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# Discrete Phonon and Zero-Phonon Optical Absorption Spectra in Alkali Halides[*]

C. B. Pierce
*Sandia Laboratory, Albuquerque, New Mexico*

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In addition to 0-phonon lines associated with the $R_2$ and $N$ bands of a number of the alkali halides at low temperature, other subsidiary peaks often occur on the high-energy side of the 0-phonon line. We have observed such peaks on the $R_2$ and $N$ bands of LiF, NaCl, KCl, and KBr, and on the $N$ bands only of NaF and KI. It is found with very few exceptions that energy separations between the 0-phonon lines and associated subsidiary peaks agree very well with theoretical normal lattice phonon energies near the zone boundary as determined by Karo and Hardy. It is felt that this is reasonable, as these are the lattice vibrations of highest probability density and of wavelength comparable to small lattice defects. The most common lattice coupling to the defects appears to be through transverse acoustical phonons propagating in $\langle 100 \rangle$ directions, although the results show that in most of the materials the defects are coupled with comparable strength to several phonon modes. Indeed, possible correlations with all normal modes are indicated in the data. The exceptions mentioned (on the $N$ bands of NaCl, KCl, and KBr) are all considerably smaller in energy than any of the lattice phonons at the zone boundary. These may be associated with pseudolocalized modes due to resonance scattering. In addition to the structure listed above, 0-phonon lines alone have been observed on the $R_2$ bands of NaF, KF, and KI.

SEVERAL recent publications[1–3] have dealt with the observation of very narrow zero-phonon optical absorption lines associated with complex electron excess color center bands in a number of the alkali halides. The primary purpose of this paper is to demonstrate that subsidiary structure often observed with these zero-phonon lines may be almost unambiguously interpreted as being associated with the excitation of a variety of normal lattice phonon modes near the first Brillouin zone boundary. Also, we present some results of measurements which verify the existence of observable zero-phonon lines in several alkali halides not previously reported.

Optical measurements were made on a Cary model 14R spectrophotometer with samples maintained near 10°K during observation. Samples were cleaved from "pure" Harshaw or Semi-Elements single crystals and colored at ambient temperature by irradiation with unfiltered 50-kV or 100-kV x rays, 400-keV or 2-MeV electrons, or reactor neutrons. In the case of NaCl, KCl, and KBr, samples were colored by all three types of irradiation. No changes were observed in line position or apparent linewidth as a function of irradiation procedure or radiation dose over several orders of magnitude. There are, naturally, different relative concentrations of the different color centers produced by these varying types of irradiation. The criterion for observing fine structure, however, seems only to be the concentration of the pertinent defect, and not its environment in the crystal so far as this environment is related to the concentration of other point defects. We do not as yet have any information about the effect of dislocations on the fine structure.

Our results are in excellent agreement with the published results of Fitchen *et al.*,[1] who reported on the existence of zero-phonon lines associated with the $R_2$ bands of LiF, NaF, NaCl, KCl, and KBr, and on a number of lines in the vicinity of the $N$ bands of some of these materials. In addition, we have verified the existence of this phenomena in several of the other alkali halides. There are some exceptions in that there are several materials in which we have so far not succeeded in observing zero-phonon lines even though there was sufficient coloring intensity that we would have expected to see fine structure. The reasons for this lack of complete generality are not known but are perhaps related to the quality of the single crystals used. The zero-phonon lines we have observed are listed in Table I. Under the heading of $N$ bands, we have included all the sharp lines in the general region of the $N$ bands although in some cases these seem too numerous to be associated with a single defect. We have omitted from this tabulation a number of occasionally observed lines which were not obviously associated with the $R_2$ or $N$ bands or which have not been found to be reproducible. Some of these are perhaps associated with

TABLE I. Zero-phonon lines observed on $R_2$ and $N$ bands of alkali halides.

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| LiF | $R_2$ | 3905 Å | KF | $R_2$ | 5892 Å | KBr | $R_2$ | 8163 Å |
| | $N$ | 4743 | | | | | $N$ | 10 972 |
| | | 4870 | KCl | $R_2$ | 7417 | | | 11 333 |
| | | 5230 | | $N$ | 9916 | | | 11 750 |
| | | | | | 10 323 | | | 13 165 |
| NaF | $R_2$ | 4478 | | | 10 668 | | | |
| | $N$ | 5455 | | | 10 772 | KI | $R_2$ | 9265 |
| | | 8217 | | | 11 959 | | $N$ | 12 387 |
| | | 8890 | | | 12 223 | | | 13 340 |
| | | 9710 | | | | | | 14 680 |
| NaCl | $R_2$ | 6325 | | | | | | |
| | $N$ | 8371 | | | | | | |
| | | 8678 | | | | | | |

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[1] D. B. Fitchen, R. H. Silsbee, T. A. Fulton, and E. L. Wolf, Phys. Rev. Letters **11**, 275 (1963).

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[3] W. VonDerÖsten, Z. Physik **174**, 423 (1963).

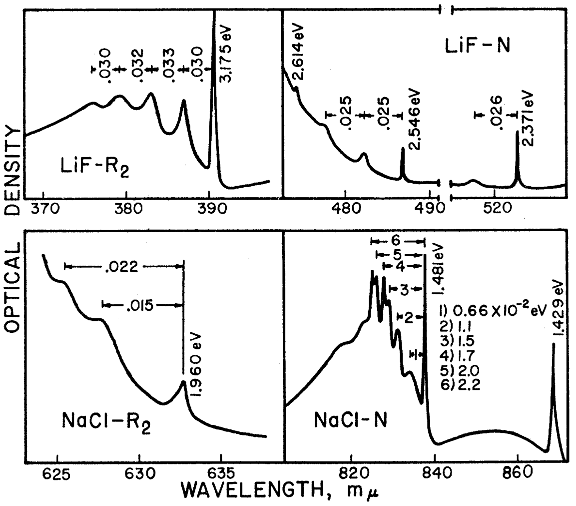

FIG. 1. Absorption spectrum of $R_2$ and $N$ bands of LiF and NaCl, showing details of fine structure due to phonon emission peaks at 10°K.

impurity complexes. A limited number of pre-irradiation background measurements have not shown any fine structure.

As has been mentioned, along with many of the zero-phonon lines a rather detailed spectrum of somewhat broader subsidiary peaks is observed superimposed on the broad band. This fine structure must be associated with lattice vibrations of some sort which are coupled with the photon absorption and electronic excitation process. One of the important questions to be answered is the exact nature of these lattice vibrations, specifically as to whether they are local modes or normal lattice phonons, and if the latter whether or not there is preferential excitation of particular modes. Previous studies of the width and temperature dependence of the usual broad color center bands have been interpreted as indicating that coupling of the optical absorption process with lattice vibrations is almost entirely through localized modes or optical phonons of small wave vector.[4] Our results are not consistent with this interpretation.

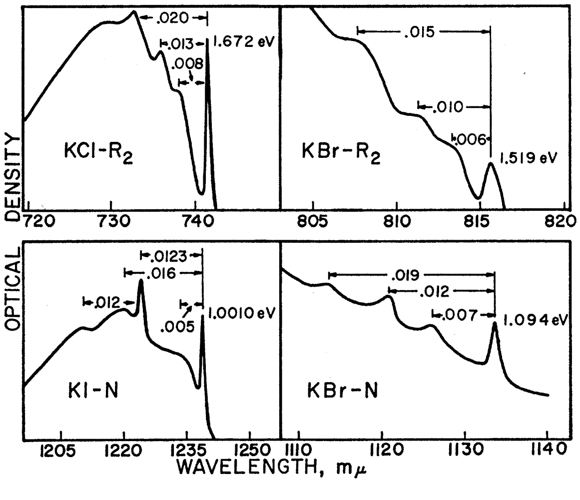

FIG. 2. Absorption spectrum of $R_2$ bands of KCl and KBr, and $N$ bands of KBr and KI, as in Fig. 1.

Representative traces showing the phonon emission peak structure observed on a number of color center bands are shown in Fig. 1 and 2. Energy separations between successive peaks or between given phonon emission peaks and their associated zero-phonon lines are given on the figures. The data are analyzed by comparing the observed energy separation of these peaks with theoretical phonon energies for all phonon modes near the zone boundary. The theoretical energies are obtained from phonon dispersion curves for all the alkali halides as theoretically determined by Karo and Hardy.[5–7] These values are shown in Table IIa. In Table IIb the experimental peak energies are listed together with the energy separation of each phonon emission peak from its zero-phonon line. Also shown are the phonon assignments given for each peak based on a direct comparison with the values in Table IIa. The theoretical phonon energies are given again in order to simplify the comparison for the reader.

The observed phonon emission peaks on the $R_2$ bands of NaCl and KCl, which are among the best resolved spectra, all agree with theoretical values of single phonon energies to within 5%. All of the listed phonon emission peaks associated with the $N$ bands of NaCl, KCl, KBr, and KI, agree with theoretical values to 10% or better (with a few possible ambiguities), with the exception of several of the lowest experimental phonon energies. These peak energy separations are all considerably lower in energy than any of the theoretical values, and are indicated with a question mark in Table IIb. It seems likely that these peaks may be associated with pseudolocalized modes due to resonance scattering.[8] The experimental values for the phonon emission peaks associated with the $R_2$ band of KBr are probably accurate to no more than 20%, since the peaks are relatively broad and are on the steeply rising side of the $R_2$ band. Within these limits there are several possible correlations, as indicated in the table.

On the $R_2$ and $N$ bands of LiF and the $N$ band of NaF, the phonon emission peak structure is approximately regularly spaced. In each case, the spacing corresponds quite well to a theoretical phonon energy, but to a different mode in each of the three cases. Thus, it appears that successive peaks should be assigned to multiple excitation of a single phonon mode.

An examination of Table IIb indicates that the most

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[4] See, e.g., James H. Schulman and W. Dale Compton, *Color Centers in Solids* (Pergamon Press, Inc., New York, 1962), Chap. 3, pp. 69–91.

[5] A. M. Karo and J. R. Hardy, Phys. Rev. **129**, 2024 (1963).

[6] J. R. Hardy and A. M. Karo, Phil. Mag. **5**, 859 (1960).

[7] J. R. Hardy, Phil. Mag. **7**, 315 (1962).

[8] J. A. Krumhansl (private communication).

TABLE II. (a) Theoretical phonon energies (in eV×$10^2$) at Brillouin zone boundary for ⟨100⟩ and ⟨111⟩ symmetry propagation directions. Energies are obtained from phonon dispersion curves of Karlo and Hardy in Refs. 5–7. TA, LA, TO, and LO refer to transverse and longitudinal acoustic, and transverse and longitudinal optic phonon modes, respectively. (b) Phonon emission peaks observed on $R_2$ and $N$ bands of alkali halides. Phonon assignments are made by comparison with (a).

(a)

| | LiF | | NaF | | NaCl | |
|---|---|---|---|---|---|---|
| | ⟨100⟩ | ⟨111⟩ | ⟨100⟩ | ⟨111⟩ | ⟨100⟩ | ⟨111⟩ |
| TA | 2.4 | 2.3 | 1.74 | 1.84 | 1.03 | 1.37 |
| LA | 3.9 | 4.2 | 2.9 | 3.8 | 1.8 | 2.0 |
| TO | 5.3 | 3.1 | 2.7 | 2.1 | 2.3 | 1.5 |
| LO | 7.5 | 8.2 | 3.4 | 4.0 | 2.7 | 3.0 |
| | KCl | | KBr | | KI | |
| | ⟨100⟩ | ⟨111⟩ | ⟨100⟩ | ⟨111⟩ | ⟨100⟩ | ⟨111⟩ |
| TA | 0.77 | 1.09 | 0.56 | 0.84 | 0.40 | 0.64 |
| LA | 1.49 | 1.82 | 0.92 | 1.13 | 0.64 | 0.80 |
| TO | 1.74 | 1.30 | 1.45 | 1.07 | 1.34 | 1.00 |
| LO | 1.87 | 1.95 | 1.66 | 1.82 | 1.53 | 1.67 |

(b)

| 0-phonon and phonon emission peak energy (eV) | Energy difference $(E_i-E_0)$ (eV×$10^2$) | Phonon assignment | Theoretical phonon energy (eV×$10^2$) |
|---|---|---|---|
| | | LiF | |
| $R_2$ | | | |
| (0) 3.175 | | | |
| (1) 3.205 | 3.0 | TO⟨111⟩ | 3.1 |
| (2) 3.238 | 6.3 | 2×TO⟨111⟩ | 6.2 |
| (3) 3.269 | 9.4 | 3×TO⟨111⟩ | 9.3 |
| (4) 3.300 | 12.5 | 4×TO⟨111⟩ | 12.4 |
| $N$ | | | |
| (0) 2.546 | | | |
| (1) 2.571 | 2.5 | TA⟨100⟩ | 2.4 |
| (2) 2.597 | 5.1 | 2×TA⟨100⟩ | 4.8 |
| (0) 2.371 | | | |
| (1) 2.397 | 2.6 | TA⟨100⟩ | 2.4 |
| | | NaF | |
| $N$ | | | |
| (0) 1.509 | | | |
| (1) 1.535 | 2.6 | TO⟨100⟩ | 2.7 |
| (2) 1.563 | 5.4 | 2×TO⟨100⟩ | 5.4 |
| (3) 1.590 | 8.1 | 3×TO⟨100⟩ | 8.1 |
| (4) 1.617 | 10.8 | 4×TO⟨100⟩ | 10.8 |
| | | NaCl | |
| $R_2$ | | | |
| (0) 1.960 | | | |
| (1) 1.975 | 1.5 | TO⟨111⟩ | 1.5 |
| (2) 1.982 | 2.2 | TO⟨100⟩ | 2.3 |
| $N$ | | | |
| (0) 1.481 | | | |
| (1) 1.488 | 0.7 | ? | |
| (2) 1.492 | 1.1 | TA⟨100⟩ | 1.03 |
| (3) 1.496 | 1.5 | TO⟨111⟩ | 1.5 |
| (4) 1.498 | 1.7 | LA⟨100⟩ | 1.8 |
| (5) 1.501 | 2.0 | LA⟨111⟩ | 2.0 |
| (6) 1.503 | 2.2 | TO⟨100⟩ | 2.3 |

(b) *continued*

| 0-phonon and phonon emission peak energy (eV) | Energy difference $(E_i-E_0)$ (eV×$10^2$) | Phonon assignment | Theoretical phonon energy (eV×$10^2$) |
|---|---|---|---|
| | | KCl | |
| $R_2$ | | | |
| (0) 1.672 | | | |
| (1) 1.680 | 0.8 | TA⟨100⟩ | 0.77 |
| (2) 1.685 | 1.3 | TO⟨111⟩ | 1.3 |
| (3) 1.692 | 2.0 | LO⟨111⟩ | 1.95 |
| $N$ | | | |
| (0) 1.037 | | | |
| (1) 1.043 | 0.6 | ? | |
| (2) 1.045 | 0.8 | TA⟨100⟩ | 0.77 |
| (0) 1.251 | | | |
| (1) 1.258 | 0.7 | TA⟨100⟩ | 0.77 |
| | | KBr | |
| $R_2$ | | | |
| (0) 1.519 | | | |
| (1) 1.525 | 0.6 | TA⟨100⟩ | 0.56 |
| (2) 1.529 | 1.0 | 2×TA⟨100⟩ | 1.12 |
| | | or LA⟨100⟩ | 0.92 |
| | | or LA⟨111⟩ | 1.13 |
| | | or TO⟨111⟩ | 1.07 |
| (3) 1.534 | 1.5 | 3×TA⟨100⟩ | 1.68 |
| | | or TO⟨100⟩ | 1.45 |
| | | or LO⟨100⟩ | 1.66 |
| $N$ | | | |
| (0) 1.094 | | | |
| (1) 1.101 | 0.7 | TA⟨100⟩ | 0.56 |
| | | or TA⟨111⟩ | 0.84 |
| (2) 1.106 | 1.2 | LA⟨111⟩ | 1.13 |
| (3) 1.113 | 1.9 | LO⟨111⟩ | 1.82 |
| (0) 1.055 | | | |
| (1) 1.058 | 0.3 | ? | |
| (2) 1.063 | 0.8 | TA⟨111⟩ | 0.84 |
| (3) 1.073 | 1.8 | LO⟨111⟩ | 1.82 |
| | | KI | |
| $N$ | | | |
| (0) 1.001 | | | |
| (1) 1.005 | 0.4 | TA⟨100⟩ | 0.40 |
| (2) 1.013 | 1.2 | TO⟨100⟩ | 1.34 |
| (3) 1.017 | 1.6 | LO⟨100⟩ | 1.53 |
| | | or LO⟨111⟩ | 1.67 |
| (4) 1.025 | 2.4 | 2×TO⟨100⟩ | 2.68 |

common coupling of the $R_2$ and $N$ centers to the lattice is through transverse acoustical phonons propagating in ⟨100⟩ directions. The next most common couplings appear to be through the transverse optical ⟨100⟩ and ⟨111⟩ phonons. Possible correlation with all eight phonon modes and propagation directions are represented in the data, however, and in a majority of the cases a given defect seems to be coupled to several phonon modes with comparable strength. Only in LiF and NaF, as mentioned above, does the coupling to a single phonon mode seem strong enough to completely predominate.

The existence of zero-phonon lines on color center bands as well as subsidiary structure associated in some way with lattice vibration is most easily understood by analogy with the Mössbauer effect. The formal analogy between the two cases is treated by Trifonov.[9] For the Mössbauer case, Visscher[10] has specifically calculated the absorption cross section for a monochromatic $\gamma$-ray beam incident on an absorber with a simple Debye spectrum of phonons. Strong absorption maxima are very clearly shown at energies corresponding to high-phonon probability densities near the cutoff frequency and at integral multiples of this frequency.

We feel that the almost universal agreement found here between observed and theoretical phonon energies must be taken as very strong experimental evidence that individual normal lattice phonons of many modes near the Brillouin zone boundary may be excited with high probability, and that a large part of the broadening of at least the $R_2$ and $N$ bands in the alkali halides is due to lattice interactions involving normal lattice phonons of appreciable wave vector. In support of these conclusions, we feel it is reasonable that excitation of phonons near the zone boundary is observed, as these are the phonons with highest density of states and also of wavelength comparable to the dimensions of the defects involved. Thus, they should be most efficiently coupled to transition processes in these defects. Also, the defects which give rise to (so far) observable fine structure are all relatively complex three-dimensional structures. It seems reasonable that if normal lattice phonons are to be excited at all in these complexes, that the transition processes should be coupled to a variety of different lattice modes.

In conclusion, we would like to acknowledge our appreciation for the efforts of a number of people who have contributed significantly to this work. We would especially like to extend our thanks to D. B. Fitchen and R. H. Silsbee for detailed discussions of their results prior to publication, to R. S. Claassen, D. K. Brice, and D. C. Wallace, in particular, and many other associates at Sandia Laboratory for many fruitful discussions, and to D. D. TerHaar for performing the major part of the experimental work.

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# Strong Axial Electron Paramagnetic Resonance Spectrum of Fe$^{3+}$ in SrTiO$_3$ Due to Nearest-Neighbor Charge Compensation

E. S. Kirkpatrick,* K. A. Müller,† and R. S. Rubins‡
*Battelle Memorial Institute, Geneva, Switzerland*

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An axial electron paramagnetic resonance (EPR) spectrum in iron-doped (cubic) strontium titanate has been observed at 3.3 and 1.85 cm wavelength with effective $g$ values $g_\perp^e = 5.993\pm0.001$ and $g_\perp^e = 5.961\pm0.001$, respectively, and $g_\parallel^e = g_\parallel = 2.0054\pm0.0007$. The same spectrum was found after charge displacement due to heat treatment in the dark or by reduction in crystals which contained, in addition to iron, other transition metal ions. The spectrum is attributed to $\Delta M = 1$ transitions of the $S_z = \pm\frac{1}{2}$ level of Fe$^{3+}(3d^5)$ in a strongly tetragonal electric crystalline field produced by local charge compensation at a nearest-neighbor oxygen site. The theory is developed for ions of half-integral spin in an axial field much greater than the Zeeman splitting. By applying the theory to the special case of $S = \frac{5}{2}$ and using the measured effective $g_\perp^e$ values and resonance magnetic fields $g_\perp = 2.0101\pm0.0008$ and a zero-field splitting parameter $|2D|$ of $2.85\pm0.15$ cm$^{-1}$ is obtained. This is the largest splitting which has so far been observed for Fe$^{3+}$ in any inorganic crystal and could be useful for submillimeter maser applications.

## I. INTRODUCTION

It has been shown by Watkins,[1] for Mn$^{2+}$ in NaCl, that impurity ions substituting for ions of different valency attract charge compensating defects in the lattice at temperatures at which the ions become mobile.

The majority of reported EPR studies of transition metal ions in the three oxide crystals SrTiO$_3$,[2] BaTiO$_3$,[3] and rutile (TiO$_2$),[4] have indicated that there is no definite evidence for local charge compensation when divalent or trivalent transition metal ions replace the tetravalent titanium ion. It seemed possible that this might be due to the high dielectric constant of these crystals, which is 100 or more at room temperature. At about 1000°K, when the ions in these oxide crystals become mobile, the dielectric constant is still an order

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[*] Present address: Harvard University, Cambridge, Massachusetts.

[†] Present address: IBM Zurich Research Laboratory, Rüschlikon-Zurich, Switzerland.

[‡] Present address: Hebrew University, Jerusalem, Israel.

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