PHYSICAL REVIEW B VOLUME 51, NUMBER 20 15 MAY 1995-II

Zero-field-splitting parameters of Cr^{2+} ion in GaAs

Yi-Yang Zhou
*Chinese Center for Advanced Science and Technology (World Laboratory), P.O. Box 8730, Beijing 100080, People's Republic of China and Institute of Solid State Physics, Sichuan Normal University, Chengdu 610066, People's Republic of China**

Fu-Zhen Li
Department of Physics, Sichuan Normal University, Chengdu 610066, People's Republic of China

(Received 8 July 1994; revised manuscript received 17 January 1995)

The zero-field-splitting (ZFS) parameters D, a, and F for Cr^{2+} ions in GaAs are studied by a molecular-orbital treatment. Viccaro, Sundaram, and Sharma's procedure is adopted in the study, taking into account all the excited spin triplets. The charge-transfer effect is shown to be significant, and the spin triplets are found to make an important contribution to ZFS. The results are compared with the previous available calculations in this system. Suggestions for future improvements are indicated.

I. INTRODUCTION

Transition-metal impurities in semiconductors have been the subject of many investigations, both experimental and theoretical. In particular, GaAs:Cr^{2+} is the most frequently studied III-V semiconductor because of its important applications in high-speed electronic circuits, photoconductors, microwave detectors, and other optoelectronic devices. It is well known[1-10] that the GaAs:Cr^{2+} system undergoes a Jahn-Teller (JT) distortion, effecting a change in symmetry from tetrahedral (T_d) to tetragonal (D_{2d}) at the Cr^{2+} site. The ground state $^5T_2$ for T_d splits into $^5B_2$ and ^5E states corresponding to D_{2d} symmetry due to the JT effect, whereas the excited state ^5E for T_d splits into $^5A_1$ and $^5B_1$ of D_{2d} symmetry (see Fig. 1). Values for the gyromagnetic parameters $g_\perp$ and $g_\parallel$ and for the zero-field-splitting (ZFS) parameter D combined with a and F were obtained from conventional electron-paramagnetic resonance (EPR) by Krebs and Stauss[1,2] and confirmed by far-infrared spectroscopic measurements made by Wagner and White.[3] The value of D was deduced from $D-a-\frac{2}{3}F$ by taking F to be zero and quoted to ±0.3%, whereas the error in a was very large.[1] From further EPR measurements, Stauss *et al.*[4] obtained $a=+0.035\pm0.26$ cm^{-1}, but F was still taken to be zero. By thermally detected EPR experiments, Bates *et al.*[9] obtained accurate values for the ZFS parameters $D=-1.895\pm0.005$, $a=0.035\pm0.002$, and $F=-0.053\pm0.009$ (cm^{-1}) in this system. However, very few detailed attempts have been made to characterize theoretically the ZFS parameters in GaAs:Cr^{2+}. A successful treatment for the EPR parameters in GaAs:Cr^{2+} was made by Viccaro, Sundaram, and Sharma.[11] They employed a molecular-orbital theory to explain these parameters as well as the charge-transfer effects in this system. The procedure of Viccaro, Sundaram, and Sharma in Ref. 11 is useful and will be adopted in the present paper. However, in their work there are the following two insufficiencies: (i) They did not deal with the parameter F (their calculated results for D and a were compared with, of course, the experimental data[4] obtained by taking F to be zero at that time); (ii) they considered the contribution of all the excited spin triplets as that of an average energy and the obtained sign for the spin-triplet contribution to D is opposite that for the spin-quintet contribution, whereas the sign for the spin-triplet contribution to a is the same as that for the spin-quintet contribution. Their expressions for the spin-triplet contributions are so rough (as shown below) that the values of a calculated by using these formulas were an order of magnitude lower than those from the experimental data. To our knowledge, a systematic study of the ZFS parameters D, a, and F in GaAs:Cr^{2+} has not appeared in literature.

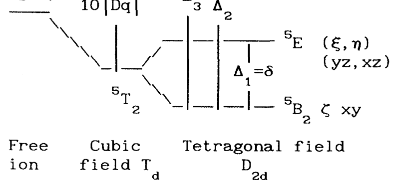

FIG. 1. Energy levels ($^5\Gamma_1$) of $3d^4$ ions in the cubic and the tetragonal crystal field.

Over the past few decades, most theoretical studies of the ZFS for $3d^4$ and $3d^6$ ions in crystals were based on the ^5D approximation, i.e., only the contributions of high-spin state ^5D of these ions to ZFS were considered and the low-spin states ^3L ($L=P,D,F,G,H$) were neglected (see, e.g., Refs. 12–27). Perturbation formulas for the ZFS parameters of $3d^4$ and $3d^6$ ions at various symmetry sites have been given up to different perturbation-order terms in ^5D approximation (see, e.g., Refs. 15, 16, 20, 21, and 27). These formulas are available to estimate ZFS parameters for these ions in ionic crystals, but they are not applicable to covalent crystals when the contribution from the spin-orbit (SO) coupling associated with the ligands is non-negligible. Vallin and Watkins[28] and Viccaro, Sundaram, and Sharma[11] suggested a molecular-orbital treatment for Cr^{2+} ($3d^4$) in tetragonal symmetry; their theory is useful for covalent crystals. However, the contribution of all the spin triplets was considered simply as that of an average energy in their works,[11,28] and the obtained spin-triplet contributions to the ZFS are rather simple compared to the detailed derivation appearing in the present paper. Recently, a series of theoretical studies[29–36] for the ZFS of $3d^4$ and $3d^6$ ions in crystals showed the important spin-triplet contribution. However, all these treatments were made by neglecting the ligand SO coupling contribution. For covalent crystals such as GaAs:Cr^{2+}, it is necessary to use a more accurate calculational method that should consider the contributions to the ZFS arising not only from the excited spin triplets of the central transition-metal ions (Cr^{2+}) but also from the SO interaction within the outermost ligands (As).

II. THEORY

In the present paper, we employ a molecular-orbital theory[11] that considers a molecular cluster Cr^{2+}-As_4 subject to the cubic crystal field (CF) and JT distortion. Because of the JT effect the Cr^{2+} experiences the tetragonal symmetry instead of the tetrahedral symmetry, which is present at the Ga site in the pure crystal. The molecular orbitals are 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[11]

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

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

where (in terms of the cubic-field representations $\theta,\varepsilon,\xi,\eta,\zeta$) 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 $\chi_{p_\pi\alpha}$, $\chi_{s\beta}$, $\chi_{p_\pi\beta}$, and $\chi_{p_\sigma\beta}$ are the appropriate symmetry combinations of the outermost s, p_σ, and p_π orbitals of the ligands (As). N_α and N_β are the normalization constants and λ_{ds}, λ_{dp_π}, and λ_{dp_σ} are the admixture coefficients. In a cubic CF, the cluster wave functions ϕ_ξ, ϕ_η, and ϕ_ζ are the degenerate one-electron orbitals representing the ground state $^5T_2$ in cubic-field representation and the cluster one-electron orbitals ϕ_θ and ϕ_ε represent the degenerate excited state ^5E (see Fig. 1). The JT distortion in GaAs:Cr^{2+} further separates the ground state $^5T_2$ into $^5B_2$ and ^5E and splits the excited state ^5E into $^5A_1$ and $^5B_1$ (see Fig. 1).

The Hamiltonian for $3d^4$ and $3d^6$ ions in tetragonal symmetry can be written as[37–39]

$$H = H_0 + H' , \tag{3}$$

with

$$H_0 = H_c(Dq) + H_t^a(\delta,\mu) + H_e^a(B,C) , \tag{4}$$

$$H' = H_t^b(\delta,\mu) + H_e^b(B,C) + H_{\mathrm{SO}}(\xi) + H_{\mathrm{SS}}(\rho) , \tag{5}$$

where H_0 is the zeroth-order Hamiltonian, H' is the perturbation term, and H_c, H_t^a, H_t^b, H_e^a, H_e^b, H_{SO}, and H_{SS}, are the cubic CF, the diagonal and the off-diagonal tetragonal CF, the diagonal and the off-diagonal electrostatic Coulomb interaction, and the SO and the spin-spin (SS) interaction terms, respectively. Dq is the cubic CF parameters and δ and μ are the tetragonal splittings of $^5T_2$ and ^5E states (see Fig. 1), respectively. B and C are the Racah electrostatic parameters and ξ and ρ denote the SO and SS coupling constants, respectively. If the interactions H_{SO} and H_{SS}, in Eq. (5) are not considered, for $3d^4$ and $3d^6$ ions in tetragonal symmetry, there are four spin-quintet ($S=2$) terms $^5\Gamma$, as mentioned above, and 33 spin-triplet ($S=1$) terms $^3\Gamma$ ($\Gamma = A_1$, A_2, B_1, B_2, and E, the irreducible representations,[40] for the tetragonal point groups C_{4V}, D_4, and D_{2d}).

For the orbital singlet ground-state case, with $^5B_2$ being the lowest (see Fig. 1), provided the first excited state lies high enough, the ZFS of the ground $S=2$ spin state is given in terms of the extended Stevens operators $O_k^q(s_x,s_y,s_z)$ (Refs. 41 and 42) as

$$H_{\mathrm{ZFS}} = B_2^0 O_2^0 + B_4^0 O_4^0 + B_4^4 O_4^4 . \tag{6}$$

The conversion between the ZFS parameters B_k^q in Eq. (6) and several other notations can be found in Rudowicz's review;[42] e.g.,

$$B_2^0 = \tfrac{1}{3}D, \quad B_4^0 = \frac{F}{180} + \frac{a}{120}, \quad B_4^4 = \frac{a}{24} \tag{7}$$

for the conventional case. Following the perturbation theory[43,44] and using the molecular-orbital wave functions (1) and (2) and the matrices of Hamiltonian (3)–(5), a detailed derivation yields the formulas of the ZFS parameters B_k^q in Eq. (6) for the ground state $^5B_2$. All the excited spin-triplet states of $3d^4$ and $3d^6$ and the SO coupling of ligands are considered. We separate these expressions of B_k^q into two parts: $B_k^q(\mathrm{I})$ and $B_k^q(\mathrm{II})$. $B_k^q(\mathrm{I})$ is just the contribution of ^5D and $B_k^q(\mathrm{II})$ is that from the combination of the spin triplets ^3L and spin quintet ^5D. Further we separate $B_k^q(\mathrm{I})$ into $B_k^q(\mathrm{I})(\mathrm{SO})$ and $B_k^q(\mathrm{I})(\mathrm{SS})$, which denote the pure SO and the pure SS plus the mixing SS-SO contributions, respectively. The SS interaction is considered only within the ^5D state because of its weakness. The formulas are given as

$$\begin{aligned} B_k^q &= B_k^q(\mathrm{I}) + B_k^q(\mathrm{II}) \\ &= B_k^q(\mathrm{I})(\mathrm{SO}) + B_k^q(\mathrm{I})(\mathrm{SS}) + B_k^q(\mathrm{II})(\mathrm{SO}) , \end{aligned} \tag{8}$$

with

$$\begin{aligned} B_2^0(\mathrm{I})(\mathrm{SO}) = {} & \frac{\zeta_1^2}{48\Delta_1} - \frac{\zeta_2^2}{12\Delta_3} - \frac{\zeta_1^3}{96\Delta_1^2} - \frac{\zeta_1\zeta_2^2}{48\Delta_1\Delta_3} - \frac{43\zeta_1^4}{5376\Delta_1^3} + \frac{\zeta_2^4}{336}\left[-\frac{11}{4\Delta_1\Delta_3^2} + \frac{31}{\Delta_3^3}\right] \\ & + \frac{\zeta_1^2\zeta_2^2}{256}\left[\frac{9}{7\Delta_1^2\Delta_2} + \frac{1}{\Delta_1^2\Delta_3} + \frac{44}{21\Delta_1\Delta_3^2}\right] , \end{aligned} \tag{9}$$

$$B_2^0(\mathrm{I})(\mathrm{SS})=-\rho-\frac{9\rho^2}{28}\left[\frac{3}{\Delta_1}-\frac{4}{\Delta_2}\right]-\frac{3\rho\zeta_1}{4\Delta_1}\,, \tag{10}$$

$$\begin{aligned}
B_2^0(\mathrm{II})(\mathrm{SO})={}&\zeta_1^2\left[\frac{1}{27\Delta_{16}}+\frac{1}{54\Delta_{19}}-\frac{1}{72\Delta_{30}}-\frac{1}{144\Delta_{33}}\right]\\
&+\zeta_2^2\left[\frac{1}{27\Delta_{15}}+\frac{1}{108\Delta_{17}}+\frac{1}{27\Delta_{18}}-\frac{1}{72\Delta_{26}}-\frac{1}{24\Delta_{27}}-\frac{1}{24\Delta_{28}}-\frac{1}{72\Delta_{29}}-\frac{1}{12\Delta_{35}}-\frac{1}{36\Delta_{36}}\right]\\
&+\zeta_1^3\left[-\frac{1}{36\Delta_1\Delta_{16}}+\frac{1}{144\Delta_1\Delta_{19}}+\frac{1}{54\Delta_{16}\Delta_{33}}-\frac{1}{216\Delta_{19}\Delta_{33}}+\frac{1}{72\Delta_{32}\Delta_{33}}-\frac{1}{288\Delta_{33}^2}\right]\\
&+\zeta_2^3\left[-\frac{1}{36\Delta_1\Delta_{15}}+\frac{1}{288\Delta_1\Delta_{17}}+\frac{1}{72\Delta_1\Delta_{18}}-\frac{1}{8\Delta_3\Delta_{27}}+\frac{1}{24\Delta_3\Delta_{29}}+\frac{1}{48\Delta_3\Delta_{33}}\right]\\
&+\zeta_1\zeta_2^2\left[\frac{1}{54\Delta_{15}\Delta_{29}}+\frac{1}{27\Delta_{16}\Delta_{29}}-\frac{1}{27\Delta_{16}\Delta_{36}}-\frac{1}{72\Delta_{17}\Delta_{27}}+\frac{1}{216\Delta_{17}\Delta_{29}}+\frac{1}{144\Delta_{17}\Delta_{33}}\right.\\
&\qquad-\frac{1}{36\Delta_{18}\Delta_{27}}-\frac{1}{108\Delta_{18}\Delta_{29}}+\frac{1}{36\Delta_{18}\Delta_{32}}+\frac{1}{36\Delta_{19}\Delta_{26}}-\frac{1}{108\Delta_{19}\Delta_{29}}-\frac{1}{54\Delta_{19}\Delta_{36}}\\
&\qquad-\frac{1}{24\Delta_{26}\Delta_{27}}+\frac{1}{72\Delta_{26}\Delta_{29}}-\frac{1}{72\Delta_{26}\Delta_{32}}-\frac{1}{24\Delta_{27}\Delta_{28}}-\frac{1}{24\Delta_{27}\Delta_{32}}\\
&\qquad-\frac{1}{24\Delta_{28}\Delta_{29}}+\frac{1}{24\Delta_{28}\Delta_{32}}+\frac{1}{72\Delta_{29}\Delta_{32}}-\frac{1}{12\Delta_{32}\Delta_{35}}-\frac{1}{36\Delta_{32}\Delta_{36}}\\
&\qquad\left.-\frac{1}{12\Delta_{35}\Delta_{36}}-\frac{1}{24\Delta_{35}^2}+\frac{1}{72\Delta_{36}^2}\right]\\
&+\zeta_1\zeta_2B\left[\frac{8}{9\Delta_{15}\Delta_{16}}+\frac{2}{9\Delta_{18}\Delta_{19}}+\frac{1}{12\Delta_{26}\Delta_{32}}-\frac{5}{12\Delta_{27}\Delta_{32}}+\frac{1}{12\Delta_{28}\Delta_{33}}+\frac{1}{12\Delta_{29}\Delta_{33}}\right.\\
&\qquad\left.-\frac{1}{6\Delta_{32}\Delta_{35}}+\frac{1}{6\Delta_{33}\Delta_{36}}\right]\\
&+\zeta_2^2B\left[-\frac{2}{27\Delta_{17}\Delta_{18}}-\frac{5}{12\Delta_{26}\Delta_{27}}-\frac{1}{6\Delta_{26}\Delta_{35}}+\frac{1}{6\Delta_{27}\Delta_{35}}+\frac{5}{12\Delta_{28}\Delta_{29}}+\frac{1}{6\Delta_{28}\Delta_{36}}+\frac{3}{18\Delta_{29}\Delta_{36}}\right]\\
&+\zeta_2^2C\left[\frac{1}{6\Delta_{27}\Delta_{35}}+\frac{1}{18\Delta_{29}\Delta_{36}}\right]+\frac{2\zeta_1^2\delta}{9\Delta_{16}\Delta_{19}}-\frac{\zeta_2^2\mu}{27\Delta_{15}\Delta_{18}}+B_2^0(\mathrm{II})(\mathrm{SO})^{(4)}\,,
\end{aligned} \tag{11}$$

$$B_4^0(\mathrm{I})(\mathrm{SO})=\frac{\zeta_1^4}{8960}\left[\frac{1}{\Delta_1^3}-\frac{3}{2\Delta_1^2\Delta_2}+\frac{16}{\Delta_3^3}\right], \tag{12}$$

$$B_4^0(\mathrm{I})(\mathrm{SS})=\frac{3\rho^2}{70}\left[\frac{6}{\Delta_1}-\frac{1}{\Delta_2}\right]+\frac{3\rho\zeta_1}{1120}\left[\frac{\zeta_1}{\Delta_1^2}-\frac{2\zeta_2}{\Delta_1\Delta_2}+\frac{16\zeta_2}{\Delta_1\Delta_3}\right], \tag{13}$$

$$\begin{aligned}
B_4^0(\mathrm{II})(\mathrm{SO}) = {} & \frac{\zeta_1^4}{26\,880\Delta_1^2}\left[\frac{1}{\Delta_7}+\frac{1}{\Delta_{13}}+\frac{16}{\Delta_{16}}-\frac{4}{\Delta_{33}}\right] \\
& +\frac{\zeta_1^2\zeta_2^2}{1680\Delta_1^2}\left[\frac{1}{32\Delta_5}+\frac{1}{32\Delta_6}+\frac{1}{16\Delta_9}+\frac{3}{16\Delta_{10}}+\frac{3}{8\Delta_{14}}+\frac{1}{\Delta_{15}}-\frac{1}{24\Delta_{17}}-\frac{3}{2\Delta_{28}}-\frac{1}{2\Delta_{29}}-\frac{1}{\Delta_{36}}\right] \\
& -\frac{\zeta_1^2\zeta_2^2}{224\Delta_1\Delta_2}\left[\frac{1}{\Delta_{27}}+\frac{1}{\Delta_{29}}+\frac{1}{\Delta_{33}}\right] \\
& -\frac{\zeta_2^4}{1260\Delta_1\Delta_3}\left[\frac{1}{\Delta_{15}}-\frac{1}{8\Delta_{17}}-\frac{1}{2\Delta_{18}}+\frac{3}{8\Delta_{26}}+\frac{9}{8\Delta_{27}}-\frac{9}{8\Delta_{28}}-\frac{1}{8\Delta_{29}}+\frac{9}{8\Delta_{35}}-\frac{1}{4\Delta_{36}}\right] \\
& +\frac{\zeta_1^2\zeta_2^2}{1260\Delta_1\Delta_3}\left[\frac{1}{\Delta_{16}}-\frac{1}{4\Delta_{19}}+\frac{3}{8\Delta_{32}}-\frac{3}{16\Delta_{33}}\right] \\
& -\frac{\zeta_2^4}{1260\Delta_3^2}\left[\frac{1}{\Delta_{15}}+\frac{1}{4\Delta_{17}}+\frac{1}{\Delta_{18}}-\frac{3}{4\Delta_{22}}-\frac{3}{2\Delta_{23}}-\frac{1}{16\Delta_{25}}+\frac{3}{8\Delta_{26}}+\frac{9}{8\Delta_{28}}-\frac{1}{32\Delta_{30}}\right. \\
& \qquad\left.-\frac{1}{32\Delta_{31}}-\frac{1}{96\Delta_{34}}+\frac{9}{4\Delta_{35}}+\frac{3}{4\Delta_{36}}\right] \\
& -\frac{\zeta_1^2\zeta_2^2}{1260\Delta_3^2}\left[\frac{1}{\Delta_{16}}+\frac{1}{2\Delta_{19}}-\frac{3}{2\Delta_{21}}+\frac{3}{8\Delta_{32}}\right]+B_4^0(\mathrm{II})(\mathrm{SO})^{(\mathrm{others})}\,, \qquad (14)
\end{aligned}$$

$$B_4^4(\mathrm{I})(\mathrm{SO})=\frac{3\zeta_1^2\zeta_2^2}{512\Delta_1^2\Delta_2}\,, \qquad (15)$$

$$B_4^4(\mathrm{I})(\mathrm{SS})=\frac{3\rho^2}{2\Delta_2}+\frac{3\rho\zeta_1}{32}\left[\frac{\zeta_1}{\Delta_1^2}+\frac{2\zeta_2}{\Delta_1\Delta_2}\right], \qquad (16)$$

$$\begin{aligned}
B_4^4(\mathrm{II})(\mathrm{SO}) = {} & -\frac{\zeta_1^4}{768\Delta_1^2}\left[\frac{1}{\Delta_7}-\frac{1}{\Delta_{13}}\right]-\frac{\zeta_1^2\zeta_2^2}{1536\Delta_1^2}\left[\frac{1}{\Delta_5}+\frac{4}{\Delta_6}-\frac{2}{\Delta_9}-\frac{6}{\Delta_{10}}-\frac{6}{\Delta_{14}}\right] \\
& +\frac{\zeta_1^2\zeta_2^2}{256\Delta_1\Delta_2}\left[\frac{2}{\Delta_{27}}+\frac{2}{\Delta_{29}}-\frac{1}{\Delta_{33}}\right]+B_4^4(\mathrm{II})(\mathrm{SO})^{(\mathrm{others})}\,, \qquad (17)
\end{aligned}$$

where

$$\zeta_1=N_{T_2}^2[\zeta_d-(\sqrt{2}\lambda_{dp_\pi}\lambda_{dp_\sigma}-\tfrac{1}{2}\lambda_{dp_\pi}^2 -2AR\lambda_{ds}\lambda_{dp_\pi})\zeta_p]\,, \qquad (18)$$

$$\zeta_2=N_{T_2}N_E\left[\zeta_d-\left[\frac{1}{\sqrt{2}}\lambda_{dp_\pi}\lambda_{dp_\sigma}+\frac{1}{2}\lambda_{dp_\pi}^2\right]\zeta_p\right], \qquad (19)$$

$$N_E^2=(1+3\lambda_{dp_\pi}^2-2\sqrt{3}\lambda_{dp_\pi}\langle\phi_{d\theta}|\chi_{p_\pi\theta}\rangle)\,, \qquad (20)$$

$$N_{T_2}^2=(1+\lambda_{ds}^2+\lambda_{dp_\pi}^2+\lambda_{dp_\sigma}^2-2\lambda_{ds}\langle\phi_{d\xi}|\chi_{s\xi}\rangle -2\lambda_{dp_\pi}\langle\phi_{d\xi}|\chi_{p_\pi\xi}\rangle-2\lambda_{dp_\sigma}\langle\phi_{d\xi}|\chi_{p_\sigma}\rangle)\,, \qquad (21)$$

$$A=-\frac{1}{2}\left\langle\chi_s\left|\frac{d}{dy}\right|\chi_{p_y}\right\rangle\,. \qquad (22)$$

In Eqs. (9)–(17), Δ_i ($i=1-36$) are energy gaps between the excited and the ground states. The designations of the states and the energies are given in Table I. The relationships of the representation notations in Table I between the cubic and tetragonal field can be found in Table A.11 of Ref. 37. The symbols ζ_d and ζ_p in Eqs. (18) and (19) are the SO coupling constants associated with the d electrons of the central transition-metal ion (Cr^{2+}) and p electrons of ligands (As), respectively. R in Eq. (18) is the distance between the central ion (Cr^{2+}) and the ligands (As). The matrix elements $\langle\,|\,\rangle$ in Eqs. (20) and (21), e.g., $\langle\phi_{d\theta}|\chi_{p_\pi\theta}\rangle$ in Eq. (20), are the two-center overlap integrals between, e.g., $\phi_{d\theta}$ and $\chi_{p_\pi\theta}$. $B_2^0\mathrm{II}(\mathrm{SO})^{(4)}$ in Eq. (11) is the fourth-order perturbation terms of $B_2^0(\mathrm{II})(\mathrm{SO})$. There are about 1000 terms in $B_2^0(\mathrm{II})(\mathrm{SO})^{(4)}$. The numerical calculations show that the contribution of $B_2^0(\mathrm{II})(\mathrm{SO})^{(4)}$ is negligible and the expression for $B_2^0(\mathrm{II})(\mathrm{SO})^{(4)}$ has not been given. It should be noted that, in the fourth-order perturbation loop[43,44] ${}^5B_2$-Γ_i-Γ_j-Γ_k-${}^5B_2$ for the rank-four ZFS parameters $B_4^0(\mathrm{II})(\mathrm{SO})$ and $B_4^4(\mathrm{II})(\mathrm{SO})$, one (e.g., Γ_i), two (e.g., Γ_i and Γ_j), and three (Γ_i, Γ_j, and Γ_k) states may be spin triplet, corresponding to the one, two, and three gaps Δ_i ($i\geq 4$) between the excited spin triplets and the ground ${}^5B_2$ in the denominator of this term, respectively. Equations (14) and (17) give only the terms in which one of the Γ_i,

Γ_j, and Γ_k states is the spin triplet and the others are expressed as $B_4^q(\mathrm{II})(\mathrm{SO})^{(\mathrm{others})}$. There are about 1000 terms for both $B_4^0(\mathrm{II})(\mathrm{SO})^{(\mathrm{others})}$ and $B_4^4(\mathrm{II})(\mathrm{SO})^{(\mathrm{others})}$. The numerical calculations show that the terms given in Eqs. (14) and (17) are the predominant contributions as compared with $B_4^q(\mathrm{II})(\mathrm{SO})^{(\mathrm{others})}$ since the energies of spin triplets are usually larger than those of spin quintets. The expressions of $B_4^q(\mathrm{II})(\mathrm{SO})^{(\mathrm{others})}$ have not consequently been given. In Eqs. (18) and (19), some terms for the two-center SO matrix elements [e.g., $\langle \phi_{d\zeta} | \zeta(r) | \chi_{p_\pi \zeta} \rangle$, where $\zeta(r)$ is the SO coupling operator] have been neglected because they are about two orders of magnitude lower than the relevant one-center SO matrix elements $\zeta_d(\mathrm{Cr}^{2+})$ and $\zeta_p(\mathrm{As})$ (Refs. 11 and 39).

Formulas (8)–(17) can be used also to study the ZFS in ionic crystals by neglecting the ligand SO contribution, i.e., taking $\zeta_1 = \zeta_2$ (or $\lambda_{ds} = \lambda_{dp_\pi} = \lambda_{dp_\sigma} = \zeta_p = 0$ and $N_E = N_{T_2} = 1$), the expressions of $B_k^q(\mathrm{I})$ and $B_2^0(\mathrm{II})$ can be reduced to those appeared in Refs. 27 and 34, respective-

TABLE I. Definition of the states and the energies for $3d^4$ and $3d^6$ ions in tetragonal symmetry. The representation notations appeared in Ref. 37.

$\Delta_i = E_i - E_0 \ (i = 1-36)$
$E_0(^5B_2[t_2^2e^2, {}^5T_2\zeta]) = 4Dq - 2Ds + Dt - 21B$
$E_1\{^5E[t_2^2e^2, {}^5T_2(\xi,\eta)]\} = 4Dq + Ds - 4Dt - 21B$
$E_2(^5A_1[t_2^3e, {}^5E\theta]) = -6Dq + 2Ds + 6Dt - 21B$
$E_3(^5B_1[t_2^3e, {}^5E\varepsilon]) = -6Dq - 2Ds + Dt - 21B$
$E_4\{^3A_1[t_2^3(^2E)e, {}^3A_1]\} = -6Dq + \frac{7}{2}Dt - 12B + 4C$
$E_5\{^3A_1[t_2^3(^4A_2)e, {}^3E\theta]\} = -6Dq + 2Ds + 6Dt - 13B + 4C$
$E_6\{^3A_1[t_2^3(^2E)e, {}^3E\theta]\} = -6Dq + \frac{7}{2}Dt - 10B + 4C$
$E_7(^3A_1[t_2^2e^2, {}^3E\theta]) = 4Dq - 2Ds + Dt - 11B + 4C$
$E_8(^3A_2[t_2^4, {}^3T_1z]) = -16Dq + 2Ds + 6Dt - 15B + 5C$
$E_9\{^3A_2[t_2^3(^2T_1)e, {}^3T_1z]\} = -6Dq - 2Ds + Dt - 11B + 4C$
$E_{10}\{^3A_2[t_2^3(^2T_2)e, {}^3T_1z]\} = -6Dq + 2Ds + 6Dt - 3B + 6C$
$E_{11}\{^3A_2[t_2^2(^3T_1)e^2(^1A_1), {}^3T_1z]\} = 4Dq - 2Ds + Dt - B + 6C$
$E_{12}\{^3A_2[t_2^2(^3T_1)e^2(^1E), {}^3T_1z]\} = 4Dq - 2Ds + Dt - 9B + 4C$
$E_{13}\{^3A_2[t_2^2(^1T_2)e^2(^3A_2), {}^3T_1z]\} = 4Dq - 2Ds + Dt - 11B + 4C$
$E_{14}(^3A_2[t_2e^3, {}^3T_1z]) = 14Dq - 14Dt - 16B + 5C$
$E_{15}(^3B_1[t_2^3e, {}^3A_2]) = -6Dq + \frac{7}{2}Dt - 8B + 4C$
$E_{16}(^3B_1[t_2^2e^2, {}^3A_2]) = 4Dq - \frac{7}{3}Dt - 2B + 7C$
$E_{17}\{^3B_1[t_2^3(^4A_2)e, {}^3E\varepsilon]\} = -6Dq - 2Ds + Dt - 13B + 4C$
$E_{18}\{^3B_1[t_2^3(^2E)e, {}^3E\varepsilon]\} = -6Dq + \frac{7}{2}Dt - 10B + 4C$
$E_{19}(^3B_1[t_2^2e^2, {}^3E\varepsilon]) = 4Dq + 2Ds - \frac{17}{3}Dt - 11B + 4C$
$E_{20}\{^3B_2[t_2^3(^2T_1)e, {}^3T_2\zeta]\} = -6Dq + 2Ds + 6Dt - 9B + 4C$
$E_{21}\{^3B_2[t_2^3(^2T_2)e, {}^3T_2\zeta]\} = -6Dq - 2Ds + Dt - 5B + 6C$
$E_{22}\{^3B_2[t_2^2(^3T_1)e^2(^3A_2), {}^3T_2\zeta]\} = 4Dq - 2Ds + Dt - 13B + 4C$
$E_{23}\{^3B_2[t_2^2(^3T_1)e^2(^1E), {}^3T_2\zeta]\} = 4Dq - 2Ds + Dt - 9B + 4C$
$E_{24}(^3B_2[t_2e^3, {}^3T_2\zeta]) = 14Dq + 4Ds - 9Dt - 8B + 5C$
$E_{25}\{^3E[t_2^4, {}^3T_1(x,y)]\} = -16Dq - Ds + 11Dt - 15B + 5C$
$E_{26}\{^3E(t_2^3(^2T_1)e, {}^3T_1(x,y)]\} = -6Dq + Ds + \frac{19}{4}Dt - 11B + 4C$
$E_{27}\{^3E[t_2^3(^2T_2)e, {}^3T_1(x,y)]\} = -6Dq - Ds + \frac{9}{4}Dt - 3B + 6C$
$E_{28}\{^3E[t_2^3(^2T_1)e, {}^3T_2(\xi,\eta)]\} = -6Dq - Ds + \frac{9}{4}Dt - 9B + 4C$
$E_{29}\{^3E[t_2^3(^2T_2)e, {}^3T_2(\xi,\eta)]\} = -6Dq + Ds + \frac{19}{4}Dt - 5B + 6C$
$E_{30}\{^3E[t_2^2(^3T_1)e^2(^1A_1), {}^3T_1(x,y)]\} = 4Dq + Ds - 4Dt - B + 6C$
$E_{31}\{^3E[t_2^2(^3T_1)e^2(^1E), {}^3T_1(x,y)]\} = 4Dq + Ds - 4Dt - 9B + 4C$
$E_{32}\{^3E[t_2^2(^1T_2)e^2(^3A_2), {}^3T_1(x,y)]\} = 4Dq + Ds - 4Dt - 11B + 4C$
$E_{33}\{^3E[t_2^2(^3T_1)e^2(^3A_2), {}^3T_2(\xi,\eta)]\} = 4Dq + Ds - 4Dt - 13B + 4C$
$E_{34}\{^3E[t_2^2(^3T_1)e^2(^1E), {}^3T_2(\xi,\eta)]\} = 4Dq + Ds - 4Dt - 9B + 4C$
$E_{35}\{^3E[t_2e^3, {}^3T_1(x,y)]\} = 14Dq - \frac{21}{4}Dt - 16B + 5C$
$E_{36}\{^3E[t_2e^3, {}^3T_2(\xi,\eta)]\} = 14Dq - 2Ds - \frac{31}{4}Dt - 8B + 5C$
$\delta = \Delta_1 = E_2 - E_0 = 3Ds - 5Dt, \quad \mu = E_4 - E_3 = -4Ds - 5Dt$

ly. These formulas are suitable for not only the fourfold (e.g., D_{2d}), but also the sixfold coordinated tetragonal symmetry such as C_{4V}, D_4, and D_{4h}; however, the molecular orbitals (1) and (2), the SO constants (18) and (19), and the normalization coefficients (20) and (21) should be changed in C_{4V}, D_4, and D_{4h} symmetry (see, e.g., Refs. 39 and 45).

A comparison between the present and previous[11,28] formulas indicates the following differences. (i) The present paper gives the perturbation formulas for $B_4^0(F/180+a/120)$ and the expression of F is obtained first. (ii) The expression of B_2^0(I), i.e., the spin-quintet contribution to the ZFS parameter D, has shown some improvement, e.g., B_2^0(I)(SO) is given up to fourth-order rather than the second-order terms in the previous works.[11,28] Also, B_2^0(I)(SS) includes the SO-SS interaction contribution. (iii) In particular the detailed expressions of B_k^q(II)(SO), i.e., the spin-triplet contributions to the ZFS parameters D, a, and F, are given in the present paper, which is very different from the previous case.[11] The following numerical calculations will show these differences in detail.

III. CALCULATIONS AND DISCUSSION

Expressions (8)–(22) are appropriate for tetragonal symmetry. They express D, a, and f as a function of the energy gaps Δ_i ($i=1$–36), the SO parameters $\zeta_d(\mathrm{Cr}^{2+})$ and $\zeta_p(\mathrm{As})$, the overlap integrals such as $\langle \phi_{d\xi} | \chi_{p_\pi \xi} \rangle$, and the admixture parameters λ_{ds}, λ_{dp_π}, and λ_{dp_σ} as well as A and R. In the present paper the values of Racah parameters $B=800$ and $C=4B=3200$ for Cr^{2+} ions[46] and the energy gaps $\Delta_1=4500$, $\Delta_2=7300$, and $\Delta_3=9700$ (in cm^{-1}) for GaAs:Cr^{2+} (Ref. 2) are adopted and the gaps Δ_j ($j=4$–36) can be obtained from Table I by using these values. The values[11] of $\zeta_d(\mathrm{Cr}^{2+})=303$ and $\zeta_p(\mathrm{As})=1256$ cm^{-1}, and $A=1.733$ Å^{-1} and $R=2.44$ Å for GaAs:Cr^{2+} are also adopted. The overlap integrals can be related to the basic integrals S_{ds}, S_{dp_σ}, and S_{dp_π} by means of the rotation-group elements, defined as[11,39]

$$\begin{aligned} S_{ds} &= \langle \phi_{d_{z'^2}} | \chi_s \rangle , \\ S_{dp_\sigma} &= \langle \phi_{d_{z'^2}} | \chi_{p_{z_i}} \rangle , \qquad (23) \\ S_{dp_\pi} &= \langle \phi_{d_{x'z'}} | \chi_{p_{x_1}} \rangle , \end{aligned}$$

where the axes systems $(x'y'z')$ for Cr^{2+} and $(x_1 y_1 z_1)$ for As have been shown in Fig. 1 and Table 1 of Ref. 11. The calculated values[11] of $S_{ds}=0.061\,81$, $S_{dp_\sigma}=-0.084\,88$, and $S_{dp_\pi}=0.068\,57$ for GaAs:Cr^{2+} are used in this work. The values of the admixture coefficients λ_{ds}, λ_{dp_π}, and λ_{dp_σ} remain unknown. Vicarro, Sundaram, and Sharma[11] obtained $\lambda_{ds}=0.6$, $\lambda_{dp_\pi}=0.08$, and $\lambda_{dp_\sigma}=0.8$ by using their perturbation formulas and fitting the experimental EPR data. From the above data the ZFS parameters are obtained, as listed in Table II, by using the previous[11] and present formulas. In Table II the ZFS parameters B_2^0, B_4^0, and B_4^4 have been transformed to D, a, and F. Comparing the results obtained by the two different formulas, denoted by A and B in Table II, one can find that (i) there is only small difference of D(I)(SS) between A and B, which is due to the mixing SO-SS ($\rho\zeta$) and the second-order SS (ρ^2) perturbation terms in the present formulas; (ii) there are obvious differences of D(I)(SO) and a(I)(SO) between A and B, showing again the importance of contributions of the third- and fourth-order perturbation approach to ZFS (Refs. 20, 21, 23, and 24) considered in the present paper; (iii) in particular, the differences of D(II)(SO) and a(II)(SO) between the previous[11] (A) and present (B) formulas are very large [e.g., the value of a(II)(SO) for B is only $\frac{1}{3}$ of that for A; particularly, the sign of D(II)(SO) for B is opposite that for A], showing, in

TABLE II. Zero-field-splitting parameters D, a, and F for GaAs:Cr^{2+} (in cm^{-1}, except r, which is dimensionless). (a) The values (Ref. 11) of $\lambda_{ds}=0.6$, $\lambda_{dp_\pi}=0.08$, and $\lambda_{dp_\sigma}=0.8$ are used, (b) the values of $\lambda_{ds}=0.5$, $\lambda_{dp_\pi}=0.3$, and $\lambda_{dp_\sigma}=0.855$ are used. A denotes values calculated by the previous (Ref. 11) perturbation formulas; B denotes values calculated by the present perturbation formulas. Experimental values are from Ref. 9.

		Calculated					Experiment
		D(I)(SS)	D(I)(SO)	D(II)(SO)	r	D	
(a)	A	−0.384	−1.642	1.341	−0.82	−0.685	
	B	−0.381	−2.182	−1.105	0.50	−3.668	−1.895±0.005
(b)	B	−0.357	−0.459	−1.071	2.33	−1.887	
		a(I)(SS)	a(I)(SO)	a(II)(SO)	r	a	
(a)	A	−0.000 10	0.000 14	0.000 21	1.50	0.000 25	
	B	−0.000 10	0.000 20	0.000 07	0.35	0.000 17	0.035±0.002
(b)	B	−0.000 68	0.023 02	0.007 83	0.34	0.030 17	
		F(I)(SS)	F(I)(SO)	F(II)(SO)	r	F	
(a)	B	0.000 08	−0.000 30	0.002 58	−8.60	0.002 36	−0.053±0.003
(b)	B	−0.001 42	−0.010 96	−0.046 81	4.27	−0.059 19	

fact, the significance of the present perturbation formulas. It should be noted that although Vicarro, Sundaram, and Sharma's above parameter data[11] are used in the present calculations, the numerical results A of D and a are different from theirs[11] because some terms for the two-center SO matrix elements in Eqs. (18) and (19) have been neglected, as mentioned above. However, this does not affect the comparison between the results A and B in Table II obtained by using the two different formulas.

Comparing the calculated values of the ZFS parameters D, a, and F with the experimental data, one can find that the values of the admixture coefficients λ_{ds}, λ_{dp_π}, and λ_{dp_σ} fitted by the previous formulas are no longer suitable for the present formulas. Following the procedure[11] of determining them, we vary λ_{ds}, λ_{dp_π}, and λ_{dp_σ} and obtain correspondingly D, a, and F from Eqs. (8)–(22). Figure 2 illustrates the variation of the ZFS parameters D, a, and F as a function of the λ_{ds}, λ_{dp_π}, and λ_{dp_σ} values. The dotted lines in Fig. 2 have been drawn to mark the experimental values. The curves marked 1, 2, and 3 correspond to the values λ_{dp_π} equal to 0.25, 0.3, and 0.35, respectively. The set of values of λ that explain best the experimental data for D, a, and F are $\lambda_{ds}=0.5$, $\lambda_{dp_\pi}=0.3$, and $\lambda_{dp_\sigma}=0.855$, which correspond to the calculated ZFS parameters $D=-1.887$, $a=0.030$, and $F=-0.059$ as compared with the experimental values $D=-1.895\pm0.005$, $a=0.035\pm0.002$, and $F=-0.053\pm0.009$ (see also Table II). Figure 2 shows clearly that by increasing λ_{ds}, the curves for D, a, and F move to the upward and right direction. This means that the larger the λ_{ds}, the larger the values of the ZFS parameters. Similarly, among the curves 1, 2, and 3 (corresponding to $\lambda_{dp_\pi}=0.25$, 0.3, and 0.35, respectively) for D, a, and F, there is a movement to the right, i.e., the values of D, a, and F increase with an increase of λ_{dp_π}. Also, on increasing λ_{dp_σ}, the values of D and a decrease; however, F decreases and then increases. It should be pointed out that the present qualitative results for the values of D altered by the variations of λ_{ds}, λ_{dp_π}, and λ_{dp_σ} are the same as the previous case;[11] however, the shapes of the present curves for D and a are quite different from the previous case.[11] These differences are due to the different perturbation formulas (in particular the spin-triplet contribution terms), as mentioned above.

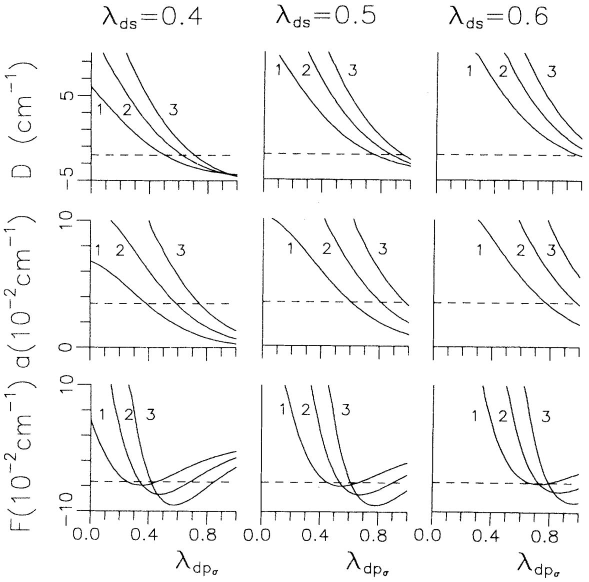

FIG. 2. Variation of the zero-field-splitting parameters D, a, and F with the admixture coefficients λ_{ds}, λ_{dp_π}, and λ_{dp_σ}. The dashed lines represent the experimental values (Ref. 9). The curves marked 1, 2, and 3 correspond to values of λ_{dp_π} equal to 0.25, 0.3, and 0.35, respectively.

From Fig. 2, the values of the admixture coefficients that correspond best to the experimental data of the ZFS parameters lie close to $\lambda_{ds}=0.5$, $\lambda_{dp_\pi}=0.3$, and $\lambda_{dp_\sigma}=0.855$, as mentioned above. The present values of λ_{ds} and λ_{dp_σ} are close to those (0.6 and 0.8) obtained by Vicarro, Sundaram, and Sharma,[11] whereas λ_{dp_π} is close to that (0.51) from Hemstreet and Dimmock's work,[11,47] but is about 40 times that (0.008) obtained by Viccaro, Sundaram, and Sharma.[11] This means that the contributions of the p_π orbitals of the ligands (As) in GaAs:Cr^{2+} are important. In addition, the present calculation shows again that the ligand s-state contributions should not be ignored in this system. These values of λ may be used in the first-order approximation to deduce the charge-transfer covalencies by means of the expressions

$$\begin{aligned}\lambda_{ds}&=\frac{2}{\sqrt{3}}S_{ds}+\gamma_{ds}\,,\\ \lambda_{dp_\pi}&=\frac{2\sqrt{2}}{3}S_{dp_\pi}+\gamma_{dp_\pi}\,,\\ \lambda_{dp_\sigma}&=\frac{2}{\sqrt{3}}S_{dp_\sigma}+\gamma_{dp_\sigma}\,,\end{aligned}\tag{24}$$

where S_{ds}, S_{dp_π}, and S_{dp_σ} are the overlap integrals defined by Eq. (23) and γ are the corresponding charge-transfer covalency parameters. The bonding orbitals are formed by combining the central-atom d orbitals with the orbitals of the ligands by means of the charge-transfer covalency parameters. The calculated values of the charge-transfer covalencies come out to be $\gamma_{ds}=0.42$, $\gamma_{dp_\pi}=0.24$, and $\gamma_{dp_\sigma}=0.95$. The present work shows again the significant charge-transfer effects in GaAs:Cr^{2+}.

Furthermore, one can estimate the contributions of the ligand SO coupling to the ZFS in GaAs:Cr^{2+}, viewing the covalency effects at a different angle. By taking $\lambda_{ds}=\lambda_{dp_\pi}=\lambda_{dp_\sigma}=\zeta_p=0$ and $N_E=N_{T_2}=1$ as mentioned above and using Eqs. (9)–(17), the values of $D=-3.149$, $a=0.074$, and $F=-0.116$ (cm^{-1}) for the contributions from the pure d orbitals of Cr^{2+} in GaAs are obtained as compared to those (-1.887, 0.030, -0.059) from the combination of d with s and p orbitals of ligands As. The large difference between the two sets of D, a, and F shows clearly the important contribution of the SO coupling associated with ligands (As) in this system. The role of the ligand SO contributions can be measured by the ratio between the *s*- and the *p*-orbital contribution and the pure *d* one,

$$R(B_k^q)=[B_k^q(dsp)-B_k^q(d)]/B_k^q(d)\ , \qquad (25)$$

where *d* and *dsp* correspond to the contribution from pure *d* orbitals and the combination of *d* with *s* and *p* orbitals, respectively. The ratios -0.40, 0.96, and -0.49 for *D*, *a*, and *F* are obtained, respectively. The negative value of the ratio corresponds to the sign of the *d*-orbital contribution being opposite that of the *s* and the *p* orbital. It is obvious that the larger the positive ratio or the smaller the negative ratio, the larger the ligand SO contributions. The large values of these ratios show the importance of the ligand SO coupling contributions to the ZFS and further reveal the strong covalency effects in this system.

Similarly, to clearly showing the spin-triplet contribution to the ZFS, the ratios between the spin-triplet and the spin-quintet contribution

$$r(B_k^q)=B_k^q(\mathrm{II})(\mathrm{SO})/B_k^q(\mathrm{I})(\mathrm{SO})\ , \qquad (26)$$

are listed in Table II. The different values of *r* obtained by using the same parameter data but the present and previous[11] formulas show the difference of these formulas and reveal, in fact, the significance of the present perturbation formulas. The large values of $r(D)$, $r(a)$, and $r(F)$ in Table II obtained by using the present formulas show the important contributions of the spin triplets in GaAs:Cr^{2+}. One may note from Table II that in this system the spin-triplet contribution to the ZFS parameter *F* is so large that neglecting this contribution one cannot obtain reasonable values of *F*. Similarly, this contribution to *D* should not be ignored in this system. However, this contribution to *a* is less than that to *D*. It has been shown recently[33] that in the tetragonal symmetry the spin-triplet contributions to the rank-four ZFS parameters B_4^q $(q=0,4)$ are, in general, larger than those to the rank-two ZFS parameter B_2^0. Following this work closely, it has been found that there exists the opposite case, i.e., $r(B_4^0)<r(B_2^0)$ for Fe^{2+} ions in the trigonal-symmetric crystal $GeFe_2O_4$.[35] This sample is for $r(B_4^4)<r(B_2^0)$ in the tetragonal symmetry.

The following two points should be noted. (i) the present values of the admixture coefficients λ are in the best fit to the experimental data for the ZFS parameters *D*, *a*, and *F* in GaAs:Cr^{2+}; these values of λ are expected to be further justified by other studies, such as phonon scattering, far-infrared measurements, and Zeeman spectroscopy measurements. We offer a few commonplace remarks by way of introduction so that others may come up with valuable opinions. (ii) λ's depend on the values of the Racah parameters *B* and *C* (Cr^{2+}), the SO parameters $\zeta_d(Cr^{2+})$ and $\zeta_p(As)$, and the overlap integrals such as $\langle\phi_{d\zeta}|\chi_{p_\pi\zeta}\rangle$ as well as *A* and *R*, as mentioned above. The values of ζ_d, ζ_p, $\langle\phi_{d\zeta}|\chi_{p_\pi\zeta}\rangle$, *A*, and *R* for GaAs:$Cr^{2+}$[11] are adopted in the present calculation. However, the following values have been quoted in the literature: $B=830-680$ and $C=3660-3090$ (in cm^{-1}) for the Cr^{2+} ion.[37–39,41,46,48] The values[46] of $B=800$ and $C=4B=3200\ cm^{-1}$ used in the above calculation are the approximate average of above data and may be rough for this system. Using various values of *B* and $C=4B$ we repeat the procedure[11] of fitting the experimental ZFS data and obtain the corresponding values of λ's that are in a best fit to the experimental data for *D*, *a*, and *F*, as listed in Table III. From this table one can see that on increasing *B*, the values of λ_{dp_π} and λ_{dp_σ} increase, whereas λ_{ds} decreases. However, the variation of λ with *B* is small and the various values of *B* do not change the main results appearing in the present paper such as the significant charge-transfer effects and the important spin-triplet contributions in this system. With further progress in theoretical treatment one expects the more exact values of the Racah parameters *B* and *C* observed in GaAs:Cr^{2+}.

In addition, it should be pointed out that the values of the gaps Δ_1, Δ_2, and Δ_3 used in the present paper were obtained by Krebs and Stauss,[1,2] who deduced them from uniaxial stress measurements. They estimated $\Delta_1=3E_{\mathrm{JT}}({}^5T_2)$ by using their measured JT coefficient $V_E=-0.85$ eV/Å and obtained Δ_2 and Δ_3 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 the Cr^{2+} center. After Krebs and Stauss, various measurements (see, e.g., Refs. 5 and 49–51) obtained different values of the JT splittings that make the values of Δ_1, Δ_2, and Δ_3 different from Krebs and Stauss's. As mentioned above, the ZFS parameters relate to the values of Δ_1, Δ_2, and Δ_3 and different values of Δ_1, Δ_2, and Δ_3 may yield different values of the admixture coefficients λ. Fortunately, this does not change the present main results. With further progress in theoretical treatment one expects the more exact data observed for the JT splittings of the energy levels. It should also be pointed out that the comprehensive set of EPR experiments on Cr^{2+} ions in GaAs obtained by Krebs and Stauss[1,2] showed the tetragonal features arising from a static JT effect; however, other works (see, e.g., Refs. 6–10 and references therein) suggested that the JT effect must be dynamic. Nahamani, Buisson, and Romestain[52] even named it the intermediate Jahn-Teller effect. Abhvani, Bates, and Pooler[7] demonstrated that the static model is a good approximation to the dynamic model for EPR and far-infrared measurements, but that the static model cannot be used to describe the results from phonon scattering and Zeeman spectroscopy experiments. The

TABLE III. Variation of the admixture coefficients λ with Racah parameters *B* and $C=4B$. The corresponding zero-field-splitting parameters in the best fit to the experimental data are also given (in cm^{-1}, except λ, which is dimensionless). The asterisk denotes a value quoted from Table I.

B	λ_{ds}	λ_{dp_π}	λ_{dp_σ}	D	a	F
830	0.49	0.31	0.86	-1.924	0.0308	-0.0599
800*	0.50	0.30	0.855	-1.887	0.0302	-0.0592
750	0.51	0.29	0.85	-1.882	0.0294	-0.0589
700	0.52	0.281	0.843	-1.876	0.0291	-0.0585

studies of, for instance, the phonon scattering and Zeeman and far-infrared spectroscopy in GaAs:Cr^{2+} are also based on the ^5D approximation (see, e.g., Refs. 6–10 and references therein). From the present calculation, the more exact treatment for the phonon-scattering and Zeeman spectroscopy results in this system should consider the spin-triplet contributions. The important spin-triplet contributions to the ZFS are due to the spin-triplet effect on the fine-structure splitting of the ground state, and this effect must influence the other related data, e.g., Mossbauer quadrupole splitting, magnetization, magnetic susceptibility as well as phonon scattering, and Zeeman spectroscopy (see, e.g., Refs. 33, 34, and 36–39).

IV. SUMMARY

In this paper, the perturbation formulas of the zero-field-splitting parameters D, a, and F up to fourth-order terms for the $^5B_2$ ground state of $3d^4$ and $3d^6$ ions in tetragonal symmetry are derived by taking account of all the spin-triplet states of these ions and the spin-orbit coupling associated with ligands. These formulas can be used to study the zero-field splittings of these ions in not only ionic but also covalent crystals and they are very different from the previous case, especially for the spin-triplet contribution terms. The present theoretical study is significant for understanding the electronic structure of the defect center Cr^{2+} in GaAs. The calculated results of D, a, and F are in good agreement with the experimental data. The present results show clearly the interesting charge-transfer effects in this system. In addition, the spin-triplet contributions to the zero-field-splitting parameters are discussed in detail. The conclusion is that these contributions are very important in GaAs:Cr^{2+} and that by neglecting these contributions one cannot obtain reasonable values of the zero-field-splitting parameters a and, in particular, D and F.

ACKNOWLEDGMENTS

This work was supported by the National Scientific Fund of China (Grant No. 19474037) and the Educational Committee of Sichuan Province of China.

---

*Mailing address.

[1] J. J. Krebs and G. H. Stauss, Phys. Rev. B **16**, 971 (1977).

[2] J. J. Krebs and G. H. Stauss, Phys. Rev. B **20**, 795 (1979).

[3] R. J. Wagner and A. M. White, Solid State Commun. **32**, 399 (1979).

[4] G. H. Stauss, J. J. Krebs, S. H. Lee, and E. M. Swiggard, Phys. Rev. B **22**, 3141 (1980).

[5] A. M. Hennel, W. Szuszkiewicz, M. Balkanski, G. Martinez, and B. Clerjaud, Phys. Rev. B **23**, 3933 (1981).

[6] M. Rezki, A. Vasson, A.-M. Vasson, A. S. Abhavani, and C. A. Bates, J. Phys. C **15**, 2207 (1982).

[7] A. M. Abhvani, C. A. Bates, and D. R. Pooler, J. Phys. C **17**, 1713 (1984).

[8] C. A. Bates and K. W. H. Stevens, Rep. Prog. Phys. **45**, 783 (1986).

[9] C. A. Bates, M. Darcha, J. Handley, A. Vasson, and A.-M. Vasson, Semicond. Sci. Technol. **3**, 172 (1988).

[10] J. A. L. Simpson, J. L. Dum, and C. A. Bates, J. Phys. Condens. Matter **2**, 8315 (1990).

[11] M. H. de A. Viccaro, S. Sundaram, and R. R. Sharma, Phys. Rev. B **25**, 7731 (1982).

[12] F. Hartmann-Boutron and P. Imbert, J. Appl. Phys. **39**, 775 (1968).

[13] Y. Hazong, Phys. Rev. B **3**, 711 (1971).

[14] J. P. Sanchez, L. Asch, and J. M. Friedt, Chem. Phys. Lett. **18**, 250 (1973).

[15] C. Rudowicz, Acta Phys. Polon. A **47**, 305 (1975); **48**, 179 (1975); **51**, 515 (1977).

[16] F. Varret, J. Phys. (Paris) Colloq. **37**, C6-437 (1976).

[17] C. Rudowicz, J. Phys. Chem. Solids **38**, 1243 (1977).

[18] C. Rudowicz, Phys. Rev. B **21**, 4967 (1980).

[19] C. Rudowicz, J. Phys. C **14**, 923 (1981).

[20] Y. Y. Zhou and M. G. Zhao, J. Phys. C **20**, 1827 (1987); **20**, 5097 (1987).

[21] Y. Y. Zhou and M. G. Zhao, J. Phys. Chem. Solids **48**, 729 (1987).

[22] Y. Y. Zhou, J. Phys. Chem. Solids **49**, 851 (1988).

[23] C. Rudowicz, J. Phys. (Paris) Colloq. **49**, C8-931 (1988).

[24] C. Rudowicz, Physica B **155**, 336 (1989).

[25] C. Rudowicz and Y. Y. Zhou, J. Magn. Magn. Mater. **111**, 153 (1992).

[26] C. Rudowicz, Y. Y. Zhou, and W. L. Yu, J. Phys. Chem. Solids **53**, 1227 (1992).

[27] C. Rudowicz and Y. Y. Zhou, J. Phys. Chem. Solids **55**, 745 (1994).

[28] J. T. Vallin and G. A. Watkins, Phys. Rev. B **9**, 2051 (1974).

[29] Y. Y. Zhou, Phys. Status Solidi B **145**, 227 (1987).

[30] Y. Y. Zhou and C. H. Ying, Phys. Rev. B **47**, 5451 (1993).

[31] C. Rudowicz, Y. Y. Yeung, and M. L. Du, J. Phys. Chem. Solids **54**, 733 (1993).

[32] C. Rudowicz, M. L. Du, Y. Y. Yeung, and Y. Y. Zhou, Physica B **191**, 323 (1993).

[33] Y. Y. Zhou and C. L. Li, Phys. Rev. B **48**, 16 489 (1993).

[34] C. Y. Jiang, M. L. Du, and Y. Y. Zhou, Phys. Rev. B **50**, 949 (1994).

[35] Y. Y. Zhou, Phys. Rev. B **50**, 7161 (1994).

[36] C. L. Li, K. Q. Zhang, and Y. Y. Zhou, Physica B (to be published).

[37] J. S. Griffith, *The Theory of Transition Metal Ions* (Cambridge University Press, Cambridge, England, 1960).

[38] C. J. Ballhomsen, *Introduction to Ligand Field Theory* (McGraw-Hill, New York, 1962).

[39] S. Sugano, Y. Tanabe, and H. Kamimura, *Multiplets of Transition-Metal Ions in Crystals* (Academic, New York, 1970).

[40] G. F. Koster, J. O. Dimmock, R. G. Wheeler, and H. Satz, *Properties of The Thirty-Two Point Groups* (MIT Press, Cambridge, MA, 1963).

[41] A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions* (Dover, New York, 1986).

[42] C. Rudowicz, Magn. Res. Rev. **13**, 1 (1987).

[43] R. M. Macfarlane, Phys. Rev. B **1**, 989 (1970).

[44] R. M. Macfarlane, J. Chem. Phys. **97**, 2066 (1976).

[45] A. S. Chakravarty, *Introduction to the Magnetic Properties of Solids* (Wiley, New York, 1980).

[46] E. Kong and S. Kremer, Z. Naturforsch. **29**, 31 (1974).

[47] L. A. Hemstreet and J. O. Dimmock, Phys. Rev. B **20**, 1527 (1979).

[48] C. A. Morrison, *Host Materials for Transition Ions* (U. S. Army Laboratory Command, Adelphi, MD, 1989).

[49] P. J. Williams, L. Eaves, P. E. Simmonds, M. O. Henry, E. C. Lightowlers, and Ch. Uihlein, J. Phys. C **15**, 1337 (1982).

[50] R. A. Vanem, K. A. Kikoin, P. A. Lyuk, and L. Ya. Pervova, Fiz. Tekh. Poluprovodn. **22**, 255 (1988) [Sov. Phys. Semicond. **22**, 155 (1988)].

[51] W. Zawadzki, P. Pfeffer, S. H. Najda, H. Yokoi, S. Takeyama, and N. Miura, Phys. Rev. B **49**, 1705 (1994).

[52] A. Nahamani, R. Buisson, and R. Romestain, J. Phys. (Paris) **41**, 59 (1980); **41**, 67 (1980).