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Defect Energy-Level Structure of PbI_2 Single Crystals

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The photoluminescence spectrum of gel-grown PbI_2 single crystals reveals features at 2.41, 2.31, 2.16, 2.13, 2.10, 1.99, 1.97, 1.94, and 1.85 eV, and the photoconductive response spectrum at 3.06, 2.41, 2.16, and 1.99 eV. An analysis of temperature quenching of the photocurrent indicates sensitizing centers located ~0.46 eV above the top of the valence band. A defect energy-level structure for PbI_2 has been proposed on the basis of this information. The results also suggest the existence of ~0.03-eV optical phonons, associated with the 2.16- and 1.99-eV emission peaks.

INTRODUCTION

A GOOD deal of interest has been shown in the potentialities of PbI_2 as a device material. There have, for instance, been publications on the photodecomposition[1,2] of PbI_2, on its potential image-recording capabilities,[3] and on its reaction to bombardment by nuclear particles.[4] However, except for the work on exciton spectra summarized by Tubbs and Forty,[5] little basic research of its physical properties has been reported, probably due to the shortage of good single-crystal specimens. Such specimens have now been grown by the recently developed hydrogel technique.[6,7] The present paper reports the results of an electro-optical investigation on them, which has yielded new information on the band and defect level structure. In particular, the correlation of new measurements of photoconductance and photoluminescence, and previously reported optical absorption measurements made on the same material has resulted in a tentative model of the defect energy levels within the forbidden gap.

SPECIMEN PREPARATION AND EXPERIMENTAL PROCEDURE

The principles and techniques of the gel method have been discussed.[6–8] Briefly, the method involves the use of a silica gel which contains one of the reagents (lead acetate) and an aqueous solution of a second reagent (potassium iodide) initially outside of the gel. This latter solution diffuses into the gel promoting PbI_2 crystal growth.

The procedure yields hexagonal platelets with areas of up to 1 cm^2 perpendicular to the c axis and thicknesses in the c direction of up to 0.5 mm. In order to promote the growth of crystals with larger dimensions in the c direction (i.e., up to 3 mm), usually at the expense of platelet area, the crystals had to be grown at 10°C rather than the more usual 45°C. Their identity and structure were verified by x-ray analysis. All specimens used in this study were of a 2*H* polytype. Spectrochemical analysis indicated trace amounts (i.e., 1–5 ppm) of Al, Ge, Si, and Mn.

The specimen was placed in a specially designed cryostat which allowed control of temperature to ±1.5°C over the range 120 to 293°K, and to ±1°C above 293°K. The measuring circuit was electrically insulated with Teflon (leakage resistance $>10^{15}\Omega$). This was necessary since the resistivity of PbI_2 at 300°K is of the order of 10^{12} Ω cm.[9,10] Currents were measured using a Keithley 610B electrometer, with its output connected to a recorder. The current was considered "in steady state" when its value did not change by more than 0.5% over a 30-min period. Electrical contact was made to the crystals by means of evaporated gold electrodes which proved to be of low resistance and ohmic. If any photovoltage was generated under single-contact illumination, it must have been less than 1 μV. The exciting radiation was provided by a Bausch and Lomb high-intensity monochromator equipped with a xenon light source.

Because during photoconductive measurements equilibrium is reached only after substantial periods (e.g., up to 2 h), consistent results are obtained only with standardized procedures. In the present case, the specimen was cooled to 120°K and allowed to remain in the dark until the dark current reached a steady state. A series of readings of photocurrent versus increasing light intensity was then taken, in each case, after allowing the photocurrent to reach a steady state. The light was then shut off and the temperature allowed to rise to the next measurement point where again the dark current was allowed to become steady. Another series of photocurrent versus increasing light-intensity

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[1] R. I. Dawood, A. J. Forty, and M. R. Tubbs, Proc. Roy. Soc. (London) **A284**, 272 (1965).

[2] R. I. Dawood and A. J. Forty, Phil. Mag. **1**, 1633 (1962).

[3] A. J. Forty, R. I. Dawood, and M. R. Tubbs, J. Sci. Instr. **41**, 274 (1964).

[4] L. T. Chadderton, H. M. Montagu-Pollock, and I. McC. Torrens, J. Appl. Phys. **34**, 3090 (1963).

[5] M. R. Tubbs and A. J. Forty, J. Phys. Chem. Solids **26**, 711 (1965).

[6] H. K. Henisch, J. Dennis, and J. I. Hanoka, J. Phys. Solids **26**, 443 (1965).

[7] J. Dennis and H. K. Henisch, J. Electrochem. Soc. **114**, 263 (1967).

[8] E. Halberstadt and H. K. Henisch (to be published).

[9] A. E. Dugan and H. K. Henisch, J. Phys. Chem. Solids **28**, 1885 (1967).

[10] R. Williams, Phys. Rev. **126**, 442 (1962).

measurements was then made. The variation in light intensity was achieved by means of neutral density filters, with spectral transmission characteristics which had previously been determined using an Eppley thermopile and a Beckman DK-2 spectrophotometer. The photocurrent was measured when flowing perpendicular to the *c* axis and the exciting radiation was incident parallel to it.

For the luminescence measurements, the single-crystal specimens were mounted over circular apertures drilled into a metal disk. The sample and sample holder were placed in a conventional cold-finger optical Dewar. The sample was excited at 4500 Å and the luminescence radiation emerging from the opposite face was focused onto the entrance slit of a 2-m grating spectrograph (Applied Research Laboratory model No. 2100). The spectrum was recorded on 35-mm Kodak high-sensitivity IR film with a dispersion of 7.19 Å/mm. The system was calibrated using mercury and iron arc spectra.

RESULTS

Figure 1 shows the photoresponse spectrum for a typical PbI_2 single crystal. The maximum at 2.41 eV corresponds to the fundamental optical absorption edge.[9] The other features at 3.06, 2.16, and 1.99 eV may be associated with the band structure or with defect levels, as discussed below.

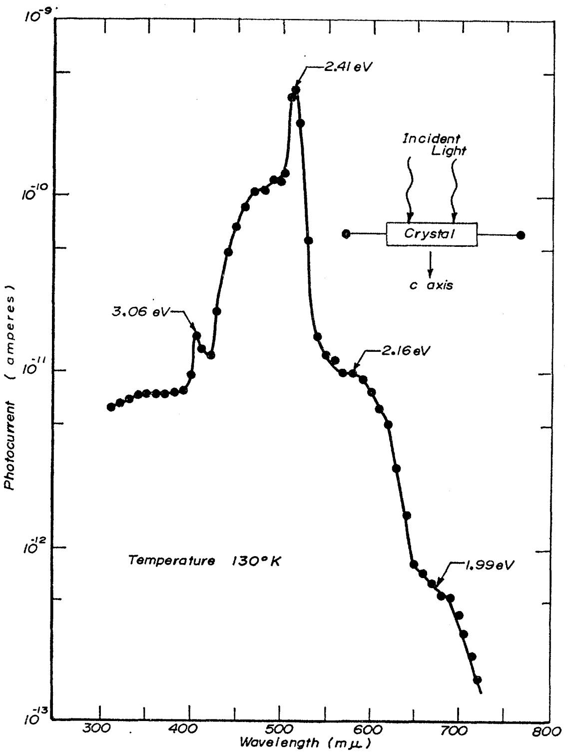

FIG. 1. Photoresponse of a PbI_2 single crystal. Excitation at 2.61×10^{13} photons/cm² sec; electrode separation: 3.5 mm; specimen thickness: 100 μ; 3 V applied.

The temperature dependence of the photocurrent over the range 120 to 293°K for various intensities of 4500 Å excitation is shown in Fig. 2. Over a limited temperature range there is a decrease of the photocurrent, a phenomenon known as "temperature quenching."[11]

Figure 3 shows a densitometer tracing of the photoluminescence spectrum of a typical PbI_2 single crystal, not corrected for the self-absorption of the specimen.

ANALYSIS OF RESULTS

The feature at 2.41 eV on Fig. 1 corresponds to radiative band-to-band transitions, or, at any rate, to transitions associated with shallow levels very close to the band edges. The results in Fig. 2 refer to steady-state excitation. A corresponding minimum in the relationship between carrier lifetime and temperature has been found to occur at approximately the same temperature.[12]

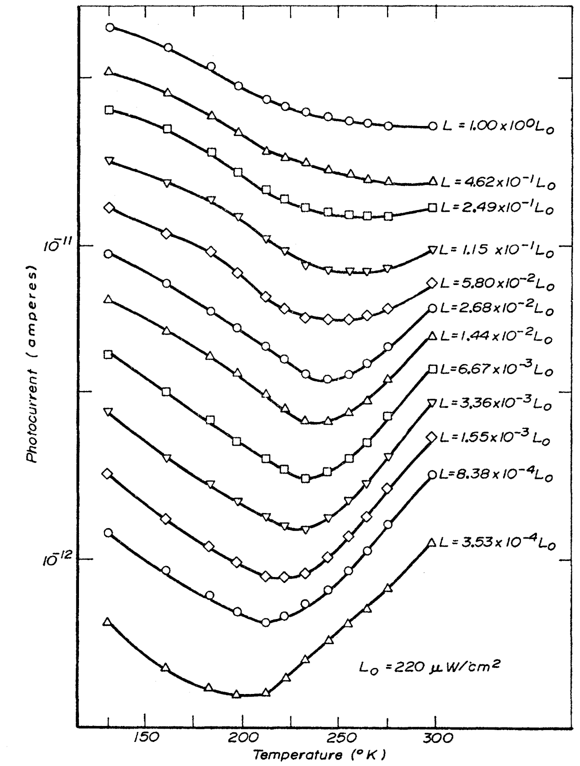

FIG. 2. Measurements of photocurrent versus temperature for a PbI_2 single crystal at various light intensities. Wavelength of exciting light is 4500 Å.

Following the procedure proposed by Rose[11] and further discussed by Bube,[13] the currents correspond-

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[11] A. Rose, RCA Rev. **12**, 362 (1951); Phys. Rev. **97**, 322 (1955).

[12] H. K. Henisch and C. Srinivasagopalan, Solid State Commun. 4, 915 (1966).

[13] R. H. Bube, *Photoconductivity in Solids* (John Wiley & Sons, Inc., New York, 1960), Chap. 11.

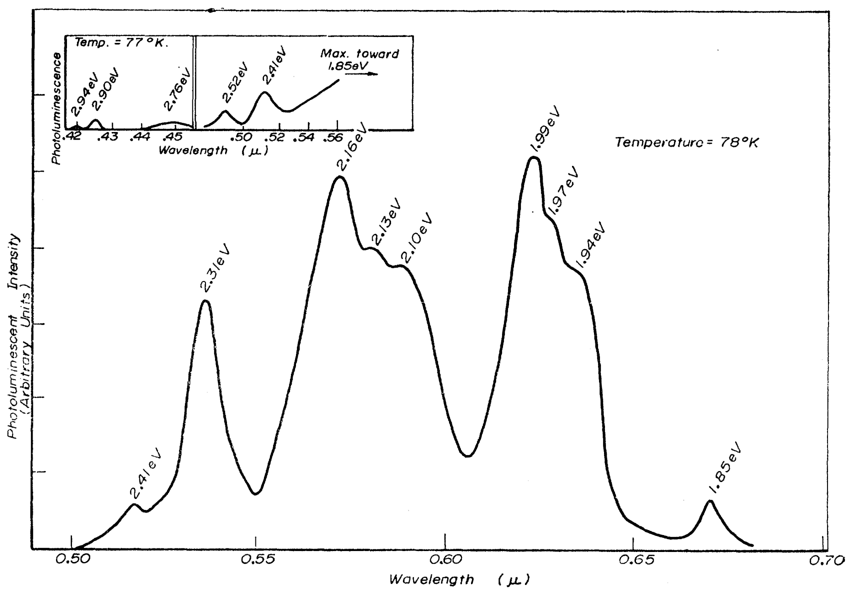

FIG. 3. Photoluminescence spectrum of a PbI_2 single crystal; insert: past results (Ref. 16).

ing to minima on Fig. 2 are on Fig. 4 plotted logarithmically as a function of reciprocal temperature. This yields a straight line, of a slope corresponding to 0.46 eV. According to Rose, this is the energy position (above the upper edge of the valence band) of the centers which, by changing their functions from recombination to trapping, are responsible for the diminishing photoconductivity with increasing temperature. Rose and Bube concerned themselves explicitly with n-type material, but the parts of their arguments here used should be generally applicable. By interpreting the results in this way, consistency can be achieved with the photoresponse and luminescence spectra, as shown below.

There is no available knowledge of the optical phonons in PbI_2, but it appears that some of the features in the photoluminescence spectrum shown in Fig. 3 are "satellites" of the main radiative features. Thus, the peaks at 2.13 and 2.10 eV are plausibly phonon replicas of the 2.16-eV feature, and the peaks at 1.97 and 1.94 eV may be similarly related to the 1.99-eV feature. This suggestion is based upon the appearance of the spectrum itself (approximately equidistant energy spacing) and upon the correlation with other measurements, inasmuch as the peaks corresponding to main features can be accommodated in a consistent energy-level scheme, whereas the peaks corresponding to "satellites" cannot. If this interpretation is correct, it indicates the presence of ~0.03-eV phonons.

Since the features at 1.99 and 2.16 eV appear to be associated with optical phonons while the 2.31-eV feature is not, the latter probably corresponds to a defect which is less tightly bound to the lattice. The feature at 1.85 eV is not strong enough to show whether phonon replicas are associated with it.

DISCUSSION AND CONCLUSIONS

Figure 5 is a model of the defect energy-level structure and of the band structure at $k=0$. It represents an augmented and amended version of one previously proposed.[9]

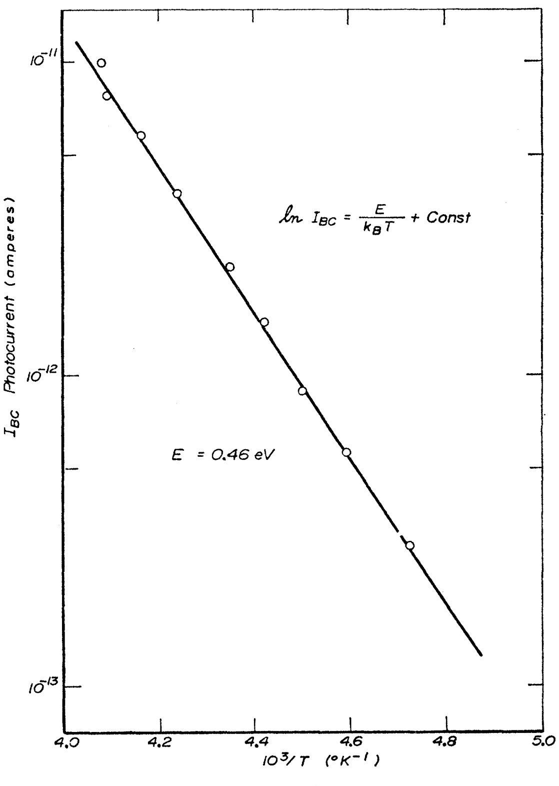

FIG. 4. Photocurrent at the breakpoint in sensitivity versus the reciprocal temperature at which the breakpoint occurs for a PbI_2 single crystal.

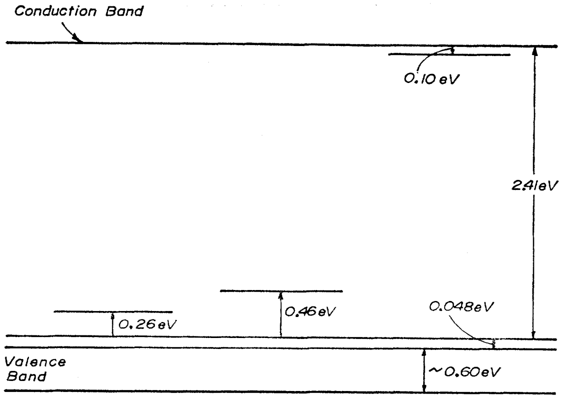

FIG. 5. Energy-level diagram showing split-valence band and defect level structure for gel-grown PbI_2 single crystals.

Valence Band Structure

As was previously reported,[9,14] the valence band of PbI_2 consists of three sub-bands due to crystal-field and spin-orbit splittings. The separation of the two upper sub-bands by 0.048 eV was determined by studying[9] the splitting of the absorption edge with polarized light (i.e., $\mathbf{E}\|c$ and $\mathbf{E}\perp c$). The feature in the photoresponse spectrum at 3.06 eV can now be explained as corresponding to a transition from the lower sub-band to the conduction band or to states in the forbidden gap very close to the conduction band. This would place the lower sub-band at a distance of approximately 0.60 eV from the top of the valence band. This, in turn, would account for an occasionally reported optical absorption feature[14] at approximately 3.1 eV. The present interpretation of the origin of the 3.06-eV absorption is favored over that previously proposed by Tubbs,[14] who ascribed it to the transition of an electron from the upper valence sub-band to a conduction band located ~0.60 eV above the main absorption edge. In this model, the main absorption edge as such was interpreted as the first exciton level. Such an interpretation is not in accord with the findings of Nikitine *et al.*[15] who determined that the ionization energy of the first exciton level was 0.033 eV.

It should be noted that earlier work[12] on the photoresponse spectrum of gel-grown PbI_2 did not detect a feature at 3.06 eV because of lower resolution. From this it was concluded that gel-grown crystals possessed a simpler structure than those prepared by other growth techniques. The present study indicates that this assumption was not justifiable since the 3.06-eV feature is due to the band structure rather than the defect structure.

Defect-Level Structure

The level at 0.26 eV above the valence band corresponds to an acceptor level responsible for the dark current carriers, as previously[9] discussed, and the level at 0.46 eV is interpreted as shown above.

The positioning of these two defect levels leads to an explanation of some of the transitions shown in the photoluminescence and photoconduction spectra. The feature at 1.99 eV in the photoresponse spectrum (Fig. 1) would correspond well to a transition from the 0.46-eV level to the conduction band. Similarly, the 2.16-eV feature could correspond to a transition from the 0.26-eV level to the conduction band. The implied energy summations are consistent with the photoresponse maximum at 2.41 eV. This, in turn, is consistent with the optical absorption edge, which is here attributed to the creation of free electron-hole pairs across the forbidden gap.

On this basis, the photoluminescence peaks at 2.16 and 1.99 eV would correspond to radiative transitions from the conduction band to the defect levels at 0.26 and 0.46 eV, respectively. The photoluminescence peak at 2.41 eV is in excellent agreement with a corresponding feature in Fig. 1.

The radiative transitions associated with energies of 2.31 and 1.85 eV are not fully explainable in terms of the defect levels at 0.46 and 0.26 eV above. The 2.31-eV peak is due to either a transition between an additional defect level ~0.10 eV below the conduction band and the valence band, or to a transition from the conduction band to a defect level ~0.10 above the valence band. The former situation is the more likely if one also considers a possible mechanism of the 1.85-eV peak. If this feature were to correspond to a radiative transition from the 0.10-eV level below the conduction band to the 0.46-eV level, then consistency would be achieved with a minimum number (one) of additional levels. In harmony with this interpretation, no feature corresponding to 1.85 eV is present in the photoconductive response spectrum.

With a defect level at 0.1 eV below the conduction band, it would be natural to expect a peak in the photoluminescence spectrum at about 2.06 eV, corresponding to a transition from the 0.1- to the 0.26-eV level. However, the phonon replicas of the 2.16-eV peak probably mask it.

It was previously suggested[9] that the 0.26-eV level may arise from a lead vacancy. Since the 0.26- and 0.46-eV centers are similar, in that they both appear to possess phonon replicas and hence are strongly coupled to the lattice, it is plausible to suggest that the 0.46-eV level is also due to the lead vacancy. This vacancy would thus produce a double acceptor level. However, without direct experimental evidence this interpretation remains speculative.

Very few comparable measurements are found in

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[14] M. R. Tubbs, Proc. Roy. Soc. (London) **A280**, 566 (1964).
[15] S. Nikitine, Mme. J. Schmitt-Burckel, J. Biellmann, and J. Ringeissen, J. Phys. Chem. Solids **25**, 951 (1964).

the literature. Photoresponse measurements by Tubbs[14] revealed features at 3.1, 2.4, and a broad feature in the region 2.13 to 2.25 eV. The latter (whose intensity was reported to vary from specimen to specimen) may well correspond to the transition discussed above, involving the 0.26-eV level of Fig. 5. The other peaks are in agreement with present results.

The previous measurements of photoluminescence are best represented by the work of Perny[16] (see inset in Fig. 3). No particular attention was paid in the past to the energy region lower than ~2.4 eV, but a peak at approximately 1.85 eV was reported, again in agreement with present results. The energy-level scheme in Fig. 5 is thus invested with a substantial measure of internal and external consistency.

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[16] G. Perny, Ann. Physik 5, 1683 (1960).

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Infrared Dispersion and Lattice Vibrations of LaF_3

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The infrared spectral emittance of oriented single crystals of LaF_3 has been measured in the range 4–125 μm. Eleven transitions have been identified whose net moments are perpendicular to the optic axis (E_u,x,y), and five additional bands were observed having net moments parallel to the optic axis (A_{2u},z). The data, taken near 4.2, 77, and 373°K, were treated by Kramers-Kronig analysis and by classical oscillator dispersion theory. The results support a crystal structure of $D_{3d}^4(P\bar{3}c1)$ which is very slightly distorted from a unit cell of $D_{6h}^3(P6_3/mcm)$ symmetry. The infrared results are in good agreement with the results of a recent Raman investigation of LaF_3.

INTRODUCTION

Lanthanum trifluoride is an important optical material which has been the subject of numerous investigations. The magnetic susceptibility and Faraday rotation,[1–4] NMR,[5,6] EPR,[7–9] and optical spectroscopy of impurities[10–14] in LaF_3 have generated considerable interest in the crystal structure and lattice vibrations. The large number of apparently conflicting studies of the crystal was recently reviewed by Bauman and Porto who undertook an investigation of the Raman spectrum.[15] In order to complement the results of the Raman studies and to further elucidate the nature of the lattice vibrations, the infrared spectrum of LaF_3 has been measured.

The crystal structure of LaF_3 has been redetermined recently by Mansmann[16] and independently, by Zalkin, Templeton, and Hopkins[17] who conclude the structure is represented by a unit cell having $D_{3d}^4(P\bar{3}c1)$ symmetry and six molecules. This differs only slightly from the structure proposed earlier by Oftedal.[18] Oftedal's unit cell also contained six molecules, but transformed according to the space group $D_{6h}^3(P6_3/mcm)$. Bauman and Porto[15] decide on the D_{3d}^4 structure and suggest that by observing the lattice vibrations of LaF_3, one should see vibrations allowed for the D_{6h}^3 symmetry and additional, less intense vibrations permitted under D_{3d}^4 in accordance with the slight departures from Oftedal's structure.

Based on the results of Bauman and Porto[15] and on the infrared analysis reported here, the bimolecular

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[1] J. Becquerel and W. J. de Haas, Proc. Acad. Sci. Amsterdam **32**, 536 (1929).

[2] W. J. de Haas and C. J. Gorter, Proc. Acad. Sci. Amsterdam **33**, 949 (1930).

[3] J. H. Van Vleck and M. H. Hebb, Phys. Rev. **46**, 17 (1934).

[4] J. Becquerel, W. J. de Haas and J. Van den Handel, Physica **1**, 383 (1934).

[5] M. Goldman and L. Shen, Phys. Rev. **144**, 321 (1966).

[6] K. Lee and A. Sher, Phys. Rev. Letters **14**, 1027 (1965).

[7] D. A. Jones, J. M. Baker, and D. F. D. Pope, Proc. Phys. Soc. (London) **74**, 249 (1959).

[8] J. M. Baker and R. S. Rubins, Proc. Phys. Soc. (London) **78**, 1353 (1961).

[9] M. B. Schulz and C. D. Jeffries, Phys. Rev. **149**, 270 (1966).

[10] W. F. Krupke and J. B. Gruber, J. Chem. Phys. **39**, 1024 (1963).

[11] E. Y. Wong, O. M. Stafsudd, and D. R. Johnston, J. Chem. Phys. **39**, 786 (1963).

[12] C. K. Asawa and M. Robinson, Phys. Rev. **141**, 251 (1966).

[13] W. M. Yen, W. C. Scott, and A. L. Schawlow, Phys. Rev. **136**, A271 (1964).

[14] S. A. Johnson, H. G. Freie, A. L. Schawlow, and W. M. Yen, J. Opt. Soc. Am. **57**, 734 (1967).

[15] R. P. Bauman and S. P. S. Porto, Phys. Rev. **161**, 842 (1967).

[16] M. Mansmann, Z. Anorg. Allgem. Chem. **331**, 98 (1964); Z. Krist. **122**, 375 (1965).

[17] A. Zalkin, D. H. Templeton, and T. E. Hopkins, Inorg. Chem. **5**, 1466 (1966).

[18] I. Oftedal, Z. Physik Chem. **5**, 272 (1929); **13**, 190 (1931).