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Theoretical investigation of the g factor in RX:V^{2+} (R = Na,K,Rb;X = Cl,Br)

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This paper presents a cluster approach to the calculation of the g factor in RX:V^{2+} (R=Na,K,Rb;X=Cl,Br), in which not only the contribution due to the spin-orbit coupling of the central transition-metal ion but also that of the ligands are included. The calculated results agree well with the available experimental data. The results show that the contribution to the g shift due to the spin-orbit coupling of the ligands is small in RCl:V^{2+} but is about 80% of that of the central transition-metal ion in RBr:V^{2+}. It suggests that the calculation of the g factor in some covalent crystals containing transition-metal ions should prefer the cluster approach over the classical crystal-field model, which accounts for only the contribution due to the spin-orbit coupling of the central transition-metal ion.

I. INTRODUCTION

In recent years there has been a great renewed interest in the theoretical investigation of the electronic structure and magnetic and optical properties of transition-metal ion impurities in a covalent host. Many works concentrate on the investigation of the multiplet structure of transition-metal ion impurities in a covalent host (see, for example, Refs. 1–6). Some works investigated the spin-Hamiltonian parameters of transition-metal ion cluster in covalent crystals. Aramburu and Moreno,[7] and Misra and Wang[8] investigated the g factor of $CuCl_4^{-2}$, $CuBr_4^{2-}$, and MAT: Cu^{2+}, and obtained a formula of the g factor for a d^1 cluster, in which the contribution due to s.o. (spin-orbit) coupling of the ligands has been included. Viccarro *et al.*[9] have given a complete theory of the spin-Hamiltonian parameters for a d^4 cluster, including covalency and Jahn-Teller effects, and interpreted the g factors and zero-field splitting parameters of GaAs: Cr^{2+}. In the present paper, we focus on the contribution due to the s.o. coupling of the ligand ions to the g factor for a d^3 cluster with octahedral symmetry.

The classical crystal-field approach can give a simple expression of the g factor of a transition-metal cluster. For a d^3 cluster, Abragam and Bleaney[10] gave a formula of the g factor involving only the energy difference between the ground state and the ${}^4T_2(t_2^3)$ state and the s.o. coupling parameter of the transition-metal ion in the crystal; Macfarlane[11] gave a third-order perturbation-theory expression of the g factor, using a strong field perturbation-loop method. In their theory, the contribution due to the s.o. coupling of the transition-metal ion is included but not those of the ligand ions. In the case of ionic crystals containing transition-metal ions, it is a good approximation and therefore is used widely in the calculation of the g factor. But in the case of covalent crystals, the neglect of the contribution due to the s.o. coupling of the ligand ions is difficult to justify. For example, Misetich and Buch[12] expected the contribution due to the s.o. coupling of the ligand ions to be large for Br^- or I^- ligand ions. In fact it has been known that the classical crystal-field model cannot agree with the experimental data of the g factors in some covalent crystals such as $CsMgX_3$:V^{2+},Ni^{2+} (X =Br,I);[13] Ni(pyrazole)$_4X_2$ and Ni(5-methyl pyrazole)$_4X_2$ (X =Br,I);[14] $CsVX_3$ (X =Br,I);[15] etc. In RX:V^{2+} (R =Na,K,Rb;X =Cl,Br),[16] for example, the covalency in the VBr_6^{4-} cluster is stronger than that in the VCl_6^{4-} cluster; and EPR experiment shows that the values of the g factor in RBr:V^{2+} are larger than that in RCl:V^{2+}; the classical crystal-field model gives results to the contrary. This error is primarily due to the neglect of the contribution due to the s.o. coupling of the ligand ions (see Sec. III).

In this paper we present a cluster approach for the calculation of the g factor in covalent crystals containing d^3 transition-metal ions, in which not only the contribution due to the s.o. coupling of the central transition-metal ion but also those of the ligand ions are included, and calculate the g shifts of RX:V^{2+} using this approach.

II. THEORETICAL MODEL

In the classical crystal-field model, the s.o. coupling interaction Hamiltonian can be given as

$$H_{\text{s.o.}} = \sum_i \zeta_c(r_i)\hat{l}_i\cdot\hat{s}_i \tag{1}$$

and the one-electron irreducible-representation basis function as

$$|\gamma\rangle = |d_\gamma\rangle \;, \tag{2}$$

where the subscript c denotes the central transition-metal ion and $|d_\gamma\rangle$ is a d function transforming as the irreducible representation γ. Using Eqs. (1) and (2) an analytical perturbation expression for the g factor of a $3d^3$ configuration with O_h symmetry was given by Macfarlane[11] as

$$\begin{aligned} g = {} & g_s - 8k\zeta/3D_1 + 2\zeta^2(k+2g_s)/9D_1^2 - 2\zeta^2(k+g_s)/3D_2^2 \\ & + 4\zeta^2(k-2g_s)/9D_3^2 - 4k\zeta^2/3D_1D_2 + 4k\zeta^2/9D_1D_3 \\ & + 4k\zeta^2/3D_2D_3 \;, \end{aligned} \tag{3}$$

where the energy denominators D_1, D_2, D_3 are, respectively, the energy differences between the excited states ${}^4T_2(t_2^2e)$, ${}^2T_2(t_2^3)$, ${}^2T_2(t_2^2e)$ and the ground state ${}^4A_2(t_2^3)$; $g_s=2.0023$ is the spin-only value; k is orbital reduction factor; ζ is the s.o. coupling parameter of the d electron in the crystal. By neglecting all the third-order terms, Eq. (3) can be reduced to

$$g=g_s-8k\zeta/3D_1\ , \tag{4}$$

which is just the simple formula given by Abragam and Bleaney.[10] In Eqs. (3) and (4), the covalency is considered by using that an orbital reduction factor $k<1$ and that the s.o. coupling parameter in the crystal is smaller than that in the free ion. It is a good approximation in the case of ionic crystal and hence is used widely.

In the case of covalent crystals, in which the s.o. coupling parameter of a ligand ion is usually large, one must rewrite Eqs. (1) and (2) in order to include the contribution due to the s.o. coupling of the ligand ions to the g factor. We take the *LCAO* orbital

$$|\Psi\rangle=\sqrt{N}\,(|d^0\rangle+b|L\rangle) \tag{5}$$

as a one-electron orbital, where $|d^0\rangle$ is the d orbital of the central transition-metal ion; $|L\rangle$ is the valence-electron orbital of the ligand ion. $|L\rangle$ has two components (the s and p orbitals), but numerical calculations[7,12] show that the contribution due to the s orbital is small, and so one can neglect the s orbital in $|L\rangle$ and take $|L\rangle=|p\rangle$. When a cluster is in an octahedral field, such as VX_6^{4-} in RX:V^{2+}, the one-electron orbital is split into two parts transforming as the t_{2g} and e_g irreducible representations of the O_h point group. So the one-electron irreducible-representation basis function can be written as

$$|\gamma\rangle=\sqrt{N_\gamma}\,(|d_\gamma^0\rangle-\lambda_\gamma|p_\gamma\rangle)\ , \tag{6}$$

where the subscript $\gamma=t_{2g}$ or e_g; N_γ and λ_γ are normalization and orbital mixing coefficients, $1>N_\gamma>0$, $1>\lambda_\gamma>0$ for the antibonding orbital of VX_6^{4-}. The zeroth-order wave functions of three-electron system in the octahedral field, which transform as irreducible representations of the O_h point group, are combined with the one-electron orbital possessing the form of Eq. (6).[17]

For the iron-group ions, the s.o. coupling interaction is weaker than either the electrostatic repulsion interaction or the cubic crystal field. So we can take the perturbation Hamiltonian as

$$\hat{H}'=\hat{H}_{\text{s.o.}}+\hat{H}_z\ . \tag{7}$$

Obviously, the s.o. coupling from the p electron of ligand ions should be included in $\hat{H}'$. The s.o. coupling interaction Hamiltonian may thus be written as

$$\begin{aligned}\hat{H}_{\text{s.o.}}&=\hat{H}_{\text{s.o.}}(d)+\hat{H}_{\text{s.o.}}(p)\ ,\\ \hat{H}_{\text{s.o.}}(d)&=\sum_i \zeta_d(r_{id})\hat{l}_i\cdot\hat{s}_i\ ,\\ \hat{H}_{\text{s.o.}}(p)&=\sum_i \zeta_p(r_{ip})\hat{l}_i\cdot\hat{s}_i\ ,\end{aligned} \tag{8}$$

and the Zeeman interaction as

$$\hat{H}_z=\mathbf{H}\cdot\mu_B(\hat{L}+g_s\hat{S})\ . \tag{9}$$

Using Eqs. (6)–(9) we can derive a perturbation-theory expression of the g factor of the ground state ${}^4A_2(t_2^3)$. The one-electron matrix elements between the d orbital of the central metal ion and the p orbital of the ligand ion are very small[18] and hence are neglected in our calculation, retaining only the matrix elements between the two d orbitals and between the two p orbitals, such as $\langle d_\gamma^0|\hat{H}_{\text{s.o.}}(d)|d_{\gamma'}^0\rangle$ and $\langle p_\gamma|\hat{H}_{\text{s.o.}}(p)|p_{\gamma'}\rangle$. The analytical expressions of the g factor of the ${}^4A_2(t_2^3)$ state obtained by using a perturbation-loop method[11] are as follows:

$$g=g_s+g(\zeta_d)+g(\zeta_p)+g(\zeta_d,\zeta_p)\ , \tag{10}$$

$$\begin{aligned}g(\zeta_d)={}&-8k_1\zeta_d^{te}/3D_1-[4k_1\zeta_d^{te}\zeta_d^{t}+2(2g_s-k_2)(\zeta_d^{te})^2]/9D_1^2+4(k_2-2g_s)(\zeta_d^{te})^2/9D_3^2-2(k_2+g_s)(\zeta_d^{t})^2/3D_2^2\\&+4k_1\zeta_d^{te}\zeta_d^{t}/9D_1D_3-4k_1\zeta_d^{te}\zeta_d^{t}/3D_1D_2+4k_1\zeta_d^{te}\zeta_d^{t}/3D_2D_3\ ,\end{aligned} \tag{11}$$

$$\begin{aligned}g(\zeta_p)={}&8k_1\zeta_p^{te}/3D_1+[4k_1\zeta_p^{te}\zeta_p^{t}-2(2g_s-k_2)(\zeta_p^{te})^2]/9D_1^2+4(k_2-2g_s)(\zeta_p^{te})^2/9D_3^2-2(k_2+g_s)(\zeta_p^{t})^2/3D_2^2\\&-4k_1\zeta_p^{te}\zeta_p^{t}/9D_1D_3+4k_1\zeta_p^{te}\zeta_p^{t}/3D_1D_2-4k_1\zeta_p^{te}\zeta_p^{t}/3D_2D_3\ ,\end{aligned} \tag{12}$$

$$\begin{aligned}g(\zeta_d,\zeta_p)={}&4(2g_s-k_2)\zeta_d^{te}\zeta_p^{te}/9D_1^2-8(k_2-2g_s)\zeta_d^{te}\zeta_p^{te}/9D_3^2-4(k_2+g_s)\zeta_d^{t}\zeta_p^{t}/3D_2^2\\&+4k_1(-1/9D_1^2+1/9D_1D_3-1/3D_1D_2+1/3D_2D_3)(\zeta_d^{te}\zeta_p^{t}-\zeta_d^{t}\zeta_p^{te})\ ,\end{aligned} \tag{13}$$

and

$$\begin{aligned}&\zeta_d^{te}=\sqrt{N_t}\sqrt{N_e}\,\zeta_d^0\ ;\quad \zeta_d^{t}=N_t\zeta_d^0\ ;\\ &\zeta_p^{te}=\sqrt{N_t}\sqrt{N_e}\,\lambda_t\lambda_e\zeta_p^0/2\ ;\quad \zeta_p^{t}=N_t\lambda_t^2\zeta_p^0/2\ ;\\ &k_1=\sqrt{N_t}\sqrt{N_e}\,(1-\lambda_t\lambda_e/2)\ ;\quad k_2=N_t(1+\lambda_t^2/2)\ ,\end{aligned} \tag{14}$$

where ζ_d^0 and ζ_p^0 are, respectively, the s.o. coupling parameters of the d electron of the central transition-metal ion and the p electron of the ligand in free ion; the subscripts t and e denote t_{2g} and e_g orbitals, respectively; g_s $(=2.0023)$ is the spin-only value; the energy denominators D_i are the differences between the excited states ${}^4T_2(t_2^2e)$, ${}^2T_2(t_2^3)$, ${}^2T_2(t_2^2e)$ and the ground state ${}^4A_2(t_2^3)$, which can either be extracted from experimental data or be calculated from following equations:

$$D_1 = 10Dq ,$$
$$D_2 = 15B + 5C , \qquad (15)$$
$$D_3 = 9B + 3C + 10Dq .$$

Taking $\lambda_t = \lambda_e = 0$ and $N_t = N_e = N$, then $g(\zeta_p) = 0$, $g(\zeta_d, \zeta_p) = 0$, and Eq. (10) returns to Macfarlane's expression Eq. (3).

It is difficult to determine the $LCAO$ coefficients N_γ and λ_γ by a molecular orbital calculation. We therefore use a semiempirical method instead. We denote the ratio of the electrostatic repulsion in crystal to that in the free ion as

$$f_\gamma = \frac{\left\langle \gamma^2 \left| \frac{e^2}{r_{12}} \right| \gamma^2 \right\rangle}{\left\langle d^2 \left| \frac{e^2}{r_{12}} \right| d^2 \right\rangle} \qquad (16)$$

and the group overlap integral as

$$S_{dp}(\gamma) = \int d_\gamma^*(1) p_\gamma(2) d\tau_1 d\tau_2 . \qquad (17)$$

When the one-electron orbital is written as Eq. (6), by using the Mulliken approximation[19] and neglecting the small terms in λ_γ^3 and λ_γ^4 from Eq. (16) we have the following approximate relation:[20]

$$f_\gamma = N_\gamma^2 [1 - 2\lambda_\gamma S_{dp}(\gamma) + \lambda_\gamma^2 S_{dp}^2(\gamma)] . \qquad (18)$$

By use of the normalization of the orbital, we have

$$N_\gamma [1 - 2\lambda_\gamma S_{dp}(\gamma) + \lambda_\gamma^2] = 1 . \qquad (19)$$

So the $LCAO$ coefficients N_γ and λ_γ could be determined from Eqs. (18) and (19), if the ratio f_γ has been obtained from experimental data. In general, one can omit the difference between t_{2g} and e_g orbitals and use Racah parameters B and C describing the electrostatic repulsion interaction. In most theoretical work (for example, Refs. 21–23), it is assumed that B/B_0 is equal to C/C_0, and $B/B_0 = N_\gamma^2$ or $B/B_0 = \overline{N}^2$ is currently used to estimate the covalency effect in the analysis of the optical spectra. Equation (18) can be seen as a correction to the relation $f_\gamma = N_\gamma^2$. For a $3d$ dominating molecular orbital, the difference between using the former and using the latter is small. In RX:V^{2+}, for example, the average difference is about 1% for N_γ and 3% for λ_γ. It means that Eq. (18) is a reasonable approximation. Since the experimental value of B/B_0 differs little from that of C/C_0 in RX:V^{2+}, we will take the average value $f = B/B_0 + C/C_0$ in the following calculation [taking $f_t = f_e = f$ (Ref. 20)].

III. RESULTS AND DISCUSSION

The optical spectra of RX:V^{2+} (R = Na,K,Rb; X = Cl,Br) were investigated by Vanhaelst *et al.*,[16,24] Kuwabara,[25] and Narayna *et al.*[26] The Racah parameters and cubic crystal-field parameter determined from the experimental data are given in Table I. The s.o. coupling parameters of V^{2+}, Cl$^-$, and Br$^-$ free ions are also given in Table I.

As is well known, it is often convenient to use the Slater orbital in computations of the overlap integral. But a reasonable s.o. coupling coefficient cannot be obtained from this orbital. On the contrary, the SCF (self-consistent field) orbital is capable of yielding a reasonable s.o. coupling coefficient. We hence use the Slater-type SCF function[27,28] to calculate the group overlap integral $S_{dp}(\gamma)$. Then the $LCAO$ coefficients N_γ and λ_γ can be determined using Eqs. (18) and (19) and the experimental values of the Racah parameters in the crystal and in the free ion. The calculated values of $S_{dp}(\gamma)$, N_γ, and λ_γ are listed in Table II. Using Eqs. (10)–(14) we can calculate the values of the g factor in RX:V^{2+}. The results are given in Table III. One can make the following observations upon an examination of Table III.

(a) If only the contribution $g(\zeta_d)$ from s.o. coupling of

TABLE I. The experimental spectral parameters (in units of cm^{-1}) and the structure parameters (in units of nm) in RX:V^{2+} (R = Na,K,Rb;X = Cl,Br).

	R[a]	B or B_0	C or C_0	Dq		ξ[b]
free V^{2+}		766[b]	2855[b]		V^{2+}	167
NaCl:V^{2+}	0.281	640[c]	2412.8[c]	784[d]	Cl$^-$	587
NaBr:V^{+}	0.298	625[c]	2356.25[c]	702[d]	Br$^-$	2460
KCl:V^{2+}	0.314	640[c]	2412.8[c]	660[e]		
KBr:V^{2+}	0.329	625[c]	2356.25[c]	591[f]		
RbCl:V^{2+}	0.327	640[c]	2412.8[c]	622[e]		
RbBr:V^{2+}	0.343	625[c]	2356.25[c]	557[f]		

[a] Reference 30.
[b] Reference 31.
[c] Reference 29.
[d] Reference 25.
[e] Reference 23.
[f] For KBr:V^{2+} and RbBr:V^{2+} the experimental data of Dq have not been found and hence the values are estimated from the following approximation that

$$\frac{Dq(\text{NaCl:V}^{2+})}{Dq(\text{NaBr:V}^{2+})} = \frac{Dq(\text{KCl:V}^{2+})}{Dq(\text{KBr:V}^{2+})} = \frac{Dq(\text{RbCl:V}^{2+})}{Dq(\text{RbBr:V}^{2+})} .$$

TABLE II. The group overlap integrals and the *LCAO* coefficients in RX:V^{2+}.

Host	f^{a}	$S_{dp}(e_g)$	$S_{dp}(t_{2g})$	N_e	N_t	λ_e	λ_t
NaCl	0.8403	0.038 42	0.010 69	0.9281	0.9197	0.3193	0.3064
NaBr	0.8206	0.034 94	0.009 06	0.9168	0.9086	0.3383	0.3264
KCl	0.8403	0.017 09	0.004 00	0.9216	0.9178	0.3093	0.3033
KBr	0.8206	0.016 25	0.003 57	0.9108	0.9069	0.3297	0.3240
RbCl	0.8403	0.012 19	0.002 69	0.9201	0.9174	0.3071	0.3027
RbBr	0.8206	0.011 25	0.002 32	0.9092	0.9065	0.3274	0.3234

[a] $f=(B/B_0+C/C_0)/2$.

the transition-metal ion is included, the g shift ($\Delta g = g - g_s$) should be arranged in the order $\Delta g(R\text{Cl:V}^{2+}) > \Delta g(R\text{Br:V}^{2+})$ (Table III, column 1). However, this is contrary to the EPR experimental data. But by including the contributions from the s.o. coupling of either the transition-metal ion or the ligand ion, the total results calculated using the cluster approach are that $\Delta g(R\text{Cl:V}^{2+}) < \Delta g(R\text{Br:V}^{2+})$ (Table III, column 4), which agree with the experimental data. We note that there are no adjustable parameters, and so one can conclude that the theoretical results agree satisfactorily in magnitude with the experimental data. (The results for KBr:V^{2+} and RbBr:V^{2+} have larger errors than for others, since their spectral parameters are estimated from an approximate relation.)

(b) The contribution $g(\zeta_d,\zeta_p)$ from the s.o. coupling of the transition-metal ion and the ligand ion is always very small (Table III, column 3). This conclusion shows itself directly in Eq. (13): First, there are no second-order terms in $g(\zeta_d,\zeta_p)$; second, terms of $(\zeta_d^{te}\zeta_p^{t}-\zeta_d^{t}\zeta_p^{te})$ are very small because of the small difference between λ_t and λ_e; third, in the three other terms there is always a term having an opposite sign to the other two terms. So $g(\zeta_d,\zeta_p)$ is always very small and can be neglected.

(c) The difference of $g(\zeta_p)$ between the Cl$^-$ and Br$^-$ ligand ions is large (Table III, column 2). For a Cl$^-$ ligand ion (NaCl,KCl,RbCl) $g(\zeta_p)$ is much smaller than $g(\zeta_d)$, and so neglecting $g(\zeta_p)$ does not result in a large error and hence the formula of the classical crystal-field model [Eq. (3) or (4)] is usable. But in NaBr:V^{2+} (or KBr:V^{2+}, RbBr:V^{2+}), $g(\zeta_p)$ is about 80% of $g(\zeta_d)$ and hence cannot be neglected.

(d) The contribution due to the s.o. coupling of the ligand ion is always opposite to that of the transition-metal ion. The smaller $|g-g_s|$ in RBr:V^{2+} are just due to the fact that a larger $g(\zeta_p)$ has an opposite sign relative to $g(\zeta_d)$.

Since the magnitude of $g(\zeta_d,\zeta_p)$ is always very small, we can take

$$g=g_s+g(\zeta_d)+g(\zeta_p) \tag{20}$$

as a good approximation. When only second-order perturbation terms are retained, we have

$$\begin{aligned} g&=g_s-8k_1\zeta_d^{te}/3D_1+8k_1\zeta_p^{te}/3D_1\\ &=g_s-8k_1(\zeta_d^{te}-\zeta_p^{te})/3D_1\ . \end{aligned} \tag{21}$$

Equation (21) is the simple expression of the g factor for a 3d center with octahedral symmetry in the cluster approach as Eq. (4) in the classical crystal-field model. By use of the cluster approach, Viccaro *et al.*[9] have given a second-order perturbation expression of the g factor for the 3d^4 center with tetrahedral symmetry, including contribution due to both one-center and two-center matrix elements. Comparing Eq. (21) with the expression of Viccaro *et al.* [Ref. 9, Eqs. (7), (8), and (11)–(14)], one finds that after neglecting the very small contribution of two-center matrix elements, the former is similar to the latter. Here, the k_1 and $(\zeta_d^{te}-\zeta_p^{te})$ in Eq. (21) correspond to the S_2 and ζ_2 in the expression of Viccaro. It shows that the contribution due to the s.o. coupling of the ligand ion in an octahedral field should be similar to that in a tetrahedral field for a 3d^n ($n=3$ or 4) center in a covalent host.

The magnitudes of λ_γ and ζ_p^0 determine $g(\zeta_p)$, e.g., the covalency and s.o. coupling parameter of the ligand ion determine the contribution due to the s.o. coupling of the ligand ion. With increasing atomic number of ligand atoms in a group, both the covalency and the s.o. cou-

TABLE III. The g shift ($g-g_s$) in RX:V^{2+}.

	Calculated values				Experimental values
Host	$g(\xi_d)$	$g(\xi_p)$	$g(\xi_d,\xi_p)$	$g-g_s$ total	Ref. 16
NaCl	−0.0467	0.0079	0.0001	−0.0387	−0.0358
NaBr	−0.0506	0.0404	0.0005	−0.0097	−0.0111
KCl	−0.0552	0.0090	0.0001	−0.0461	−0.0412
KBr	−0.0599	0.0462	0.0007	−0.0130	−0.0167
RbCl	−0.0585	0.0094	0.0001	−0.0490	−0.0433
RbBr	−0.0635	0.0485	0.0008	−0.0142	−0.0209

pling parameter increase. Obviously for a ligand ion, a large atomic number results in a large contribution due to the s.o. coupling to the g factor. In the halogen group, for example, there are two orders from fluorine to iodine:

covalency: $F^- < Cl^- < Br^- < I^-$;

s.o. coupling parameter (in unit cm^{-1}) :

$$F^-(220) < Cl^-(587) < Br^-(2460) < I^-(5060) \ .$$

The $g(\zeta_p)$ must be in order:

$g(\zeta_p)$: $F^- < Cl^- < Br^- < I^-$.

So we can conclude that the classical crystal-field model is applicable in the case of the F^- ligand but only the cluster approach is applicable in the case of the I^- ligand. Noticing the magnitude of the s.o. parameter of the I^- ion, we can infer from the case of the Br^- ligand ion that $g(\zeta_p)$ can even be equal to, or larger than, $g(\zeta_d)$ in the case of the I^- ligand ion. It can explain reasonably that $g > g_s$ in some crystal having I^- ligand ions, such as $CsVI_3$ ($g = 2.06$),[15] $CsMgI_3$:V^{2+} ($g = 2.04$).[13]

It must be pointed out that by only introducing the covalency factor N or orbital reduction factor k, the classical crystal-field model is inadequate for obtaining a reasonable g shift in the case of large $g(\zeta_p)$. In the average covalency factor model,[21,22] the values of the Racah parameters and the s.o. coupling parameter in crystals are related with that in free ion as

$$B = \bar{N}^2 B_0 \ , \quad C = \bar{N}^2 C_0 \ , \quad \zeta = \bar{N}\zeta_d^0 \ . \tag{22}$$

This means the change of the spectra parameters is related to the change of the s.o. coupling parameter. Neglecting the direct contribution due to the ligand p electron (taking $\lambda_\gamma = 0$) in Eq. (14), the orbital reduction factor k is equal to the coefficient N (it is called average covalency factor in Refs. 21 and 22). If Eq. (4) is written as

$$g = g_s - 8\lambda / D_1 \ , \tag{23}$$

where λ is the s.o. coupling parameter of the d^3 ion in a crystal, the λ should be related to the λ_0 of the free ion by $\lambda = kN\lambda_0 = \bar{N}^2\lambda_0$. In order to obtain a g factor agreeing with the EPR experimental data from Eq. (23), Vanhaelst *et al.*[16] suggested that one must take $\lambda/\lambda_0 = 0.66$ in NaCl:V^{2+} and 0.17 in NaBr:V^{2+}. It can be easily determined that the Racah parameters $B = 130$ cm^{-1} and $C = 485$ cm^{-1} obtained from the ratio λ/λ_0 in NaBr:V^{2+} are too small and hence are in contradiction with the experimental optical spectra. Therefore it shows that the neglect of the contribution due to the s.o. coupling of the ligand ion is not justified.

IV. CONCLUSION

This work presents a cluster approach for the calculation of the g factor in RX:V^{2+} ($R =$ Na,K,Rb;$X =$ Cl,Br). With this model, the calculated results are found to agree well with experimental data. In RCl:V^{2+}, the contribution due to the s.o. coupling of the ligand ion, $g(\zeta_p)$, is small (about 15%) and hence the classical crystal-field model (the Macfarlane or Abragam-Bleaney formula) is applicable. But in RBr:V^{2+}, $g(\zeta_p)$ is about 80% of $g(\zeta_d)$ and has an opposite sign relative to $g(\zeta_d)$. And hence one should prefer the cluster approach, in which the contribution due to the s.o. coupling of the ligand ion is included, in the investigation of the g shift of RBr:V^{2+}, over the classical crystal-field model.

In our work the theoretical formula is obtained for the three-electron system in a strong octahedral field. So the formula can be used in covalent crystals containing not only V^{2+} ions but also Cr^{3+} ions (three electron) or Co^{2+} ions (three hole). Since $\zeta_d^0 = 273$ cm^{-1} for the Cr^{3+} ion and $\zeta_d^0 = 533$ cm^{-1} for the Co^{2+} ion, the relative contribution due to $g(\zeta_p)$ to $g(\zeta_d)$ in the case of the Cr^{3+} or Co^{2+} ion is smaller than that in the case of the V^{2+} ion. A simple estimate (omitting the change of λ_γ from the case of V^{2+} ion) shows that in the case of the Br^- ligand ion, for example, the ratio of $g(\zeta_p)$ to $g(\zeta_d)$ is about 48% for the Cr^{3+} ion and 25% for the Co^{2+} ion. It means that the neglect of the contribution due to the s.o. coupling of the ligand ion is also not justified in covalent crystals containing Cr^{3+} ions or Co^{2+} ion.

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