# Contribution of the Orbit-Lattice Interaction to the Splitting of the $^8S_{7/2}$ Ground State*

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A calculation of the static contribution of the orbit-lattice interaction to the ground-state splitting of rare-earth $S$-state ions is made, and the effects of mixing due to spin-orbit coupling are treated explicitly. Both the zero-point and the temperature-dependent phonon contributions are determined, and it is shown that, for $Gd^{3+}$ in $CaF_2$, the splitting produced by these terms (a) is approximately three orders of magnitude smaller than the measured value, (b) has the opposite sign to the observed splitting, and (c) possesses (by itself) an incorrect temperature behavior. Consequently, in agreement with our initial calculations, which did not include spin-orbit coupling corrections, we conclude that the static orbit-lattice interaction is not responsible for the ground-state splitting of $S$-state ions.

## I. INTRODUCTION

IN a recent paper[1] this writer investigated the possibility that the orbit-lattice interaction $V_{OL}$ might be the proper mechanism to explain the ground-state splitting of rare-earth $S$-state ions in cubic crystalline hosts. It was demonstrated that this interaction produced no splitting of the $^8S_{7/2}$ ground state if the matrix elements were unaffected by the mixing caused by spin-orbit coupling. By including these mixing effects, Huang[2] has recently calculated the ground-state splitting of $Gd^{3+}$ in $CaF_2$ from this mechanism and found a splitting which was smaller than the experimental value[3] by a factor of 40 and smaller by only a factor of 4 than the calculated splitting due to the crystalline field.[4] In this paper we amend our previous calculation[1] to include the spin-orbit mixing and show that, contrary to Huang's results,[2] the splitting produced by $V_{OL}$ (a) differs in magnitude from the experimental value[3] by a factor of $2.6\times10^3$, (b) is opposite in sign to the observed splitting, and (c) exhibits (by itself) an incorrect behavior with temperature.

## II. CALCULATION

The $^8S_{7/2}$ ground multiplet of a rare-earth ion in the $4f^7$ configuration splits in a cubic environment into two doublets $\Gamma_6$, $\Gamma_7$, and a quartet $\Gamma_8$, whose wave functions are given in terms of the magnetic substates $|M\rangle$ as[5]

$$|\Gamma_6,1\rangle=(5/12)^{1/2}|\tfrac{7}{2}\rangle+(7/12)^{1/2}|-\tfrac{1}{2}\rangle,$$
$$|\Gamma_7,1\rangle=(\tfrac{3}{4})^{1/2}|-\tfrac{5}{2}\rangle-\tfrac{1}{2}|\tfrac{3}{2}\rangle,$$
$$|\Gamma_8,1\rangle=(7/12)^{1/2}|\tfrac{7}{2}\rangle-(5/12)^{1/2}|-\tfrac{1}{2}\rangle. \quad (1)$$

In our initial work,[1] the spin-orbit coupling corrections to the free-ion wave functions and energies were neglected, and the energy shifts $E(\Gamma_i)$ arising from the effective orbit-lattice interaction were determined from the expression

$$E(\Gamma_i)=\sum_J E_J(\Gamma_i), \quad (2)$$

where

$$E_J(\Gamma_i)=\sum_{L,M_J''}\langle\Gamma_i|V_{OL}|{}^6L_JM_J''\rangle \times\langle{}^6L_JM_J''|V_{OL}|\Gamma_i\rangle/(E_{8S}-E_{6L}). \quad (3)$$

The sum is over all excited states of the ion, but since $V_{OL}$ is expressed in lowest order in spherical harmonics of order two, and since the lowest order nonvanishing reduced matrix element[6] of the operator $U^2$ in the $4f^7$ configuration is $\langle{}^6P\|U^2\|{}^6D\rangle$, the sum over the excited states in Eq. (3) is restricted to the $^6D_J$ states with $J=\frac{3}{2}$–$\frac{9}{2}$ (matrix elements involving $^6D_{1/2}$ vanish). We had introduced the $^6P_{7/2}$ state by a first-order perturbation in the spin-orbit coupling, i.e., the perturbed ground state $|{}^8S_{7/2}M)$ was written[2,7]

$$|{}^8S_{7/2}M)=0.9866\,|{}^8S_{7/2}M\rangle+0.1618\,|{}^6P_{7/2}M\rangle+\cdots. \quad (4)$$

Equation (3) then became

$$E_J(\Gamma_i)=\sum_{MJ''}\langle\Gamma_i|V_{OL}|{}^6D_JM_J''\rangle \times\langle{}^6D_JM_J''|V_{OL}|\Gamma_i\rangle\left[\frac{(0.1618)^2}{E_{8S}-E_{6D}}\right], \quad (5)$$

in which it is understood here that the states $|\Gamma_i\rangle$ are linear combinations of the $|{}^6P_{7/2}M\rangle$ states of Eq. (1).

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[1] T. J. Menne, J. Phys. Chem. Solids **28**, 1629 (1967).
[2] Chao-Yuan Huang, Phys. Rev. **159**, 683 (1967).
[3] C. Ryter, Helv. Phys. Acta **20**, 353 (1957).
[4] R. Lacroix, Arch. Sci. (Geneva) Fasc. Spec. Ampere **11**, 141 (1958).
[5] C. Kittel and J. M. Luttinger, Phys. Rev. **73**, 162 (1948).
[6] C. W. Nielson and G. F. Koster, *Spectroscopic Coefficients for the $p^n$, $d^n$, and $f^n$ Configurations* (M. I. T. Press, Cambridge, Mass., 1963), p. 192.
[7] B. G. Wybourne, Phys. Rev. **148**, 317 (1966).

In Table I are recorded the Eq. (5) values of $E_J(\Gamma_i)$ expressed in terms of $E_{7/2}(\Gamma_6)$ and determined by using the long-wavelength approximation with $E_{6_D}-E_{8_S}=42\,845$ cm$^{-1}$ for all $J$. As demonstrated in Ref. 1 from more general arguments, $E(\Gamma_i)=\sum_J E_J(\Gamma_i)=$ const(126/55) for all $i=6$–8, and hence there is a net shift but no splitting when the $^6D_J$ states are assumed to be degenerate in $J$. The spin-orbit-coupling corrections required to remove the degeneracy in the $^6D_J$ states were initially neglected because states of an ion with a half-filled shell are degenerate in first-order perturbation, and consequently the first nonvanishing correction to $E(^6D_J)$, for example, is of second order in the spin-orbit coupling. It was expected that these small corrections would yield a negligible value for the splitting, since the calculated value of $E_{7/2}(\Gamma_6)$ was $-2.28\times10^{-3}$ cm$^{-1}$ for $Gd^{3+}$ in $CaF_2$. This value is already a factor of 60 smaller than the measured splitting[3] of 0.149 cm$^{-1}$. It is shown in the next paragraph that this suspicion was correct.

To account for the spin-orbit coupling corrections, we simply write

$$E(\Gamma_i)=\sum_J E_J(\Gamma_i)\alpha_J{}^2 \times(E_{6_D}-E_{8_S})/[E(^6D_J)-E(^8S_{7/2})], \quad (6)$$

in which $\alpha_J$ is the coefficient of the unperturbed $|\,^6D_J\rangle$ state in the expression for the perturbed $|\,^6D_J)$ state given in Eq. (1) of Huang,[2] $E(^6D_J)-E(^8S_{7/2})$ are the experimental energies provided by Wybourne[7] and also recorded by Huang,[2] and the $E_J(\Gamma_i)$ are listed in Table I. From Eq. (6) we find that the zero-point phonon contribution to the energy shift of $Gd^{3+}$ in $CaF_2$ is

$$\begin{aligned}E(\Gamma_6)&=-4.0287\times10^{-3}\text{ cm}^{-1},\\ E(\Gamma_8)&=-4.0505\times10^{-3}\text{ cm}^{-1},\\ E(\Gamma_7)&=-4.0869\times10^{-3}\text{ cm}^{-1}.\end{aligned} \quad (7)$$

First, note that in agreement with Huang's findings,[2] $\Gamma_6$ lies highest and $\Gamma_7$ lowest. However, contrary to Huang's claim, this order is in direct disagreement with experiment, where it is observed that the quantity

$$8\delta=E(\Gamma_6)-E(\Gamma_7) \quad (8)$$

is negative,[8–10] and hence $\Gamma_7$ lies highest and $\Gamma_6$ lowest. Secondly, we find from Eq. (7) that

$$8\delta=+5.82\times10^{-5}\text{ cm}^{-1}, \quad (9)$$

which is a factor of $2.6\times10^3$ smaller than the measured value[3] $8\,|\,\delta\,|=0.149$ cm$^{-1}$, and $2.6\times10^2$ times smaller than Lacroix's value[4] calculated from the point-charge crystal-field model. It is seen then that the orbit-lattice interaction, even when corrected for the mixing arising from spin-orbit coupling, makes a negligible contribution to the ground-state splitting of rare-earth $S$-state ions.

Of further interest is the fact that an interaction possessing cubic symmetry will split an eightfold degenerate state such that the ratio

$$R=[E(\Gamma_6)-E(\Gamma_8)]/[E(\Gamma_8)-E(\Gamma_7)] \quad (10)$$

has a value near 0.60. Indeed, Ryter[3] has found experimentally that $R=0.596$ for $Gd^{3+}$ in $CaF_2$. Thus, an evaluation of $R$ provides some measure of the correctness and accuracy of a particular calculation. Huang's values[2] for $E(\Gamma_i)$ yield $R=0.91$, whereas we obtain the value $R=0.598$ from Eq. (7).

In the calculations discussed above we have considered only the zero-point phonon contribution to the ground-state splitting. By including the temperature-dependent lattice vibrations in the long-wavelength approximation, we obtain

$$8\delta=\left[5.82\times10^{-5}+6.91\times10^{-15}T^4\int_0^{\Theta/T}\frac{x^3dx}{e^x-1}\right]\text{cm}^{-1}, \quad (11)$$

where $\Theta$ is the Debye temperature. Thus, for $\Theta=475$°K and $T=293$°K, $8\delta=9.58\times10^{-5}$ cm$^{-1}$, which is still negligible compared with the measured[3] and calculated[4] values. Moreover, Eq. (11) exhibits an increase in the zero-field splitting with temperature in contrast to its observed behavior[11,12] and the behavior expected from lattice expansion.

In his calculation of the $S$-state splitting arising from the orbit-lattice interaction, Huang[2] has evidently employed the Debye spectrum and the short-wavelength approximation, i.e., $kR\gg1$, where $k$ is the phonon wave vector and $R$ is the interionic distance, whereas in our calculations above the long-wavelength approximation ($kR\ll1$) was used. To determine the effect of these approximations on the magnitude of the splitting, we performed a short calculation of the ratio of the zero-

TABLE I. Energy shifts $E_J(\Gamma_i)$ arising from each state in the $^6D_J$ multiplet. They are determined from Eq. (5) in units of $E_{7/2}(\Gamma_6)$.

| $E_J(\Gamma_i)$ \ $J$ | $\frac{3}{2}$ | $\frac{5}{2}$ | $\frac{7}{2}$ | $\frac{9}{2}$ | $\Sigma_J E_J(\Gamma_i)$ |
|---|---|---|---|---|---|
| $E_J(\Gamma_6)$ | 42/275 | 171/550 | 1 | 91/100 | 126/55 |
| $E_J(\Gamma_7)$ | 18/175 | 2349/3850 | 45/77 | 153/154 | 126/55 |
| $E_J(\Gamma_8)$ | 258/1925 | 1629/3850 | 65/77 | 137/154 | 126/55 |

[8] J. M. Baker and F. I. B. Williams, Proc. Roy. Soc. (London) **A267**, 283 (1962).
[9] F. I. B. Williams, Proc. Roy. Soc. (London) **A283**, 445 (1965).
[10] F. G. Wakim and A. W. Nolle, Bull. Am. Phys. Soc. **9**, 244 (1964).
[11] W. Low and D. Shaltiel, J. Phys. Chem. Solids **6**, 315 (1958).
[12] Sook Lee, T. J. Menne, and D. P. Ames, Bull. Am. Phys. Soc. **12**, 1043 (1967).

point phonon splitting determined from the long-wavelength approximation to that determined from the short-wavelength approximation and obtained a value of four. Thus, both approximations yield the same order of magnitude for the ground-state splitting when used in conjunction with the Debye spectrum.

## III. CONCLUSIONS

We have demonstrated that, even when admixtures arising from spin-orbit coupling are included, the orbit-lattice interaction yields a ground-state splitting for $CaF_2:Gd^{3+}$ which is orders of magnitude smaller than the measured value, gives the incorrect order of the levels, and increases instead of decreases with temperature. Consequently, in concurrence with our initial findings[1] on this subject, it is concluded that the orbit-lattice interaction, without configuration mixing, may be eliminated as a possible mechanism which is responsible for the splitting of the ground level of $S$-state ions.

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# Transverse Stimulated Emission in Liquids*

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Stimulated Brillouin scattering transverse to the laser beam, external to the laser cavity and free from frequency-dependent feedback, has been studied using a specially designed laser. The laser beam is focused by a cylindrical lens so that the direction of maximum gain is transverse to the beam. The hypersonic velocities of several liquids have been measured at high power levels without frequency-pulling effects. Transverse filaments have been observed, and an approximate measurement of the power contained in a single filament has been obtained. A stimulated anti-Stokes scattering in benzene has also been observed, which has a 200-MHz frequency shift. This scattering is tentatively identified as stimulated thermal Rayleigh scattering.

## I. INTRODUCTION

WE have studied stimulated Brillouin scattering transverse to the laser beam and external to the laser cavity. With this arrangment no *frequency-dependent* feedback occurred in either the longitudinal or transverse direction. This experiment has been made possible by the design and construction of a mode-selected 350-MW ruby laser whose spectral width is approximately 300 MHz. With this device we have been able to observe stimulated Raman and stimulated Brillouin scattering transverse to the laser beam in almost any liquid without any external resonator. Thus, it has been possible to measure the hypersonic velocities of the liquids at high power levels without the frequency pulling usually involved. Because of the good separation of the incident and scattered light, we have been able to observe light shifted by less than 0.01 $cm^{-1}$ from the laser frequency. It has also been possible to study the spatial distribution of light intensity in the scattering region.

Several studies of stimulated scattering in liquids have been carried out in which the direction of the stimulated scattering was not parallel to the laser beam.[1–4] Dennis and Tannenwald[1] used a transverse resonator external to the laser cavity to study stimulated Raman scattering emitted at 90° to the laser beam. Dennis[2] observed stimulated Brillouin scattering in a transverse resonator, but the observed frequency shift was somewhat ambiguous because of the multimode nature of the laser source. Takuma and Jennings[3] studied stimulated Brillouin scattering in an off-axis external resonator at small angles to the laser beam. In the latter experiment two frequency shifts were observed, corresponding to the two angles from the forward laser beam direction. Pine[4] has studied stimulated Brillouin scattering from many different liquids using an external transverse resonator. His experiments were performed with a laser with sufficiently good mode selection to allow unambiguous determination of the Brillouin shift and threshold phenomena. Pine pointed out the difficulty with frequency-pulling effects caused by the external resonator. Frequency pulling by the laser resonator has also been noted[5,6] in longitudinal

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[1] J. Dennis and P. Tannenwald, Appl. Phys. Letters **5**, 58 (1964).
[2] J. Dennis, Lincoln Laboratory, Solid State Research Report No. ESD-TDR-65-31, 1964 (unpublished).
[3] H. Takuma and D. Jennings, Appl. Phys. Letters **5**, 239 (1964).
[4] A. Pine, Phys. Rev. **149**, 113 (1966).
[5] R. G. Brewer, Appl. Phys. Letters **9**, 51 (1966).
[6] T. A. Wiggins, R. V. Wick, D. H. Rank, and A. H. Guenther, Appl. Opt. **4**, 1203 (1965).