Circular Dichroism in the Urbach Region of KI†

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Measurements of the circular dichroism in the low-energy tail of the first exciton absorption peak in KI are presented and discussed. The magnitude of the observed dichroism allows the rms splitting of the $P_{3/2}$-like hole to be evaluated. The result is that the cubic part of the Urbach perturbation is at least 15 times larger than the noncubic part.

THE optical-absorption coefficient on the low-energy tail of many exciton-absorption peaks follows the empirical Urbach Rule[1]:

$$\alpha(E)=\alpha_0 \exp[-\sigma(E_p-E)/kT], \quad (1)$$

where σ is of order unity. This rule is valid for energies as much as 1–2 eV below the exciton peak in alkali halides. Very few hard facts are known about the nature of the electronic states which give rise to this absorption or the type of lattice distortion responsible for the large energy shifts.[2]

This paper reports measurements of the circular dichroism in the Urbach region of KI. The interpretation of these measurements gives information about the amount by which the orbital degeneracy of the p-like hole is split by noncubic parts of the lattice interaction.

The lowest-energy exciton in KI is made up of an s-like electron bound to a $P_{3/2}$-like hole. Coupling these states to cubic lattice distortions will shift the s and p energies; noncubic distortions will split the $P_{3/2}$ state. Moran[3] has discussed the effect of noncubic lattice distortions on a spin-orbit-split p state. The effect on the $P_{3/2}$ state is to split the four-fold degenerate state into two Kramers doublets having wave functions $U_{1,2}{}^{+}=2^{-1/2}(|\frac{3}{2}\ \frac{3}{2}\rangle\pm|\frac{3}{2}\ -\frac{1}{2}\rangle)$ plus magnetic conjugates $U_{1,2}{}^{-}=2^{-1/2}(|\frac{3}{2}\ -\frac{3}{2}\rangle\pm|\frac{3}{2}\ \frac{1}{2}\rangle)$. In order to calculate the effect of a magnetic field on the optical absorption in the Urbach region, we use these free-atom eigenstates to obtain an approximate result. The $P_{1/2}$ exciton is 1 eV higher in energy, and so should only be mixed in slightly by the noncubic interactions which is shown by comparison with the experimental results to be small compared with 1 eV. The mixing of the $P_{1/2}$ and $P_{3/2}$ states by the magnetic field also produces only a small correction.

Let the splitting between states $U_1{}^{+}$ and $U_2{}^{+}$ be Δ. The magnetic field has two effects: It splits the two states and it mixes them. We describe the change in optical properties by expanding the absorption coefficient in powers of the applied magnetic field, keeping only the first term. The requirement that the observed properties must be invariant under all operations which leave the crystal macroscopically invariant yields the result that the splitting term cannot contribute to the dichroism.[4] Only the mixing term remains invariant and can contribute.

In the presence of the magnetic field, the two states $U_1{}^{+}$ and $U_2{}^{+}$ are changed to first order in the magnetic field as follows:

$$\begin{aligned} U_1{}^{+} &\rightarrow U_1{}^{+}+U_2{}^{+}\langle U_2{}^{+}|\beta H(L_z+2s_z)|U_1{}^{+}\rangle/\Delta \\ &= U_1{}^{+}+(\gamma\beta H/\Delta)U_2{}^{+}, \quad (2) \\ U_2{}^{+} &\rightarrow U_2{}^{+}-(\gamma\beta H/\Delta)U_1{}^{+}. \end{aligned}$$

The optical absorption is given by

$$\alpha\sim\textstyle\sum_i |\langle 0|P_{\pm}|SU_i\rangle|^2\delta(E_i-h\omega),$$

where $|0\rangle$ represents the crystal with no excitons, $P_{\pm}$ is the dipole operator for right and left circular polarization, and $|SU_i\rangle$ is the exciton wave function. The change in absorption is then given by

$$\frac{\alpha_+(E)-\alpha_-(E)}{\alpha(E)}\equiv\frac{\Delta\alpha}{\alpha}=4\frac{\gamma\beta H}{\Delta}. \quad (3)$$

The average splitting of the $P_{3/2}$ state by noncubic lattice distortions can thus be determined by measuring the circular dichroism.

The value of γ, the Zeeman-interaction matrix element connecting the states U_1 and U_2 obtained using the free-atom eigenstates, is $\frac{4}{3}$. Two arguments can be made that the correct value for the exciton is not far from the free-atom value. First, the magnitude of the spin-orbit splitting of the excitons in alkali halides is nearly the same as in the free atom. Second, the observed Faraday rotation in the visible range,[5] when fit with the Becquerel formula, gives a g value of about 85% of the free-atom value for KI and similar values for other alkali halides. This estimate is used for the purpose of the present analysis, while we recognize that a recent interesting report of a small g value for RbI has been made based on reflectivity measurements.[6] It would be valuable to carry out a Faraday-rotation

† Work supported by the National Science Foundation.
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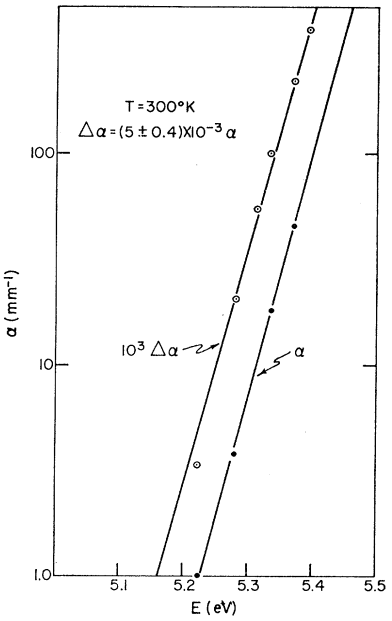

FIG. 1. α and $\Delta\alpha$ plotted on a logarithmic scale against photon energy for a room-temperature sample.

measurement on RbI to verify the smallness of g for this material.

Note that the upper of the two split states always prefers one circular polarization over the other, regardless of whether the upper state is U_1 or U_2, while the lower state always prefers the other polarization. If the splitting were large enough, absorption would only occur to the lower of the two states. As the splitting approaches zero, there is cancellation between the upper- and lower-state contributions and the observable signal remains finite.

To include the partial cancellation for small splittings, we must assume a distribution for the splitting. The experimental results support a Gaussian distribution. Let the probability of the average exciton energy E be

$$P(E)=\exp[-\sigma(E_p-E)/kT],$$

in accordance with Eq. (1). Now assume that the probability of a splitting Δ occurring varies as

$$P(\Delta)=\exp[-(\Delta/\Gamma)^2].$$

Then the total probability of absorbing light at energy E is proportional to

$$\alpha(E)\sim\int_0^\infty [P(E+\tfrac{1}{2}\Delta)+P(E-\tfrac{1}{2}\Delta)]P(\Delta)d\Delta \Big/ \int_0^\infty P(\Delta)d\Delta.$$

In a magnetic field, the difference in absorption between left and right circular polarizations is proportional to

$$\Delta\alpha(E)\sim 4\beta\gamma H\int_0^\infty [P(E+\tfrac{1}{2}\Delta)-P(E-\tfrac{1}{2}\Delta)](d\Delta/\Delta) \Big/ \int_0^\infty P(\Delta)d\Delta,$$

so

$$\frac{\Delta\alpha(E)}{\alpha(E)}=\frac{4\gamma\beta H}{2kT/\sigma}\int_0^\infty e^{-b^2x^2}\frac{\sinh x}{x}dx \Big/ \int_0^\infty e^{-b^2x^2}\cosh x dx$$
$$=\frac{4\gamma\beta H}{2kT/\sigma}e^{-1/4b^2}\,{}_1F_1(\tfrac{1}{2};\tfrac{3}{2};1/4b^2), \quad (4)$$

where $x=\sigma\Delta/2kT$, $b=2kT/\Gamma\sigma$, and ${}_1F_1(\frac{1}{2};\frac{3}{2};1/4b^2)$ is a confluent hypergeometric function.[7] Equation (4) is used to obtain a value for Γ, and hence $\Delta^2=\frac{1}{2}\Gamma^2$, from the measured $\Delta\alpha/\alpha$. For the data presented in this paper, the correction due to partial cancellation is fairly small ($\simeq$30%), so the assumption of a Gaussian distribution for Δ is not too critical.

The measurements were carried out by transmitting a light beam through a KI sample parallel to the field of a 4-in. electromagnet. The polarization of the beam was modulated from left to right circularity by transmitting the beam through a fused-quartz rod with applied uniaxial strain.[8] The light source was a 450-W xenon lamp. Two grating monochromators were used in series to reduce scattered light. The temperature of the sample was varied from 300–640°K, with a small oven having quartz windows which was placed in the gap of the magnet. The magnetic field strength was 15 kG and the measurements were made by reversing the field so the effective field change was 30 kG. Both the absorption coefficient and the change in absorption due to the field were measured for several energies at each temperature. A graph showing typical results is presented in Fig. 1. Altogether, ten "good" measurements were made, and the resulting averaged values of Δ^2 are plotted as a function of E_p-E in Fig. 2, where E_p is the energy of the exciton peak, and E is the photon energy used. The values of E_p used were corrected for thermal expansion of the crystal, so that E_p-E represents only the dynamical part of the total exciton energy shift with temperature.

The principal experimental difficulty encountered was the deterioration of sample surfaces with time. The surfaces were protected either with an evaporation film of MgF2 or by melting the KI between quartz plates. These steps were necessary to produce usable results, but they still did not eliminate surface deterioration. The rate of deterioration increased with temperature. This is responsible for higher temperatures not

[7] I. S. Gradshteyn and I. W. Rhyzhik, *Tables of Integrals, Series, and Products* (Academic Press Inc., 1966), p. 495

[8] S. N. Jasperson and S. E. Schnatterly, Rev. Sci. Instr. **40**, 761 (1969).

being used and for the increase in uncertainty in the value of Δ with E_p-E.

The change in reflectivity in the magnetic field can be ignored because of the smallness of the reflectance loss compared with the absorption loss for the range of energy and sample thicknesses used. This was verified by observing that there was no measurable circular dichroism for energies just below those used in the experiment, where the reflectance is nearly the same but the absorption coefficient is much smaller. The fact that impurities and defects were not contributing significantly to the absorption was determined by verifying that the absorption coefficient had the right magnitude and slope at the energy and temperature used. In addition, most of the measurements were made above room temperature, so it was possible to verify that before warming the sample only reflection losses were present, while afterward there was significant absorption as well.

The general result of the experiment is that the splitting of the p state is small compared with the shift in energy in the Urbach region. The Urbach perturbation thus appears to be mostly cubic.

To be more specific, the data can be used to evaluate parameters in a configuration-coordinate model. The energy to create an exciton can be expanded in a power series in the amplitude of lattice distortions:

$$E(Q)-E(0)=\sum_i A_iQ_i+\sum_{ij} B_{ij}Q_iQ_j+\cdots. \quad (5)$$

The linear term gives rise to a Gaussian-shape absorption band, the second moment of which is given by $\sum_i A_i\langle Q_i^2\rangle$. The quadratic term gives rise to a shift in the first moment of the exciton absorption band with temperature and, as pointed out by Toyozawa,[9] can also produce Urbach's rule. The splitting of the p state is due to the noncubic parts of both interactions. Thus

$$\begin{aligned}\langle E^2\rangle&=A_C^2\langle Q_C^2\rangle+A_{NC}^2\langle Q^2{}_{NC}\rangle\\&\qquad+B^2\langle Q^2\rangle_C{}^2+B_{NC}^2\langle Q^2\rangle_{NC}{}^2,\\\langle E\rangle&=B_C\langle Q^2\rangle_C,\\E_p-E&=B_C\langle Q^2\rangle_{Cloc},\\\langle\Delta^2\rangle_{loc}&=A_{NC}^2\langle Q^2{}_{NC}\rangle_{loc}+B_{NC}^2(\langle Q^2\rangle_{loc})_{NC}{}^2,\end{aligned} \quad (6)$$

where a subscript C refers to cubic and NC refers to noncubic lattice distortions, $\langle E^2\rangle$ is the second moment of the exciton band, and $\langle E\rangle$ is the first moment of the exciton band. The brackets indicate the usual thermal average, while $\langle\ \ \rangle_{loc}$ indicates a local average, that is, a mean square value of lattice distortion corresponding to a given value of E_p-E. If we assume that $\langle Q_{NC}{}^2\rangle_{loc}=\beta\langle Q^2\rangle_{Cloc}$, and $\langle Q^2\rangle_{NCloc}=\beta'\langle Q^2\rangle_{Cloc}$, then

$$\begin{aligned}\langle\Delta^2\rangle_{loc}&=(A_{NC}^2/B_C)\beta(E_p-E)\\&\qquad+(B_{NC}^2/B_C{}^2)\beta'^2(E_p-E)^2.\end{aligned} \quad (7)$$

[9] Y. Toyozawa, Prog. Theoret. Phys. (Kyoto) **22**, 455 (1959); *ibid.*, Suppl. **12**, 111 (1959).

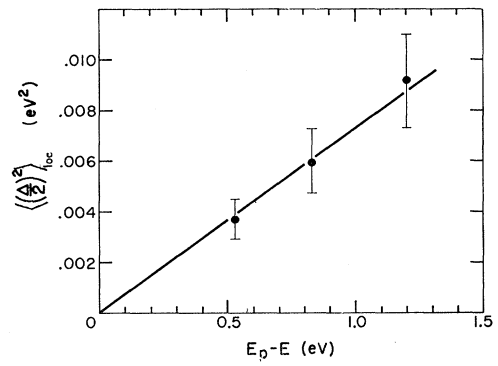

FIG. 2. Mean-square splitting of the $P_{3/2}$-like hole state plotted against photon energy measured from the exciton peak.

Hence we expect Δ^2 to increase linearly with E_p-E due to the linear coupling term, and quadratically due to the second-order term. The data indicate that the linear term dominates. In fact, there is no indication of any noncubic second-order interaction at all. The uncertainties in the measurements allow the following upper limit to be placed on B_{NC}:

$$\beta'B_{NC}/B_C\leq 0.06. \quad (8a)$$

That is, the cubic part of the second-order interaction is larger than the noncubic part by at least a factor of 15. Either the noncubic parts of the lattice distortions are small in the Urbach region (β' is small), or the strength of the non-cubic Urbach term in the configuration-coordinate Hamiltonian is weak (B_{NC} is small).

From the slope of the graph in Fig. 2, another ratio of parameters can be obtained:

$$(A_{NC}{}^2/B_C)\beta=0.0075\pm0.001\text{ eV}. \quad (8b)$$

Two other equations relating the parameters in the configuration-coordinate Hamiltonian can be obtained from Martienssen's measurements of the width and peak position of the first exciton peak as a function of temperature.[10] Correcting the peak shift for thermal expansion we find

$$\begin{aligned}A_C{}^2\langle Q_C{}^2\rangle+A_{NC}{}^2\langle Q_{NC}{}^2\rangle&=5.0\times10^{-5}\text{ eV}^2/^\circ\text{K}\\B_C\langle Q^2\rangle_C&=9\times10^{-4}\text{ eV}/^\circ\text{K}.\end{aligned} \quad (9)$$

There is, unfortunately, no direct way of comparing Eq. 8(b) with Eq. 9, since the relation between $\langle Q_C{}^2\rangle$, the mean-square amplitude of the totally symmetric modes and $\langle Q^2\rangle_C$, the cubic part of the mean-square amplitude of all lattice modes, is not known.

If we believe Fig. 2 rigorously, then the p-state splitting is not involved at all with the Urbach coupling mechanism, and $\langle(\frac{1}{2}\Delta)^2\rangle_{loc}$ is just the noncubic part of

[10] W. Martienssen, J. Phys. Chem. Solids **2**, 257 (1957).

the second moment of the exciton. The three points shown in Fig. 2 were measured at 300, 440, and 600°K, respectively. Comparing with Martienssen's measurements of the width of the exciton peak as a function of temperature, we find $\langle E_{NC}^2\rangle \simeq \langle E_C^2\rangle$. This is very close to the corresponding result for F centers.

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Soft-Mode Damping and Ultrasonic Attenuation at a Structural Phase Transition

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The soft-mode damping and the ultrasonic attenuation at a displacive phase transition has been calculated with the help of a model Hamiltonian. The soft-mode damping parameter Γ is finite at the transition temperature, whereas the ultrasonic attenuation α is singular. For sound frequencies $\omega \ll \Gamma$, the ultrasonic attenuation is proportional to the sound frequency squared with critical exponents $\eta = 0.5$ and 1.5, respectively, for weakly damped and strongly overdamped soft-mode frequencies. A comparison is made with previous calculations based on the Silvermann model.

I. INTRODUCTION

A MODEL Hamiltonian has recently been constructed to describe displacive structural phase transitions in perovskite-type crystals of the form ABO_3 involving rotations of the BO_6 octahedra.[1,2] The model Hamiltonian is expressed in terms of localized displacement fields $\mathbf{R}(l)$ associated with each unit cell where $\mathbf{R}(l)$ is an axial vector describing the rotations of the oxygen octahedra about the cell center.

From the model Hamiltonian, the behavior of the soft dynamical modes associated with the phase transition and the static angular displacement have been calculated as functions of temperature.[2]

The displacements of the oxygen octahedra are coupled to the static strains.[3,4] This interaction is important in determining both the amount of distortion and the form of the eigenfrequencies of the coupled system.[3,4]

In this paper, we present the results for the attenuation of the acoustic phonons and the soft optical phonons due to their mutual interaction. A model Hamiltonian may be constructed by expanding the potential energy of the strained crystal in terms of the strain and the oxygen-ion displacement fields. Then, making use of the transformation given in Ref. 2 connecting the oxygen-ion displacements and the operators $\mathbf{R}(l)$, the Hamiltonian takes the form[5]

$$H=\sum G_{\alpha\beta ij\lambda\lambda'}[e_{\alpha\beta}(l)+e_{\alpha\beta}(l')]\gamma_{ij}(ll') \times[R_\lambda(l)R_{\lambda'}(l')+R_\lambda(l')R_{\lambda'}(l)], \quad (1)$$

where $e_{ij}(l)$ are localized strain tensor components. There are four independent coupling constants $G_{\alpha\beta ij\lambda\lambda'}$, and these are listed in the Appendix. The coupling function $\gamma_{ij}(ll')$ is a symmetric matrix. When expressed in terms of its Fourier transform,

$$\gamma_{ij}(ll')=(1/N)\sum_{\mathbf{q}} e^{i\mathbf{q}\cdot[\mathbf{x}(l)-\mathbf{x}(l')]}\gamma_{ij}(\mathbf{q}), \quad (2)$$

it has the simple form

$$\gamma_{ij}(\mathbf{q})=\tfrac{1}{2}(1-\cos q_i a) \quad \text{for} \quad i=j,$$
$$\gamma_{ij}(\mathbf{q})=\tfrac{1}{2}(1-\cos q_k a) \quad \text{for} \quad i\neq j\neq k, \quad (3)$$

where i, j, and k refer to the three Cartesian coordinates. The vector $\mathbf{X}(l)$ denotes the center of the lth unit cell.

Because

$$\gamma_{ij}(q=0)=0, \quad (4)$$

the Hamiltonian vanishes when all the octahedra rotate in phase as required on physical grounds. We also note that

$$\gamma_{ij}(\mathbf{q}_R)=1 \quad (5)$$

for all i and j, where $\mathbf{q}_R$ is the wave vector at the R corner of the Brillouin zone.

The Hamiltonian Eq. (1) has the proper symmetry and transformation properties appropriate for the cubic

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[2] E. Pytte and J. Feder, Phys. Rev. **187**, 1077 (1969).
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[4] J. Feder and E. Pytte (to be published).

[5] A more detailed derivation of the model Hamiltonian will be presented in Ref. 4.