–(16) have been appropriately assigned so as to correspond to the notations of Vallin and Watkins.[9] The symbols E_1, E_2, and E_3 stand for the energies, with respect to the ground state $^5B_2$, of the states ^5E, $^5A_1$, and $^5B_1$ in the tetragonal symmetry, respectively (see Fig. 2), and E is the average energy of the excited triplet states[9,15] measured from the ground state. It is worth noting that the energy values E_2 and E_3 have interchanged their roles in the present case from those of Ref. 9 since the levels $^5B_1$ and $^5A_1$ have been inverted in case of GaAs:Cr^{2+}. The symbols $\zeta_{d,d}$ and $\zeta_{p,p}$ in the above expressions are the spin-orbit coupling constants associated with the d electrons of Cr^{2+} and $4p$ electrons of As, respectively, which may be evaluated by means of the integral[16]

$$\zeta_{l,l} = \int u_{nl}(r)\zeta(r)u_{nl}(r)\,dr \ , \qquad (20)$$

where $u_{nl}(r)$ is r times the radial orbital (with the quantum numbers nl) of the atom or ion concerned and $\zeta(r)$ is the r-dependent spin-orbit coupling operator:

$$\zeta(r) = \frac{\mu_B^2}{a_0^3}\frac{1}{r}\frac{dV(r)}{dr} \ , \qquad (21)$$

with $V(r)$ as the potential experienced by an electron at position given by

$$V(r) = \left[\frac{d^2u_{nl}(r)}{dr^2} \Big/ u_{nl}(r)\right] - \frac{l(l+1)}{r^2} + E_{nl} \ , \qquad (22)$$

where E_{nl} is the orbital energy. Since $\zeta(r)$ depends on $dV(r)/dr$, E_{nl} in Eq. (22) effectively does not contribute to the spin-orbit coupling constant. The matrix element $\langle \phi_{d_{xy}} | \zeta(r) | \chi_{p_\pi\zeta} \rangle$ in Eqs. (7)–(14) is the two-center nonlocal integral of the spin-orbit coupling operator $\zeta(r)$ [Eq. (21)] between the Cr^{2+} wave functions $\phi_{d_{xy}}$ and the As wave functions $\chi_{p_\pi\zeta}$. The matrix element $\langle \phi_{d_{xy}} | \chi_{p_\pi\zeta} \rangle$ is the two-center overlap integral between $\phi_{d_{xy}}$ and $\chi_{p_\pi\zeta}$. Other matrix elements in Eqs. (7)–(16) carry similar meaning.

In the following section we have used Eqs. (7)–(22) to investigate $g_{\parallel}$, $g_{\perp}$, D, and a for GaAs:Cr^{2+}.

III. CALCULATIONS, RESULTS, AND DISCUSSION

The expressions (7)–(16) are appropriate to the tetragonal symmetry and depend on the various one- and two-center matrix elements such as $\zeta_{d,d}(Cr^{2+})$, $\zeta_{pp}(\mathrm{As})$, $\langle \phi_{d_{xy}} | \zeta(r) | \chi_{p_\pi\zeta} \rangle$, the overlap integrals such as $\langle \phi_{d_{xy}} | \chi_{p_\pi\zeta} \rangle$, and on the admixture parameters λ_{ds}, λ_{dp_σ}, and λ_{dp_π}.

For the evaluation of the various matrix elements we have adopted the atomic orbitals of Cr^{2+} as given by Clementi[17] and the atomic orbitals of As as calculated by Bagus, Gilbert, and Roothan.[18] The spin-orbit matrix elements such as $\zeta_{d,d}$, $\langle \phi_{d\zeta} | \zeta(r) | \chi_{p_\pi\zeta} \rangle$, etc., have been calculated by a method similar to the one used previously[16] in context with the magnetic properties of Fe^{3+} and Mn^{2+} in solids and making use of the general expression for the α function[19] for the expansion of a Slater orbital from one center onto the other. The overlap matrix elements which occur in the normalization constants N_α and N_β and in Eqs. (7)–(14) have been calculated by employing a general analytical expression for the overlap between two Slater orbitals.[19]

The calculated values of the one-center spin-orbit integrals have been listed in Table II. The distance R between Cr^{2+} and As is taken as 2.44 Å for GaAs considering that Cr^{2+} is located at a Ga site. The calculated values of $\zeta_{d,d}(Cr^{2+})$ and $\zeta_{pp}(\mathrm{As})$ come out to be 303 cm^{-1} and 1256 cm^{-1}, respectively, which compares favorably with the corresponding available values,[20] 236 cm^{-1} and 1273 cm^{-1}. We have used our calculated values for analyzing $g_{\parallel}$, $g_{\perp}$, D, and a. The overlap matrix elements (calculated by means of the general analytical expression[19] for the overlap integrals between two Slater orbitals) have been listed in Table III, for $R(Cr^{2+}\text{-}\mathrm{As}) = 2.44$ Å. Actually, S_{dp_π}, S_{dp_σ}, and S_{ds} basic integrals have been tabulated in Table III and have been defined as

$$S_{dp_\pi} = \langle \phi_{d_{x'z'}} | \chi_{p_{x_1}} \rangle \ , \qquad (23)$$

$$S_{dp_\sigma} = \langle \phi_{d_{3z'^2-r^2}} | \chi_{p_{z_1}} \rangle \ , \qquad (24)$$

$$S_{ds} = \langle \phi_{d_{3z'^2-r^2}} | \chi_s \rangle \ , \qquad (25)$$

where $\phi_{d_{x'z'}}$ are the Cr^{2+} $3d$ orbitals of $x'z'$ type in the axes system $x'y'z'$ located at Cr^{2+} site and parallel to x_1, y_1, z_1 axis system located at the ligand site 1; $\chi_{p_{x_1}}$ is the As p orbital of the type x at site 1. $\phi_{d_{3z'^2-r^2}}$ and $\chi_{p_{z_1}}$ have been defined similarly. The two-center overlap matrix elements such as $\langle \phi_{d\zeta} | \chi_{p_\pi\zeta} \rangle$ appearing in Eqs. (7)–(16) are related to the basic overlap integrals by means of the rotation-group elements. The two-center spin-orbit matrix elements are about 2 orders of magnitude lower in magnitude than the relevant one-center spin-orbit matrix elements and therefore

TABLE II. Tabulation of one-center spin-orbit coupling constants (in units of cm^{-1}) useful for evaluations of $g_{\parallel}$, $g_{\perp}$, D, and a and comparison with published results.

$\zeta_{d,d}(Cr^{2+})$	$\zeta_{p,p}(\mathrm{As})$	Reference
303	1256	present
236	1273	Abragam and Bleaney[a]

[a] See Ref. 20.

TABLE III. Table of overlap integrals between the Cr^{2+} and As wave functions involved in the evaluations of the expressions for the spin-Hamiltonian parameters $g_{\|}$, $g_{\perp}$, D, and a.

S_{dp_π}	S_{dp_σ}	S_{ds}
0.061 81	−0.084 88	0.068 57

have not been listed. The calculated values of the parameters ρ and A as defined in Eqs. (17) and (19) have been given in Table IV. As for the energy values (Fig. 2) we have taken $E_1 = 4500\ \text{cm}^{-1}$, $E_2 = 7300\ \text{cm}^{-1}$, and $E_3 = 9700\ \text{cm}^{-1}$ as deduced by Krebs and Stauss.[2] The energy E has been estimated to be of the order of $20\,000\ \text{cm}^{-1}$.[9,15]

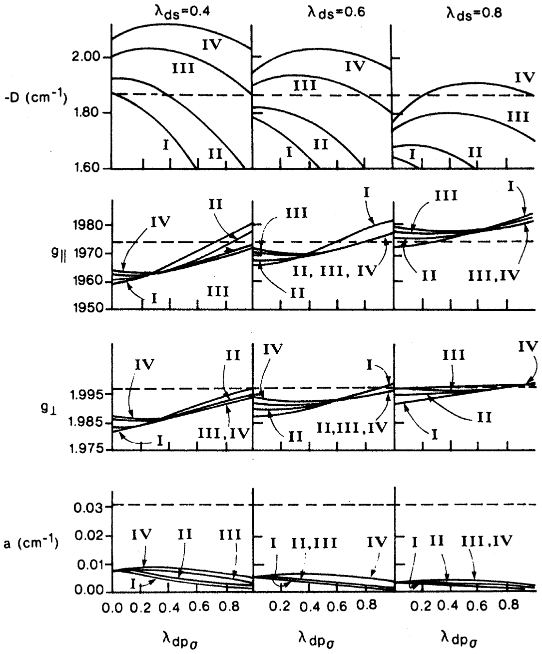

FIG. 3. Shows variations of the spin-Hamiltonian parameters D, $g_{\|}$, $g_{\perp}$, and a, with the admixture coefficients λ_{ds}, λ_{dp_σ}, and λ_{dp_π}. Only the curves for $\lambda_{ds} = 0.4$, 0.6, and 0.8 are shown for representative purposes. The curves marked I, II, III, and IV correspond to the values of λ_{dp_π} equal to 0.0, 0.04, 0.08, and 0.1, respectively. The dashed lines represent the experimental values (Ref. 2) of the spin-Hamiltonian parameters.

The evaluation of the expressions (7)−(16) requires, further, the values of λ_{ds}, λ_{dp_σ}, and λ_{dp_π}. Since they are unknown at present, we follow the procedure of determining them from the available experimental data. To this end, we vary λ_{ds}, λ_{dp_σ}, and λ_{dp_π} and obtain correspondingly $g_{\|}$, $g_{\perp}$, D, and a from Eqs. (7)−(16). Figure 3 illustrates the variation of the spin-Hamiltonian parameters as a function of λ_{ds}, λ_{dp_σ}, and λ_{dp_π} values. The dotted lines in Fig. 3 have been drawn to mark the experimental values. The set of values of λ which explain best the experimental data for $g_{\|}$, $g_{\perp}$, D, and a are $\lambda_{ds} = 0.6$, $\lambda_{dp_\sigma} = 0.8$, and $\lambda_{dp_\pi} = 0.08$ which correspond to the calculated spin-Hamiltonian parameters $g_{\|} = 1.975$, $g_{\perp} = 1.995$, $D = -1.865$, $a = 0.0043$ as compared with the experimental values $g_{\|} = 1.974 \pm 0.003$, $g_{\perp} = 1.997 \pm 0.002$, $D = -1.860 \pm 0.0016$, and $a = 0.031 \pm 0.013$ (see also Table V). The numerical values of normalization constants N_E and N_{T_2} associated with the above set of λ values have been presented in Table IV. As for the variations of $g_{\|}$, $g_{\perp}$, D, and a parameters with λ_{ds}, λ_{dp_σ}, and λ_{dp_π} parameters, Fig. 3 reveals that by increasing λ_{dp_π} the value of $|D|$ increases, while the values of $g_{\|}$ and $g_{\perp}$ increase if $\lambda_{dp_\sigma} < 0.3$ and decrease if $\lambda_{dp_\sigma} > 0.3$. Also, on increasing λ_{ds} the value of $|D|$ decreases, whereas the values of $g_{\|}$ and $g_{\perp}$ increase. The values of a are not significantly altered by the variations of λ_{ds}, λ_{dp_σ}, and λ_{dp_π}. Thus the set of values of the admixture coefficients that correspond best to the experimental values of the spin-Hamiltonian parameters lie close to $\lambda_{ds} = 0.6$, $\lambda_{dp_\sigma} = 0.8$, and $\lambda_{dp_\pi} = 0.08$ as mentioned above. These values of λ's may now be used in the first-order approximation to deduce the charge-transfer covalencies, by means of the expressions

$$\lambda_{dp_\sigma} = \frac{2}{\sqrt{3}} S_{dp_\sigma} + \gamma_{dp_\sigma} , \tag{26}$$

$$\lambda_{dp_\pi} = \frac{2\sqrt{2}}{3} S_{dp_\pi} + \gamma_{dp_\pi} , \tag{27}$$

$$\lambda_{ds} = \frac{2}{\sqrt{3}} S_{ds} + \gamma_{ds} , \tag{28}$$

TABLE IV. List of the calculated parameters A, ρ. The normalization constants N_E and N_{T_2} which explain best the observed spin-Hamiltonian parameter have also been given.

A (Å^{-1})	$\rho(Cr^{2+})$ (cm^{-1})	N_E	N_{T_2}
1.733	0.128	1.0044	0.6969

TABLE V. Comparison of the calculated values of the spin-Hamiltonian parameters $g_{\parallel}$, $g_{\perp}$, D, and a for GaAs:Cr^{2+} with the experimental values. The admixture parameters which correspond to the calculated values have also been listed.

λ parameters			Spin-Hamiltonian parameters				
λ_{ds}	λ_{dp_σ}	λ_{dp_π}	$g_{\parallel}$	$g_{\perp}$	D	a	Reference
0.6	0.8	0.08	1.975	1.995	−1.865	+0.0043	present calculations
0	0.9	0.07	1.986	1.990	−1.879	+0.005	present calculations
0.369	0.509	0.045	1.966	1.988	−1.860	+0.01	present calculations
experiment			1.974(3)	1.997(2)	−1.860(16)	0.031(13)	Krebs and Strauss[a]

[a] See Ref. 1.

where S_{dp_σ}, S_{dp_π}, and S_{ds} have been defined by Eqs. (23)–(25) and γ's are the corresponding charge-transfer covalency parameters. The above equations have been obtained by imposing the condition that the antibonding orbitals [Eqs. (1) and (2)] are orthogonal to the bonding orbitals which could be formed by combining the central-atom d orbitals with the orbitals of the ligands by means of the charge-transfer covalency parameters. The numerical factors appearing in Eqs. (26)–(28) are due to the rotation-group elements to appropriately relate the pertinent parameters. The calculated values of the charge-transfer covalencies come out to be $\gamma_{ds}=0.522$, $\gamma_{dp_\sigma}=0.8988$, and $\gamma_{dp_\pi}=0.0217$.

As mentioned earlier the nonlocal contributions arising from the spin-orbit interaction are negligible. As for the distant contributions arising from this interaction, they depend on the λ values and come out to be about 20% of the local contribution which is due to the fact that such contributions are greatly reduced by the second-order effect of the λ parameters even though the spin-orbit coupling constant of As is about four times that of Cr^{2+}. Thus, in general, it is important to consider the effect of the distant terms in such calculations.

In case one neglects completely the ligand s-state contributions (see Fig. 3 for extending the calculated values for $\lambda_{ds}\rightarrow 0$), the best set of the other parameters could be fixed in the vicinity of $\lambda_{dp_\sigma}=0.9$ and $\lambda_{dp_\pi}=0.07$, although the calculated values would then be somewhat unsatisfactory (see Table V) compared with the experimental values as could be judged from the curves plotted in Fig. 3. This shows that the ligand s-state contributions are important and should not be ignored.

The values of λ's ($\lambda_{ds}=0.6$, $\lambda_{dp_\sigma}=0.8$, and $\lambda_{dp_\pi}=0.08$) as deduced above to explain the experimental data in the best possible way are, indeed, very high in magnitude.[21(a)] In an attempt to search for a better set we have selected another set of values of the admixing parameters, viz., $\lambda_{ds}=0.369$, $\lambda_{dp_\sigma}=0.509$, and $\lambda_{dp_\pi}=0.045$ (see also Table V) with only a fair agreement with the experimental data. This new set yields the calculated values: $g_{\parallel}=1.966$, $g_{\perp}=1.988$, $D=-1.860$, and $a=+0.01$, which are not in as good an agreement with the experimental values as those from the previous set (see Table V). The new set still gives a high[21(a)] value of λ_{dp_σ}. In short, it appears that, with the experimental data at hand, it is hard to obtain acceptable values of the admixing parameters.

The experimental data we have used and which give rise to our numerical values of the admixture parameters are those of Krebs and Stauss[2] who deduce E_1, E_2, and E_3 from uniaxial stress measurements. They estimate $E_1=3E_{\text{JT}}(^5T_2)$ by using their measured Jahn-Teller coefficient $V_E=-0.85$ eV/Å. Then they obtained E_2 and E_3 by employing the model calculations of Vallin *et al.*[7] and fitting with the above E_1 value by considering that the zero-phonon line at 6760 cm^{-1} and the absorption peak at 7300 cm^{-1} both arise from the $^5T_2$-^5E cubic field transition of this same Cr^{2+} center. It is apparent that these values are illustratative rather than definitive,[21(b)] mainly due to the large experimental error bars on E_1.

Recent Zeeman studies[22,23] have demonstrated that the above-mentioned 6760-cm^{-1} zero-phonon line is due to a Cr center located at a site with trigonal rather than tetragonal symmetry. This is possible provided that the center observed in these studies is not the isolated center seen in EPR experiments. In addition, Clerjaud *et al.*[24] have discovered a new set of zero-phonon lines around 6620 cm^{-1} which are conceived to be due to the isolated Cr^{2+} center. Accounting for this observation and based on their detailed optical absorption measurements at low temperature with different amounts of *n* or *p* doping in samples, Hennel *et al.*[25] have concluded that $E_{JT}(^5T_2) \leq 660$ cm^{-1}; consequently, $E_1 \leq 2000$ cm^{-1}, $E_3 - E_2 \leq 320$ cm^{-1} and $E_2 \simeq 6620$ cm^{-1} and, hence, $E_3 \simeq 6940$ cm^{-1}. Clearly, the E_i values deduced by Hennel *et al.* are considerably lower than the values given by Krebs and Stauss.[2] The reduction factors for E_1, E_2, and E_3 are 0.44, 0.91, and 0.71, respectively.

If one believes in the reduction in the energy values as discussed above and repeats our calculations, it is obvious from Eqs. (7)–(19) that the admixture parameters would be reduced significantly. References 22–25 are recent experimental observations and have appeared in the literature after completing the present calculations. It is suggested that the future calculations should be directed towards not only improving the theory but also incorporating the latest experimental data.

As mentioned in Sec. I, Hemstreet and Dimmock[10] have performed calculations for the electronic energy states of substitutional Cr^{2+} in GaAs in the strong-field coupling limit by modifying the normalization constants of the *e* and t_2 type orbitals. Their method essentially consists of multiplying the free-electron <u>*d*</u> orbitals of the Cr^{2+} ion by factors $\sqrt{R_{ee}}$ or $\sqrt{R_{tt}}$ depending on whether the orbital belongs to the *e* symmetry or to the t_2 symmetry. They took $R_{ee} = 0.63$ and $R_{tt} = 0.21$ from their $X\alpha$-scattered wave-cluster method and found that $^5T_2$ and ^5E states of Cr^{2+} are separated by 0.6 eV in agreement with the cubic field splitting 0.68 eV. Careful analysis shows that their wave functions contain only part of our wave functions taken in the present treatment. Explicitly, our local part of the wave functions, namely, $N_E\phi_{d\epsilon}$ and $N_{T_2}\phi_{d\xi}$ of Eqs. (1) and (2), are effectively equivalent to the modified wave functions used by Hemstreet and Dimmock. This leads us to compare our λ values with the λ's contained in Hemstreet and Dimmock's parameters R_{ee} and R_{tt}. Making use of the calculated value of the overlap integrals (Table III) and Eq. (15) we obtain $\lambda_{dp_\pi} = 0.51$ or -0.38. Both of these values are very large in magnitude relative to the expected value of this parameter or to the one obtained by our treatment. One of the reasons for this large value may be the neglect of Jahn-Teller splitting of ^5E and $^5T_2$ levels in Ref. 10. It is not possible to obtain other parameters λ_{ds} and λ_{dp_σ} from the parameters of Ref. 10 since the connecting Eq. (16) for N_{T2}^2 (equal to R_{tt}) is the only available equation with two unknowns. Moreover, since it requires also the value of λ_{dp_π} with an obtained value which is too high, the other parameters based on this are likely to be doubtful. Since all the λ parameters are not possible to be deduced from the R_{ee} and R_{tt} values of Ref. 10, we compare our values of N_E^2 and N_{T2}^2 (R_{ee} and R_{tt}) which are obtained, for our best set of λ values, to be 1.009 and 0.486, respectively. These values are quite different from the corresponding values 0.63 and 0.21 of R_{ee} and R_{tt} of Ref. 10. There are two reasons for this difference: one is mainly due to the consideration in Ref. 10 of only the *d* orbitals of Cr^{2+} with modification of the normalization constants; the other is due to the neglect of Jahn-Teller distortion in Ref. 10.

Though the treatment used here is analogous to the one considered by Vallin and Watkins,[9] it must be noted that they have neglected completely the *s* orbitals of the ligands, and, as far as the formalism is concerned, they have not included the nonlocal terms. Further, they have analyzed their data in terms of a single parameter *k*, and assumed the same charge transfers for all the compounds (ZnS, ZnSe, ZnTe, CdTe) investigated. Also, it must be noted that the role of the *s*-state functions included in the present treatment is not primarily to affect the normalization constants as it is clear from Eqs. (7)–(19), where λ_{ds} parameter appears explicitly in the expressions besides in the normalization constants. Our calculations show that the *s* orbitals of the ligands are even more important than the p_π orbitals, since the overlap of the *s* orbitals with the *d* orbitals of the central ion is found to be larger in magnitude than that of the p_π orbitals.

In the present analysis we have neglected the ligand-ligand overlap effects and the parts of the distant matrix elements which involve ligand-ligand interactions. In addition, the contributions arising from the "nonlocal" and "distant" terms due to spin-spin interactions have been omitted. Though such effects are expected to influence the covalency parameters only slightly, they may be important for explaining the spin-Hamiltonian parameters more precisely and must be investigated.

Also, the explicit changes in the cluster wave functions consequent to the distorted geometry of the molecular cluster produced by the Jahn-Teller distortion have been ignored in our calculations for simplicity. The consideration of such modifications would not only remove the restriction of retaining the same λ_{dp_π} parameter in Ψ_α and Ψ_β cluster wave functions in Eqs. (1) and (2), but would also alter other admixture parameters, and consequently improve the theory substantially.

IV. CONCLUSIONS

The spin-Hamiltonian parameters, namely, the g factors, zero-field splitting D, and cubic field parameter a of GaAs:Cr^{2+} have been analyzed theoretically in the framework of a molecular cluster subjected to the cubic crystal field and the Jahn-Teller energy-level splittings, and the values of the covalency parameters due to s and p orbitals of ligands have been deduced from the calculations. The present study is very significant for understanding the electronic structure of the defect center Cr^{2+} in GaAs. We find that large covalency parameters are needed to interpret the observed spin-Hamiltonian parameters. Even with large covalency effects, the cubic field parameter a is explained only in sign and its calculated value is an order of magnitude too low. The main cause for high value of covalencies appears to be in employing the experimentally observed values of the Jahn-Teller splittings of the ^5E and $^5T_2$ cubic field energy levels, which have been discovered to be too high in view of the most recent careful estimates of Jahn-Teller splittings from detailed optical absorption measurements at low temperatures with different amounts of n or p doping in samples by Hennel *et al.*[25] If one adopts the new values of the Jahn-Teller splittings in calculations, the covalencies are expected to be reduced as discussed in Sec. III.

For further progress in theoretical treatment it is suggested to form new wave functions compatible with the distorted geometry of the cluster and utilize the latest and more exact observed data for the Jahn-Teller splittings of the energy levels.

The calculations are underway in our group for GaAs:Cr^{2+} with modifications of the wave functions of the molecular cluster consistent with the displaced positions of the atoms constituting the cluster in confirmation with the observed Jahn-Teller tetragonal distortion. The shift of the position of the atoms will be determined with the aid of the latest experimentally estimated Jahn-Teller splittings of the $^5T_2$ and ^5E energy levels and the improvised covalency parameters will be obtained to explain the optical as well as the EPR experimental data. It might be remarked that care must be taken to admix also the s and p_σ type (allowed by symmetry) of orbitals of the ligands in the θ and ϵ type of cluster orbitals, which are otherwise absent in the undistorted cluster wave functions and that the admixtures, in general, would be different in different symmetry orbitals because of the distorted geometry of the cluster. Also, in the refined calculations the ligand-ligand interaction terms in various matrix elements involving spin-spin and spin-orbit interactions and the ligand-ligand overlap effects would be required to understand the nature of the defect center Cr^{2+} in GaAs. Further improvements could be made by retaining also the nonlocal and distant terms in the matrix elements involving the spin-spin interaction following the procedure of Refs. 14 and 16. One then expects better agreement of the calculated results with the experimental data and a reliable estimate of the covalency parameters, which would be valuable for evaluating the (remaining) electronic excited states of the center using the generalized Coulomb and exchange matrix elements[11,26] to gain information as to the electronic structure of the center.

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