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Roles of the Van Vleck Orbit-Lattice Interaction in an *S*-State Ion

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Using the Van Vleck orbit-lattice interaction, we show that the phonon-induced shift of a spectral line is proportional to the Debye-Waller factor. Based on this result, we propose a convenient method of measuring the Debye temperature. We show also that the orbit-lattice interaction is not the mechanism to account for the discrepancy between the theoretical and experimental g values of the ground state. Within our approximation, we have found the phonon-induced ground-state splitting of Gd^{3+} in CaF_2 at $T=293°\mathrm{K}$ to be 3.6×10^{-3} cm^{-1} with a correct sign. This is smaller than the experimental value by a factor of 40, and is smaller than the theoretical estimate by a factor of 4.

I. INTRODUCTION

For many years, the investigation on the physical properties of the S-state ions has been a major subject of study in physics. The difficulties incurred in these ions were recently reviewed by Wybourne,[1] and the reader is referred to his paper for a complete coverage of the references pertinent to this subject.

Even though the theory we shall present in this paper is applicable to any paramagnetic ions, for simplicity we shall restrict ourselves to Gd^{3+} in CaF_2. The lowest electronic configuration of Gd^{3+} is $(4f)^7$ and the ground-state multiplet is ${}^8S_{7/2}$. Assuming the $4f$ wave functions to be hydrogenic and taking into account the spin-orbit interaction, Wybourne found the following wave functions:

$$\begin{aligned}
|{}^8S_{7/2}M) &= 0.9866\,|{}^8S_{7/2}M\rangle + 0.1618\,|{}^6P_{7/2}M\rangle + \cdots,\\
|{}^6P_{7/2}M) &= 0.8514\,|{}^6P_{7/2}M\rangle - 0.1503\,|{}^8S_{7/2}M\rangle\\
&\quad - 0.4038\,|{}^6D_{7/2}M\rangle + \cdots,\\
|{}^6D_{9/2}M) &= 0.9604\,|{}^6D_{9/2}M\rangle + \cdots,\\
|{}^6D_{7/2}M) &= -0.8696\,|{}^6D_{7/2}M\rangle + \cdots,\\
|{}^6D_{5/2}M) &= 0.8755\,|{}^6D_{5/2}M\rangle + \cdots,\\
|{}^6D_{3/2}M) &= 0.9287\,|{}^6D_{3/2}M\rangle + \cdots,
\end{aligned} \tag{1}$$

where $|\,)$ and $|\,\rangle$ denote the perturbed and unperturbed wave functions, respectively. The energies associated with these wave functions are[1,2] 0, 32105, 39562, 40574, 40901, and 40754 cm^{-1}, respectively. We shall use these wave functions and energies for our later calculations. Let

$$a = \frac{\langle {}^6P_{7/2}|\Lambda|{}^8S_{7/2}\rangle}{E({}^6P_{7/2}) - E({}^8S_{7/2})}, \tag{2}$$

where Λ is the spin-orbit interaction. Evaluating the matrix element, we can rewrite Eq. (2) as[3,4]

$$a = (14)^{1/2}\zeta/32105 = 0.1725, \tag{3}$$

where[1] $\zeta = 1480$ cm^{-1} was used in the last computation. We can now express the g value of the ${}^8S_{7/2}$ ground state as

$$g = (1-a^2)g({}^8S_{7/2}) + a^2 g({}^6P_{7/2}) = 1.994, \tag{4}$$

where $g({}^8S_{7/2}) = 2.0023$ and $g({}^6P_{7/2}) = 1.7159$ were used. Wybourne carried out the calculation to the second order and found $g = 1.99454$. This value is high compared to 1.991 for gadolinium ethyl sulphate determined experimentally by Hutchison *et al.*[5] In Sec. III, we shall use Eqs. (2) and (4) to calculate the phonon-induced g shift, wishing to account for the discrepancy between theory and experiment.

According to McCumber and Sturge,[6] the temperature-dependent shift of a spectral line is caused by the two-phonon Raman process involving virtual transitions. The effective interaction of this process can be explicitly written as

$$V_{\mathrm{eff}} = \sum_p \frac{V_{\mathrm{ol}}|p)(p|V_{\mathrm{ol}}}{E_i - E_p}, \tag{5}$$

where i and p denote the initial and intermediate states, respectively, and V_{ol} is the Van Vleck orbit-lattice interaction.[7] It can be expressed as

$$V_{\mathrm{ol}} = \sum_j v_j Q_j, \tag{6}$$

in which v_j and Q_j are the jth electronic operator and the jth normal coordinate, respectively. Inoue[8] also used this effective interaction to calculate the phonon-induced g shifts of Tm^{2+} and Ho^{2+} in CaF_2. In Sec. II, we shall use Eq. (5) to calculate the phonon-induced shift of the ${}^6P_{7/2}$ state. Since the lattice vibrations in a crystal will distort the crystal symmetry, the dynamic crystalline field potential will remove the degeneracy of the electronic state. In view of this, we shall calculate the phonon-induced splitting of the ground state in Sec. IV.

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II. PHONON-INDUCED SHIFT OF $^6P_{7/2}$

In the f^7 configuration, there are 327 SLJ states. As a result, calculations including all these states are not possible. However, we could still estimate our theoretical value with some accuracy. From the table compiled by Nielson and Koster,[9] for the f^7 configuration the nonvanishing reduced matrix element in the lowest order connecting the ^6P state is $\langle{}^6P\|U^2\|{}^6D\rangle=(3/14)^{1/2}$, where U^2 is related to the spherical harmonics by

$$U_m{}^n=[4\pi/(2n+1)]^{1/2}Y_n{}^m.$$

In consequence of this, the intermediate states are then those ^6D_J states with $J=\frac{1}{2}$ to $\frac{9}{2}$, and only the electronic operators v_j to second order are needed to be considered in the following calculations. We can now write the phonon-induced shift of the $^6P_{7/2}$ state as

$$\delta E({}^6P_{7/2}M)=\sum_{J'=\frac{1}{2}}^{9/2}\sum_{M'=-J'}^{+J'}\sum_{j,j'} \times\frac{({}^6P_{7/2}M|v_jQ_j|{}^6D_{J'}M')({}^6D_{J'}M'|v_{j'}Q_{j'}|{}^6P_{7/2}M)}{E({}^6P_{7/2})-E({}^6D_{J'})}, \quad (7)$$

where, for convenience, we omit the phonon wave functions. For Gd^{3+} in CaF$_2$, the Gd^{3+} ion sits at the center of a cube with eight fluorine ions occupying the eight corners of the cubic XY_8 molecular cluster. The electronic operators for this case have been computed.[10] Following the argument presented earlier, only the first terms of the electronic operators given in Eq. (10) of Ref. 10 are needed in our theoretical estimate of the spectral shift. In order to estimate the matrix elements in Eq. (7), the standard formula by Elliott *et al.*[11] will be used. It is

$$\langle SLJM|U_m{}^n|S'L'J'M'\rangle =(-1)^{M+S+L'}[(2J+1)(2J'+1)]^{1/2}\begin{pmatrix} J & J' & n\\ -M & M' & m\end{pmatrix} \times\begin{Bmatrix} L & J & S\\ J' & L' & n\end{Bmatrix}\langle SL\|U^n\|S'L'\rangle\delta(S,S'), \quad (8)$$

where $(\cdots)$ and $\{\cdots\}$ denote the 3-j and 6-j symbols, respectively. The 3-j and 6-j symbols can be obtained from the tables prepared by Rotenberg *et al.*[12]

According to Van Vleck, the normal coordinate Q_j can be regarded as linear functions of the normal coordinates q_i associated with the phonons. Hence,

$$Q_j=\sum_{i=1}^{3N} a_{ji}q_i. \quad (9)$$

Here N is the total number of atoms in the crystal, and a_{ji} are the appropriate coefficients. Above the liquid-nitrogen temperatures, the phonons with large wave vectors k are well excited. Because the phonon density of states with larger values of k is higher, the phonons of large k are more important in the spectral line shift. Hence, a_{ji} should be computed for the phonons of large k. We thus find[13,14]

$$\langle a_{ji}a_{j'i'}\rangle_{\text{av}}\simeq\tfrac{1}{3}\delta_{jj'}\delta_{ii'}, \quad (10)$$

for all j, j', i, and i'.

Following the standard procedure, we can now reduce Eq. (7) to the following form:

$$\delta E({}^6P_{7/2}M)=A(M)B(T), \quad (11)$$

where

$$A(M)=\sum_{J'=\frac{1}{2}}^{9/2}\sum_{M'=-J'}^{+J'}\sum_{j=2}^{9} \times\frac{({}^6P_{7/2}M|v_j|{}^6D_{J'}M')({}^6D_{J'}M'|v_j|{}^6P_{7/2}M)}{E({}^6P_{7/2})-E({}^6D_{J'})}, \quad (12)$$

$$B(T)=\frac{h}{12\pi^2M}\sum_{i=1}^{3N}[1+2N(\nu_i)]/\nu_i, \quad (13)$$

in which ν_i is the frequency of the ith phonon mode, $N(\nu_i)$ is the Bose-Einstein factor evaluated at $E=h\nu_i$, and M is the mass of the crystal. It is interesting to note that Eq. (13) is proportional to the Debye-Waller factor.[15] For the convenience of the later discussions, we shall separate the zero-point phonon contribution from the temperature-dependent contribution. Hence Eq. (11) can be written as

$$\delta E({}^6P_{7/2}M)=\delta E(0)+\delta E(T), \quad (14)$$

where

$$\delta E(0)=A(M)b(0), \quad (15)$$

$$\delta E(T)=A(M)b(T), \quad (16)$$

with

$$b(0)=\frac{h}{12\pi^2M}\sum_{i=1}^{3N}1/\nu_i, \quad (17)$$

$$b(T)=\frac{h}{6\pi^2M}\sum_{i=1}^{3N}N(\nu_i)/\nu_i. \quad (18)$$

In the Debye approximation, we can replace the summation by the integration as

$$\sum_{i=1}^{3N}=9N(h/k_B\Theta_D)^3\int_0^{k_B\Theta_D/h}\nu^2d\nu. \quad (19)$$

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Here Θ_D is the Debye temperature and k_B is Bolzmann's constant; Eq. (18) becomes

$$b(0)=3h^2n/8\pi^2\mu k_B\Theta_D\,, \tag{20}$$

$$b(T)=\frac{3h^2n}{2\pi^2\mu k_B\Theta_D}\left(\frac{T}{\Theta_D}\right)^2\int_0^{\Theta_D/T}\frac{zdz}{e^z-1}\,, \tag{21}$$

where μ is the mass of the atoms in a unit cell, and n is the number of atoms per unit cell.

Let us now try to derive an expression for the spectral line shift contributed by the optical phonons in a crystal. In this case, we have to express Q_j in terms of the normal coordinate q_{i_r} associated with the ith optical-phonon mode in the rth optical branch as[13,14]

$$Q_j=\sum\nolimits_r\sum_{i_r=1}^{N/n}a_{ji_r}q_{i_r}. \tag{22}$$

As pointed out by the author[13] and others,[16] the optical phonons with large values of k are the most important. In view of this, we also have[13]

$$\langle a_{ji_r}{}^2\rangle_{\text{av}}\simeq\tfrac{1}{3}\,, \tag{23}$$

for all j and r. By the same procedure used earlier, we find the spectral line shift of the $^6P_{7/2}$ state induced by the optical phonons to be

$$\delta E_{\text{op}}(^6P_{7/2}M)=\delta E_{\text{op}}(0)+\delta E_{\text{op}}(T)\,, \tag{24}$$

with

$$\delta E_{\text{op}}(0)=A(M)b_{\text{op}}(0)\,, \tag{25}$$

$$\delta E_{\text{op}}(T)=A(M)b_{\text{op}}(T)\,, \tag{26}$$

$$b_{\text{op}}(0)=\frac{h}{12\pi^2M}\sum\nolimits_r\sum_{i_r=1}^{N/n}1/\nu_{i_r}\,, \tag{27}$$

$$b_{\text{op}}(T)=\frac{h}{6\pi^2M}\sum\nolimits_r\sum_{i_r=1}^{N/n}N(\nu_{i_r})/\nu_{i_r}. \tag{28}$$

Because only those optical phonons with large values of k are important, we may further approximate ν_{i_r} by the optical-phonon frequency of the rth optical branch at the Brillouin-zone boundary ν_{rB}. This is essentially the Einstein approximation weighted with the optical-phonon frequency at the Brillouin-zone boundary. With this approximation, Eqs. (27) and (28) become

$$b_{\text{op}}(0)\simeq\frac{h}{12\pi^2\mu}\sum\nolimits_r 1/\nu_{rB}\,, \tag{29}$$

$$b_{\text{op}}(T)\simeq\frac{h}{6\pi^2\mu}\sum\nolimits_r N(\nu_{rB})/\nu_{rB}. \tag{30}$$

As in Ref. 13, for the very narrow optical branches, we can further replace ν_{rB} by the optical-phonon frequency of the rth branch at $k=0$.

TABLE I. Temperature shift of the $^6P_{7/2}$ state of Gd^{3+} in CaF_2.

T°K	77	293	500	700	1000	1300
Total temperature shift (cm^{-1})	∼0.1	13.2	26.3	39.5	59.7	79.8
Temperature shift by optical phonons (cm^{-1})	∼0.07	2.2	5.1	8.1	12.2	17.7

For CaF_2, the lattice constant[17] is 5.75×10^{-8} cm, the effective charge of a corner ion of the cubic molecular cluster is e, $n=3$, and[18] $\Theta_D=474$°K. Hence, using Eqs. (12), (15), and (20), the zero-point phonon contribution to the shift of the $^6P_{7/2}$ state is

$$\delta E(0)=16.8\ \text{cm}^{-1}. \tag{31}$$

This is only 0.05% of $E(^6P_{7/2})$-$E(^8S_{7/2})$. In order to calculate the optical-phonon contribution, we shall assume the solid to be elastically isotropic, and hence the optical-phonon frequencies at the symmetry point X calculated by Ganesan and Srinivasan[19] will be used. They are $\nu_{1l}=4.48\times10^{12}$, $\nu_{1\text{t}}=6.67\times10^{12}$, $\nu_{2l}=11.9\times10^{12}$, and $\nu_{2\text{t}}=10.5\times10^{12}$ cps. Using these and Eqs. (12), (25), and (29), we find the zero-point optical-phonon contribution to the shift of $|^6P_{7/2}\rangle$ to be

$$\delta E_{\text{op}}(0)\simeq4.5\ \text{cm}^{-1}. \tag{32}$$

Comparing Eq. (32) with Eq. (31), we find that about 27% of the zero-point phonon-induced shift is contributed by the optical phonons. In Table I, we tabulate the temperature-dependent shifts of $|^6P_{7/2}\rangle$ based on Eqs. (12), (16), (21), (26), and (30) from 77 to 1300°K.

Let us now concentrate our attention to the phonon-induced shift of the ground $^8S_{7/2}$ state. To the lowest order, we have

$$\delta E(^8S_{7/2}M)=\sum_{J'=\frac{1}{2}}^{9/2}\sum_{M'=-J'}^{+J'}\sum_{j=2}^{9}\times\frac{(^8S_{7/2}M|v_jQ_j|^6D_{J'}M')(^6D_{J'}M'|v_jQ_j|^8S_{7/2}M)}{E(^8S_{7/2})-E(^6P_{7/2})}. \tag{33}$$

Because the Van Vleck orbit-lattice interaction connects only $|^6P\rangle$ and $|^6D\rangle$, $\delta E(^8S_{7/2}M)$ will be small compared with $\delta E(^6P_{7/2}M)$. Consequently, $\delta E(^6P_{7/2}M)$ will represent the phonon-induced shift of the spectral line connecting $|^8S_{7/2}\rangle$ and $|^6P_{7/2}\rangle$. No data on the temperature dependence of the spectral line shift of Gd^{3+} in CaF_2 are available. However, Dieke and Leopold[20] found that the shift of the A_1 component of $^6P_{7/2}$ of $GdCl_3\cdot6H_2O$ from 1.7 to 273°K is 6.18 cm^{-1}. In want of the electronic operators and normal coordinates

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appropriate to this crystal, the direct comparison of theory with experiment is not possible. Nevertheless, this shift is in the same order of magnitude with the shift for Gd^{3+} in CaF_2 at 293°K given in Table I. Therefore, we may conclude that theory and experiment agree to within one order of magnitude.

III. PHONON-INDUCED g SHIFT

In view of the success in interpreting the g shifts of Tm^{2+} and Ho^{2+} in CaF_2 by Inoue,[8] we shall attempt to calculate the phonon-induced g shift of Gd^{3+}. In order to do this, let us write

$$E({}^6P_{7/2}M)=E_P(0)+\delta E({}^6P_{7/2}M)\,, \tag{34}$$

where $E_P(0)$ is the energy of $|{}^6P_{7/2}\rangle$ calculated from the Slater integrals.[1,4] Hence, Eq. (2) can be written as

$$a(T)\simeq a(0)-\delta a\,, \tag{35}$$

where, from Eq. (3),

$$\begin{aligned} &a(0)=0.1725\,,\\ &\delta a=a(0)\delta E({}^6P_{7/2}M)/E_p(0)\,. \end{aligned} \tag{36}$$

In terms of these notations, we can rewrite Eq. (4) in the following form:

$$g(T)=g(0)+\delta g\,, \tag{37}$$

in which $g(0)$ is the g value neglecting the phonon contribution, and

$$\delta g=0.5725[a(0)]^2\delta E({}^6P_{7/2}M)/E_P(0)\,. \tag{38}$$

At room temperatures, $\delta E({}^6P_{7/2}M)\sim 30$ cm^{-1}, and hence

$$\delta g\sim +1.5\times 10^{-6}\,, \tag{39}$$

which is far too small to be meaningful. It also does not have the correct sign to account for the discrepancy pointed out in Sec. I.

IV. PHONON-INDUCED SPLITTING OF THE ${}^8S_{7/2}$ GROUND STATE

In a cubic field, the ground-state multiplet ${}^8S_{7/2}$ splits into two doublets Γ_6, Γ_7 and a quartet Γ_8. The zeroth-order wave functions of these states are[21]

$$\begin{aligned} &|\Gamma_6,1\rangle=(5/12)^{1/2}|M=\tfrac{7}{2}\rangle+(7/12)^{1/2}|M=-\tfrac{1}{2}\rangle\,,\\ &|\Gamma_7,1\rangle=(\tfrac{3}{4})^{1/2}|M=-\tfrac{5}{2}\rangle-\tfrac{1}{2}|M=-\tfrac{3}{2}\rangle\,,\\ &|\Gamma_8,1\rangle=(7/12)^{1/2}|M=\tfrac{7}{2}\rangle-(5/12)^{1/2}|M=-\tfrac{1}{2}\rangle\,. \end{aligned} \tag{40}$$

Using Eqs. (1), (33), and (40), we can calculate the phonon-induced shifts of these three states. After some tedious computations, we find the zero-point shifts to be

$$\begin{aligned} &\delta E(\Gamma_7)=0.0812\ \text{cm}^{-1}\,,\\ &\delta E(\Gamma_8)=0.0823\ \text{cm}^{-1}\,,\\ &\delta E(\Gamma_6)=0.0833\ \text{cm}^{-1}\,. \end{aligned} \tag{41}$$

These theoretical estimates show that Γ_7 is the lowest, and Γ_6 the highest. This result is in agreement with the conclusion made by Wakim[22] based on his experimental data. From these estimates, the zero-point phonon contribution to the ground-state splitting is

$$\delta E(\Gamma_6)-\delta E(\Gamma_7)=2.1\times 10^{-3}\ \text{cm}^{-1}\,. \tag{42}$$

At $T=293$°K, we find the phonon-induced splitting to be 3.6×10^{-3} cm^{-1}. Note that this splitting is smaller than Ryter's experimental value,[23] 0.149 cm^{-1}, by a factor of 40, but it is only a factor of 4 smaller than the theoretical value, 0.015 cm^{-1}, calculated by Lacroix,[24] who used the standard sixth-order perturbation involving the nearest-neighbor point-charge static-crystalline field potential and the spin-orbit interaction. Therefore, we may conclude that phonons play an important role in the zero-field splittings of the S-state ions.

V. DISCUSSION

In Sec. II, we showed that the phonon-induced shift of a spectral line is proportional to the Debye-Waller factor. This result suggests to us a convenient method of measuring the Debye temperature of some transparent crystals. Because of the severe anharmonicity in the crystal at high temperatures, the direct comparison of theory with experiment will be difficult. However, this difficulty can be overcome by using some crystals doped with S-state ions, such as alkali halides whose Debye-Waller factors are known.[25]

In Sec. IV, we showed that lattice vibrations are responsible for at least a part of the ground-state splitting. We should be aware that this splitting vanishes if $|{}^6D_J\rangle$ with $J=\frac{3}{2}$ to $\frac{9}{2}$ are degenerate. This result was first shown by Huber.[26] Hence, the splitting is very sensitive to the spin-orbit interaction by which the degeneracy in $|{}^6D_J\rangle$ is removed. Furthermore, in this calculation, we considered only 15 of the 327 *SLJ* states. In consequence, we should like to emphasize that the calculation made in Sec. IV is only an approximation to the truth.

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