Spin-Hamiltonian Parameters as a Function of Pressure-Induced and Cation-Induced Changes in Nearest-Neighbor Distance for Europium-151 in Alkaline Earth Fluorides*

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The electron-paramagnetic-resonance spectra of the systems $CaF_2:{}^{151}Eu^{2+}$, $SrF_2:{}^{151}Eu^{2+}$, $BaF_2:{}^{151}Eu^{2+}$ have been studied at a pressure of 26 kbar. These spectra were interpreted in terms of the usual phenomenological spin Hamiltonian with parameters g (spectroscopic splitting factor), b_4 and b_6 (crystalline-field parameters), and A (hyperfine splitting factor). The variations of b_4 and b_6 with pressure were compared with their variations with cation, and a consistent interpretation of the differences was found in terms of local lattice distortions about the impurity europium ions. This model leads to the relationships $b_4 \propto \delta^{-8.8}$, $b_6 \propto \delta^{-13.6}$ between the crystalline-field parameters and the nearest-neighbor distance δ.

I. INTRODUCTION

THE nature of the interaction of an imbedded paramagnetic ion with the crystalline field of a solid, including nuclear effects, has been of considerable interest for many years. This interest stems from the successful implantation of such ions into a crystal lattice and the possibility of studying those interactions by electron-paramagnetic-resonance (EPR) techniques,[1,2] with consequent enhancement of our understanding of the solid state. In particular, the dependence of certain spin-Hamiltonian parameters upon the nearest-neighbor distance from the paramagnetic ion is rather different for different bonding models.[3,4] An experimental determination of this dependence, therefore, provides useful data for the better theoretical understanding of the nature of the coupling between the atoms of the solid.

In the systems $CaF_2:Eu^{2+}$, $SrF_2:Eu^{2+}$, and $BaF_2: Eu^{2+}$, the nearest neighbors to the cations are eight fluorine atoms in a cubic array about the cation at the center.[5] They would seem, therefore, to provide the necessary dependence of the spin-Hamiltonian parameters upon nearest-neighbor distance (δ), since the lattice parameters for the pure crystals are in the ratio of $5.4626:5.7996:6.2001$.[6] In fact, Title[7] has measured one of the spin-Hamiltonian parameters[8] (b_4) for these systems. He interpreted his results to imply an approximate inverse fifth-power dependence of b_4 on δ, a result which seemed to support an electrostatic model of non-overlapping charges (point charge) for the crystal in

which the electrostatic potential occurred linearly in the perturbation process.

The results of our experiment present evidence that another interpretation of Title's work is necessary, an interpretation which takes into account a distortion of the local cell surrounding the paramagnetic ion. A preliminary effort to take this distortion into account yields a -8.8 power dependence of b_4 on δ. This power should be compared to -10, suggested by Watanabe[9] for a quadratic dependence of the perturbation on the point-charge potential. (It should also be noted that Powell, Gabriel, and Johnston[10] have pointed out some errors in Watanabe's calculations.) In our work, the lattice spacings of the cubic systems named above are altered by subjecting the crystals to hydrostatic pressure. A comparison of the changes in the spectra induced by pressure with those induced by changes in cation has yielded information on the distortion of the lattice imposed by the cation impurity. It has also provided information about the variation of the spin-Hamiltonian parameters with cell size in the crystals.

In Sec. II the experimental arrangement is discussed. Section III presents the results of our measurements and of the reduction of the data. In Sec. IV our interpretation of these results is discussed.

II. EXPERIMENT

The high-pressure measurements were made using the method of Gardner and co-workers.[11,12] In this method, the sample under study is confined by a high-friction gasket in a nearly hydrostatic medium (indium) between two dielectric Bridgman anvils, one of which serves as a microwave cavity. An accurate determination of the pressure at 26 kbar was made possible by the presence near the sample of a bismuth strip whose resistance was monitored. This same strip carried the

[1] B. Bleaney and K. W. H. Stevens, Rept. Progr. Phys. **16**, 108 (1953).
[2] K. D. Bowers and J. Owens, Rept. Progr. Phys. **18**, 304 (1955).
[3] J. D. Axe and G. Burns, Phys. Rev. **152**, 331 (1966).
[4] R. E. Watson and A. J. Freeman, Phys. Rev. **156**, 251 (1967).
[5] R. W. G. Wycoff, *Crystal Structures* (Interscience Publishers, Inc., New York, 1963) 2nd ed., Vol. I.
[6] Natl. Bur. Std. (U. S.) Circ. No. 539, Vol. I, pp. 69–72; Vol. V, pp. 67–68.
[7] R. S. Title, Phys. Letters **6**, 13 (1963).
[8] J. M. Baker, B. Bleaney, and W. Hayes, Proc. Roy. Soc. (London) **A247**, 141 (1958).

[9] H. Watanabe, Phys. Rev. Letters **4**, 410 (1960).
[10] M. J. D. Powell, J. R. Gabriel, and D. F. Johnston, Phys. Rev. Letters **5**, 145 (1960).
[11] J. H. Gardner *et al.*, Rev. Sci. Instr. **34**, 1043 (1963).
[12] H. M. Nelson, D. B. Larson, and J. H. Gardner, J. Chem. Phys. **47**, 1994 (1967).

current for the magnetic field modulation at the sample. Measurements were made at the pressure of the Bi I–II transition which occurs at 26 kbar.[13] By careful observation of the bismuth resistance curve before and after the EPR spectra were run, it was determined that the pressure during all measurements for which data was used remained within 4% of the Bi I–II transition pressure (i.e., ±1 kbar).

The measurements under ambient conditions were made using a Varian model V-4531 multipurpose cavity in place of the pressure cavity described above. This change allowed the narrowing of the gap in the 12-in. magnet from 4 to 2 in., with a corresponding increase in the homogeneity and precision of measurement of the magnetic field strength in the ambient pressure case. The magnetic field strength was measured in both cases by a Varian model F-8A nuclear fluxmeter with the probe placed as near to the position of the sample as possible (about 1 in.). A calibration was made of the magnetic field at the position of the sample relative to that at the position of the probe. The frequencies of the fluxmeter and the X-band klystron were measured with a Hewlett-Packard model 5245L frequency counter with appropriate adapting units for the frequencies measured.

The samples of CaF_2:[151]Eu^{2+}, SrF_2:[151]Eu^{2+}, and BaF_2:[151]Eu^{2+} were obtained from Harshaw Chemical Co. They were grown with 0.1 at.% of [151]Eu. The use of a single isotope [151]Eu gives rise to well-resolved spectra. The overlapping of some lines in prior investigations[14,15] owing to the presence of two hyperfine spectra is avoided here.

III. RESULTS

Typical spectra are shown in Figs. 1–6. The derivative of the absorption is plotted as a function of magnetic field strength. The magnetic field is parallel to the [100] direction of the crystal. It is seen that each of the spectra consists of seven groups of electronic transitions;
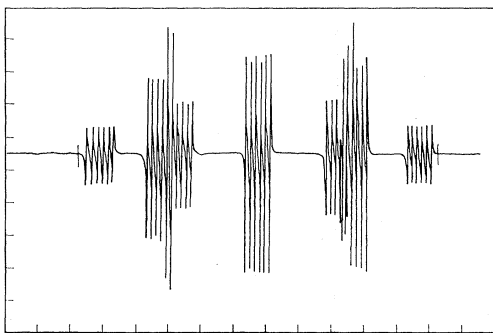
FIG. 1. EPR spectrum of CaF_2: [151]Eu^{2+} at ambient temperature and pressure with the magnetic field parallel to the [100] direction of the crystal (scan: 3750 G centered at 3322 G).

[13] R. N. Jeffery, J. D. Barnett, H. B. Vanfleet, and H. T. Hall, J. Appl. Phys. **37**, 3172 (1966).
[14] H. J. Glaser and D. Geist, Z. Naturforsch. **A20**, 842 (1965).
[15] T. J. Menne, D. P. Ames, and S. Lee, Phys. Rev. **169**, 333 (1968).

the six lines of each group comprise the hyperfine structure. Although there is some overlapping in four of the groups, three of them are completely resolved. The hyperfine structure appears to be completely resolved except perhaps in the outermost groups of the spectrum for BaF_2:[151]Eu^{2+}.

The model used in processing the data was the phenomenological spin Hamiltonian[8,14]

$$H = H_{cryst} + H_Z + H_{hf}$$
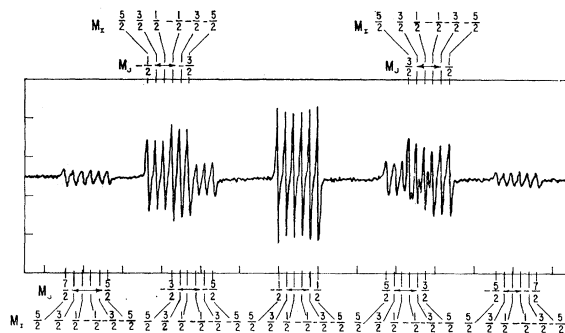
FIG. 2. EPR spectrum of SrF_2: [151]Eu^{2+} at ambient temperature and pressure with the magnetic field parallel to the [100] direction of the crystal (scan: 2500 G centered at 3367 G). The quantum numbers associated with each of the transitions are indicated.
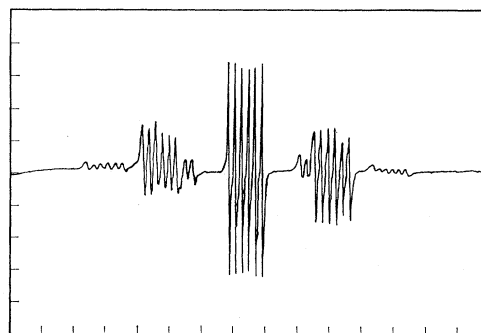
FIG. 3. EPR spectrum of BaF_2: [151]Eu^{2+} at ambient temperature and pressure with the magnetic field parallel to the [100] direction of the crystal (scan: 2500 G centered at 3400 G).
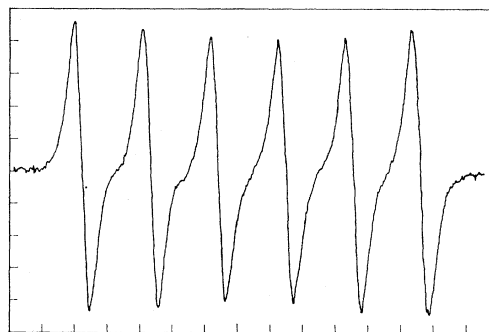
FIG. 4. $M_J = \frac{1}{2} \leftrightarrow -\frac{1}{2}$ transition group in CaF_2: [151]Eu^{2+} at 26 kbar and ambient temperature with the magnetic field parallel to the [100] direction of the crystal (scan: 250 G centered at 3325 G).

FIG. 5. $M_J = -\frac{1}{2} \leftrightarrow -\frac{3}{2}$ transition group in BaF_2: $^{151}Eu^{2+}$ at 26 kbar and ambient temperature with the magnetic field parallel to the [100] direction of the crystal (scan: 250 G centered at 2810 G).

FIG. 6. $M_J = \frac{7}{2} \leftrightarrow \frac{5}{2}$ transition group in SrF_2: $^{151}Eu^{2+}$ at 26 kbar and ambient temperature with the magnetic field parallel to the [100] direction of the crystal (scan: 250 G centered at 2305 G).
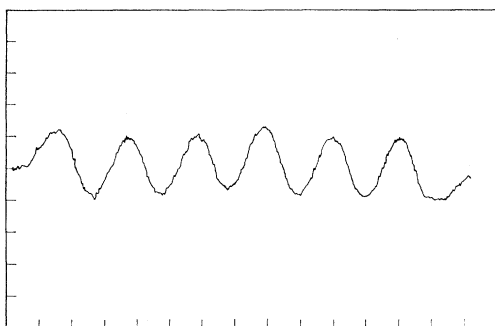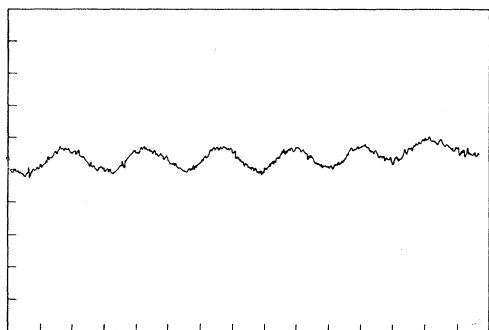
where

$$H_{\text{cryst}} = (b_4/60)(\mathcal{O}_4{}^0 + 5\mathcal{O}_4{}^4) + (b_6/1260)(\mathcal{O}_6{}^0 - 21\mathcal{O}_6{}^4), \quad H_Z = g\beta\mathbf{H}\cdot\mathbf{S}, \text{ and } H_{\text{hf}} = A\mathbf{I}\cdot\mathbf{S}.$$

The $\mathcal{O}$'s are the operator equivalents introduced by Stevens.[8,16] The energy levels of $^{151}Eu^{2+}$ were obtained within the ground state $^8S_{7/2}$ manifold by an exact diagonalization of the 8×8 matrix for $H_{\text{cryst}} + H_Z$, followed by a second-order perturbation calculation for H_{hf}. The constants A, b_4, b_6, and g were regarded as adjustable parameters whose values were chosen by a least-squares fit to the theoretical expression for energy differences for all the transitions observed (see below). The appropriate transition associated with each of the 42 lines is shown in Fig. 2, where the states are labeled by $M_J = \frac{7}{2}, \cdots, -\frac{7}{2}$ and $M_I = \frac{5}{2}, \cdots, -\frac{5}{2}$.

The criterion used to determine the best values of the spin-Hamiltonian parameters to fit the experimental data was the minimization of the function

$$F(A, b_4, b_6, g) = \sum_{i=1}^{42} C_i(W_i - h\nu_i)^2.$$

In this expression, W_i is the energy difference for the ith transition. The experimental values of the magnetic

[16] K. W. H. Stevens, Proc. Phys. Soc. (London) A65, 209 (1952).

fields at resonance enter into its evaluation. The quantity ν_i is the experimentally measured microwave frequency, and C_i is a weighting factor. Each term in the sum would vanish, of course, for an exact theory and a perfect measurement. The function F is minimized by a Newtonian method which is iterated until self-consistency is obtained.

The values of the parameters obtained by this method are shown in Tables I and II. In Figs. 7 and 8, respectively, $\log_{10}|b_4|$ versus $\log_{10}\delta$, and $\log_{10}|b_6|$ versus $\log_{10}\delta$ are plotted. The averages of the values from Tables I and II are used with the range of variation indicated by the vertical bars. The nearest-neighbor distances δ are those of the host lattices. At 26 kbar, the nearest-neighbor distances are obtained for the host crystals assuming constant isothermal compressibilities which were computed from adiabatic elastic-constant data for the host crystals.[17,18] No allowance for a different compressibility around the impurity site was made in this computation. A log-log plot is used in anticipation of a power dependence of b_4 and b_6 upon δ.

It can be seen from Tables I and II that there is little variation in g either as a function of pressure or of

TABLE I. Spin-Hamiltonian parameters at ambient temperature and pressure.

Crystal	Run No.	$\lvert A \rvert$ (10^{-4} cm^{-1})	$\lvert b_4 \rvert$ (10^{-4} cm^{-1})	$\lvert b_6 \rvert$ (10^{-4} cm^{-1})	g
CaF$_2$	1	32.76	55.47	0.2386	1.99095
	2	32.77	55.45	0.2360	1.99099
	3	32.78	55.54	0.2353	1.99100
	4	32.77	55.52	0.2359	1.99099
	5	32.78	55.54	0.2350	1.99101
	6	32.77	55.52	0.2358	1.99101
SrF$_2$	1	32.34	44.66	0.1778	1.99171
	2	32.33	44.67	0.1792	1.99171
	3	32.39	44.67	0.1763	1.99166
	4	32.38	44.67	0.1776	1.99166
BaF$_2$	1	31.90	35.21	0.1381	1.99179
	2	32.03	35.22	0.0971	1.99186

TABLE II. Spin-Hamiltonian parameters at 26 kbar and ambient temperature.

Crystal	Run No.	$\lvert A \rvert$ (10^{-4} cm^{-1})	$\lvert b_4 \rvert$ (10^{-4} cm^{-1})	$\lvert b_6 \rvert$ (10^{-4} cm^{-1})	g
CaF$_2$	1	32.43	60.48	0.3045	1.991
	2	32.74	60.89	0.2651	1.989
	3	32.58	60.91	0.2882	1.990
	4	32.57	60.67	0.2863	1.990
	5	32.61	60.77	0.2962	1.990
	6	32.66	60.69	0.2772	1.990
SrF$_2$	1	32.09	49.98	0.2065	1.991
	2	32.30	49.99	0.2055	1.990
	3	32.10	49.92	0.2127	1.990
	4	32.30	50.06	0.2109	1.990
	5	32.23	50.08	0.2121	1.990
BaF$_2$	1	30.04	38.57	1.235	1.993
	2	30.30	38.82	1.191	1.993
	3	30.28	39.19	1.099	1.993

[17] P. J. Ho and A. L. Ruoff, Phys. Rev. 161, 864 (1967).
[18] D. Gerlich, Phys. Rev. 135, A1331 (1964); 136, A1366 (1964).

cation, and we have not considered an interpretation of its change. The variation in the hyperfine constant A with nearest-neighbor distance is small, and even appears to be of one sign under increasing pressure and of the opposite sign when induced by changing the cation from Ba to Sr to Ca. This effect, if real, is unexpected.

It should be noted that the values of the hyperfine constant A in Table I differ from the value given by Baker et al.[8] by more than their stated uncertainty. It seems to us that these differences can be attributed to differences in the method of data reduction. Although Baker et al. do not state their data-reduction method, we have been able to obtain a value within their stated uncertainty by reducing our data by the method of Menne et al.[15] Two sources are present for the differences in the results of the methods: (1) neglect of third and higher-order terms in expansion of square roots, and (2) choice of the weighting factors C_i to be used in minimizing F. We have used the value 1 for resolved lines, and the value 0 for overlapping lines. In any case it would appear that our uncertainty on A would have to be $\pm 0.4 \times 10^{-4}$ cm^{-1}.

IV. DISCUSSION

In Fig. 7, where δ refers to the undoped host lattice, the points corresponding to 26 kbar do not lie on the same straight line as those corresponding to ambient pressure. One might infer from this result that changing the nearest-neighbor distance through a pressure change produces a different effect from that induced by changing the nearest-neighbor distance through changing the cation. However, it is also possible to interpret this result as the effect of an altered lattice in the neighborhood of the impurity europium ion.[19] Under the hypothesis that such a local distortion is present and that it is predominantly a cation-size effect, one would expect less distortion near the europium site in SrF$_2$:Eu^{2+} than in either CaF$_2$:Eu^{2+} or BaF$_2$:Eu^{2+}, because Sr^{2+} and Eu^{2+} have nearly the same ionic radius (see Table III).[20] We have taken, therefore, as a first approximation to the variation of the crystalline-field parameter b_4 with nearest-neighbor distance δ, the pressure-induced variation in SrF$_2$:Eu^{2+}; assuming $\log_{10}|b_4|$ to be linear in $\log_{10}\delta$, we compute a slope of -8.79 (Fig. 7).

TABLE III. Ionic Radii of investigated ions.[a]

Ion	Ionic radius (Å)
Ca^{2+}	1.04
Sr^{2+}	1.20
Ba^{2+}	1.38
Eu^{2+}	1.18

[a] See Refs. 19 and 20.

[19] T. Rewaj, Fiz. Tverd. Tela **9**, 2978 (1967) [English transl.: Soviet Phys.—Solid State **9**, 2340 (1968)].
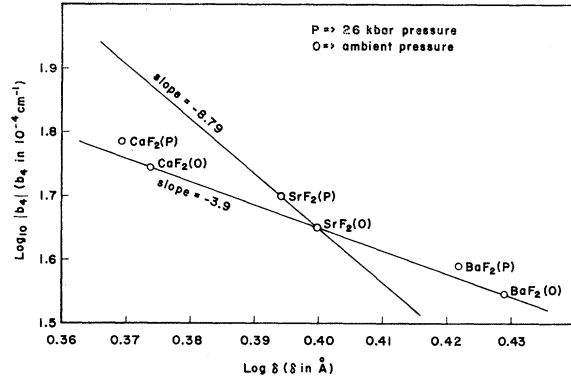[20] J. Sierro, Helv. Phys. Acta **36**, 507 (1963).

FIG. 7. $\log_{10}|b_4|$ versus $\log_{10}\delta$, without taking into account distortion at impurity sites.
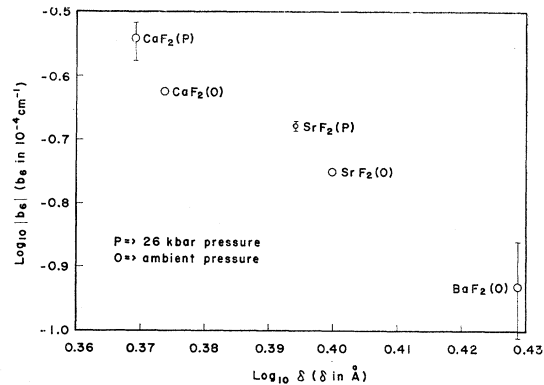

FIG. 8. $\log_{10}|b_6|$ versus $\log_{10}\delta$, without taking into account distortion at impurity sites. Flags indicate the extremes of the measurements shown in Tables I and II.

We have made a preliminary attempt to justify this choice by consideration of the following model.

The europium ion is considered to lie at the center of a cube at the corners of which lie the fluorine ions. The side-length of the cube is considered to be given by that equilibrium distance predicted by a Born-Mayer theory.[21,22] This theory is to be applied to the tetrahedron in the crystal having a fluorine ion at the center, a europium ion at one vertex, and host cations at the other three vertices, that is, the following energy expression is to be minimized as a function of fluorine position in the tetrahedron:

$$E = be^{-r/\rho} + 3b'e^{-r'/\rho'},$$

where r and r' are the fluorine-europium interionic distance and the fluorine-host cation interionic distance, respectively. The constants b and ρ, corresponding to the europium ion, and b' and ρ', corresponding to the host cation, are evaluated[23] for pure crystals of EuF$_2$ or of CaF$_2$, SrF$_2$, or BaF$_2$ from dielectric data[24] and those

[21] M. Born and J. E. Mayer, Z. Physik **75**, 1 (1932).
[22] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Clarendon Press, Oxford, 1954), p. 33.
[23] J. D. Axe, Phys. Rev. **139**, A1215 (1965).
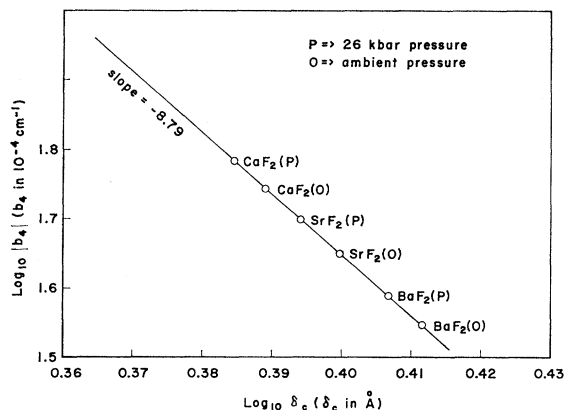[24] D. R. Bosomworth, Phys. Rev. **157**, 709 (1967).

FIG. 9. $\log_{10}|b_4|$ versus $\log_{10}\delta_c$. The CaF$_2$ points and the BaF$_2$ points are adjusted horizontally to lie on the straight line through the SrF$_2$ points of Fig. 7. Abscissas of the CaF$_2$ points and BaF$_2$ points indicate the corrected values for the nearest-neighbor distance to the europium impurity ion in these crystals.

same values are used here. They were assumed to be constant with pressure. The influence of the next-nearest-neighboring fluorine ions upon the position of the fluorine ion within the tetrahedron is neglected in this model, and it would therefore be expected that the change in the size of the lattice cell due to the presence of the europium impurity ion would be overestimated.

Although this model tends to overcorrect for the lattice distortion, it does lend credence to the above choice of slope; the corrected value for the slope of the line $\log_{10}|b_4|$ versus $\log_{10}\delta$ is -8.82 for SrF$_2$:Eu^{2+}, a 1% correction. Inasmuch as the uncertainty in pressure is about $\pm4\%$ (i.e., ±1 kbar), it can be shown that this correction is less than the uncertainty in the value of the slope. By contrast, the same model yields a correction to the slope $\log_{10}|b_4|$ versus $\log_{10}\delta$ of about 10% for CaF$_2$:Eu^{2+} and about 5% for BaF$_2$:Eu^{2+}.

If the nearest-neighbor distances to the europium ion in CaF$_2$:Eu^{2+} and BaF$_2$:Eu^{2+} are adjusted so that the
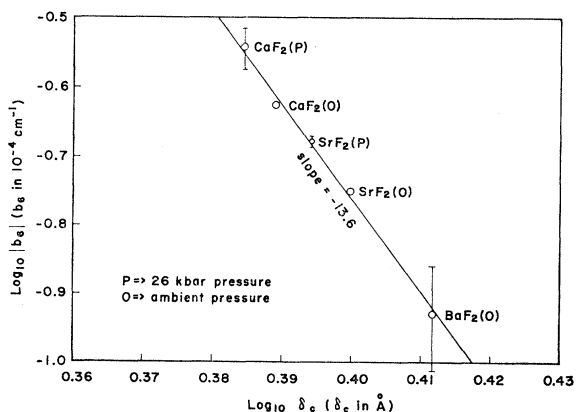

FIG. 10. $\log_{10}|b_6|$ versus $\log_{10}\delta_c$. The values of δ_c are the corrected values obtained from Fig. 9. Flags indicate the extremes of the measurements shown in Tables I and II.

values of $\log_{10}|b_4|$ for these crystals lie on the straight line passing through the points for SrF$_2$:Eu^{2+} as in Fig. 9, then the adjusted values δ_c are as shown in Table IV. We note an enlargement of about 4% in the nearest-neighbor distance about the Eu^{2+} impurity for CaF$_2$:Eu^{2+} and a contraction of about 4% for that nearest-neighbor distance in BaF$_2$:Eu^{2+}. These results are for ambient temperature and pressure. The validity of this assignment of nearest-neighbor distances δ_c for CaF$_2$:Eu^{2+} and BaF$_2$:Eu^{2+} is further supported by the fact that a straight line is obtained when $\log_{10}|b_6|$ is plotted against $\log_{10}\delta_c$ (rather than $\log_{10}\delta$). This is shown in Fig. 10.

The flags indicate the extremes of the measurements shown in Tables I and II in the cases where the variation in those measurements is enough to show on the scale of the graph. The slope of the line which is least-squares fitted to the 23 measured values of Tables I and II is -13.6. The slope $\log_{10}|b_6|$ versus $\log_{10}\delta_c$ would be -14 for a quadratic dependence of the perturbation on a point-charge electrostatic potential.

TABLE IV. Nearest-neighbor distance to cation in host crystal and near an impurity cation at ambient pressure.

Crystal	δ(host) (Å)	δ(impurity) (Å)
CaF$_2$	2.366[a]	2.450
SrF$_2$	2.512	2.512
BaF$_2$	2.685	2.580

[a] See Ref. 6.

The principal conclusion that we have drawn from our work is that distortion of the host lattice in the neighborhood of an impurity ion is a consistent interpretation of the experimental results for the materials studied. A quantitative estimate of the amount of distortion is provided by assuming it is primarily an ion-size effect. On the basis of that interpretation, the crystalline-field parameters are found to vary with nearest-neighbor distance in the following way:

$$d(\log_{10}|b_4|)/d(\log_{10}\delta_c) = -8.8,$$
$$d(\log_{10}|b_6|)/d(\log_{10}\delta_c) = -13.6.$$

We have drawn no conclusions about the specific nature of the perturbation which produces the splitting in the ground state of the S-state europium ions except to note that the slope of $\log_{10}|b_4|$ versus $\log_{10}\delta_c$ seems to provide added evidence that perturbation cannot be from simple point charges.

The temperature dependence of b_4 has been measured by Rewaj[19] for CaF$_2$:Eu^{2+}, SrF$_2$:Eu^{2+}, and BaF$_2$:Eu^{2+}. Under the assumption that the thermal expansion of the crystal played the dominant role in the variation of b_4, he found the slope of the line $\log_{10}|b_4|$ versus $\log_{10}\delta$ to be, respectively, -16.3, -21.2, and -23.8 for the above

crystals. These slopes are two to three times larger in magnitude than that obtained in our high-pressure experiments for which we similarly assumed that the variation in nearest-neighbor distance is the major influence effecting the variation in b_4. The rather large difference in slope obtained from temperature data and from pressure data would seem to imply that thermal expansion and/or compressibility does not play the dominant role in the variation of b_4. It should be pointed out that the slope in question is a rather sensitive function

of the nearest-neighbor distance, but that insofar as the difference in its values, as computed from temperature data and from pressure data, is real, then that fact may be significant in a theoretical understanding of the EPR of this S-state ion.

Imperfectly Mode-Locked Laser Emission and Its Effects on Nonlinear Optics

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The output of an ideally mode-locked laser, namely, one having equal phase angles of the modes, consists of a train of bandwidth-limited short pulses. The influence of deviations from equal phase angles on the laser output is investigated. Random distributions of the phases of the modes around equal phase angles introduce only limited fluctuating background, whereas the duration of the pulses remains bandwidth-limited. A systematic deviation of the phase angles at least quadratic with mode number is necessary for lengthening of the pulses. The results obtained by the superposition of these two effects are consistent with the experiments published so far. The efficiency of second- and higher-harmonic generation is discussed by help of the moments of the intensity probability distributions. It is shown how these distributions change as a result of harmonic generation and optical mixing. From intensity-correlation measurements, the moments of the intensity probability distribution can be obtained directly, as well as information on the time behavior of the light field. Experimental arrangements used to measure intensity correlations are described.

I. INTRODUCTION

A LASER light source is believed to emit a coherent light beam of intensity varying slowly in time, but only if the laser oscillates in a single mode. However, if the laser oscillates in several axial modes (off-axial modes are not considered, since their addition only introduces geometrical problems), the light intensity is modulated and becomes, with an increasing number of independently oscillating modes, more and more irregularly fluctuating. It can be shown that in the limit of an infinite number of independent modes, the emission becomes completely "chaotic," like a Gaussian light field, as predicted by Mandel and Wolf,[1] and has the same fluctuations as the light of a thermal source transmitted through a suitable narrow-band optical filter.

The fluctuations in the laser intensity are of great importance for nonlinear interactions of light,[2-5] since the efficiency of such interactions depends on the instantaneous intensities of the light fields. The influence of statistical fluctuations of the intensity on optical second- and higher-harmonic production,[2,3] as well as on optical mixing, arising from multimode oscillation, is discussed. It will be demonstrated that the average efficiency of the harmonic generation of lasers with several modes oscillating simultaneously depends predominantly on the kind of intensity fluctuations. For these reasons, the intensity fluctuations of multimode lasers and of higher harmonics generated by multimode lasers will be discussed.

Recently, several authors investigated the time

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[5] N. Bloembergen, Am. J. Phys. **35**, 989 (1967).