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The apparent spin-lattice relaxation time for the EPR of H atoms in damaged HD at 1.2°K and 24 GHz which have been achieved with an added impurity of O₂ are sufficiently short to permit substantial dynamic polarization of the nuclei, both protons and deuterons, if the relaxation times of the NMR are as long as several hundred seconds. Relaxation times for the magnetic resonance of protons of 8000 sec at 1.2°K have been found by Hardy and Gaines⁷ in extremely pure HD, and preliminary evidence⁸ indicates that relaxation times for magnetic resonance of protons and deuterons at 1.2°K and 8.6 kG up to 300 sec are possible in HD with added impurities. If such times persist in HD with O₂ impurity, the dynamic polarization induced into protons and deuterons will be limited by the fractional width of the EPR which might be reduced at higher fields.

Production of trapped radicals other than O₂D from impurities other than O₂ by reaction with unstably trapped D atoms in damaged solid HD at 4.2°K was demonstrated by spectrum (h). Spectrum (h) was observed at 4.2°K for radiation-damaged solid HD prepared from a commercial gas without chemical purification which was known to contain substantial amounts of O₂, N₂, CO₂, Ar, diethyl ether, and unidentified organic compounds. It displayed resonances of trapped H atoms and a broad, complex distribution of resonances attributed to trapped radicals. Reso-

nances of the unstable D atoms had disappeared before this spectrum was recorded; however, amplitudes of the resonances of H atoms and radicals did not decrease significantly after storage for two months at 4.2°K. Although the radicals present in this spectrum have not been specifically identified, substantial production of several species which were stably trapped in an environment suitable for observing their EPR was distinctly indicated.

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BAND STRUCTURE AND ULTRAVIOLET OPTICAL PROPERTIES OF SODIUM CHLORIDE*

C. Y. Fong

Department of Physics, University of California, Berkeley, California

and

Marvin L. Cohen†

Department of Physics and Inorganic Materials Research Division,
Lawrence Radiation Laboratory, University of California, Berkeley, California

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The empirical pseudopotential method is used to calculate the electronic band structure and the frequency-dependent dielectric function, $\epsilon_2(\omega)$, of NaCl. The results allow an identification of the interband transitions responsible for the prominent structure in the measured optical spectrum.

In this Letter, we report the first application of the empirical pseudopotential method¹ (EPM) to an alkali-halide crystal. This calculation allows an analysis of the measured optical spectrum² of NaCl and an identification of the interband transitions responsible for the prominent

optical structure. The analysis of the optical data is made by comparing the calculated and measured frequency-dependent dielectric function, $\epsilon_2(\omega)$, and this comparison shows good agreement between experiment and theory for both the location in energy and the shape of the promi-

nent optical structure.

The optical spectrum of NaCl is similar to that of MgO,^{3,4} and it was therefore expected that the electronic band structures of these materials should be similar. This is, in fact, what was found.

In applying the EPM it is assumed that the Hamiltonian for an electron in a solid consists of a kinetic energy term plus a weak effective potential. The potential is expanded in reciprocal lattice vectors, and the Fourier coefficients or form factors for the potential are chosen to give energy levels in agreement with experiment. For convenience, in crystals with two atoms per unit cell, the origin is taken at the Na site and the potential is factored into a symmetric part and an antisymmetric part. The symmetric part is the average potential of the two atoms, and the antisymmetric part represents the difference between the two potentials.

The starting set of pseudopotential form factors for the symmetric¹ part of the potential were obtained by scaling the silicon potential for the lattice constant of NaCl, $a = 5.63 \text{ \AA}$. The antisymmetric¹ part of the potential was obtained by scaling the MgO form factors. These form factors were then adjusted slightly to give a few of the observed band gaps. The numerical values for the form factors used are $V^S(200) = -0.083 \text{ Ry}$, $V^S(220) = -0.0186 \text{ Ry}$, $V^S(222) = 0.0477 \text{ Ry}$, $V^A(111) = 0.1448 \text{ Ry}$, and $V^A(311) = -0.0255 \text{ Ry}$.

In the calculation, we use $E_1 = 11.1 \text{ eV}$ and $E_2 = 32.1 \text{ eV}$. The convergence of the energy gaps

at Γ , X , and L is of the order of 0.1 eV when we increase E_1 from 11.1 to 13.1 eV . The variation of gap energies is insensitive to the variation of E_2 for values above 30 eV .

The resulting band structure is given in Fig. 1. The lowest valence band is included for completeness, but it is not expected that the EPM will give the energies of this band accurately. The minimum in the conduction band and the maximum in the valence band are both at Γ . The fundamental gap $\Gamma_{15} - \Gamma_1$ was adjusted to 8.97 eV to agree with the gap determined experimentally. The band structure bears an overall similarity to the band structure of MgO, but some of the energy splittings are different (e.g., the $\Gamma_{15} - \Gamma_1$ gap in MgO is 7.77 eV). Another difference between MgO and NaCl is that there is less dispersion in the energies of the various bands as a function of wave vector. The major difference, however, is the relative lowering of the upper conduction bands (bands 6 through 10). These bands contain d -wave components, and they are lowered to such an extent that in the calculation we find that the X_3 level lies below the X_1 level. It is difficult to check this ordering experimentally.

Using the calculated band structure and pseudo-wave functions (wave functions calculated with the pseudopotential), we have computed the imaginary part of the frequency-dependent dielectric function, $\epsilon_2(\omega)$. The theoretical and experimental² curves from 7 to 18 eV are given in Fig. 2 and the energies of the prominent optical struc-

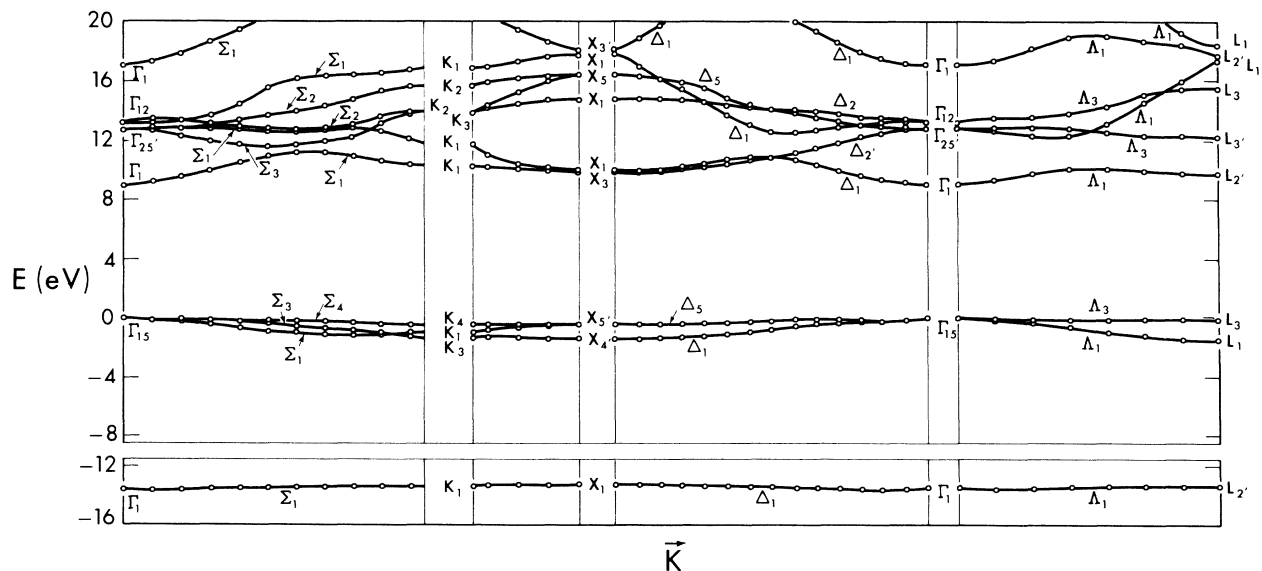


FIG. 1. Electronic band structure of NaCl.

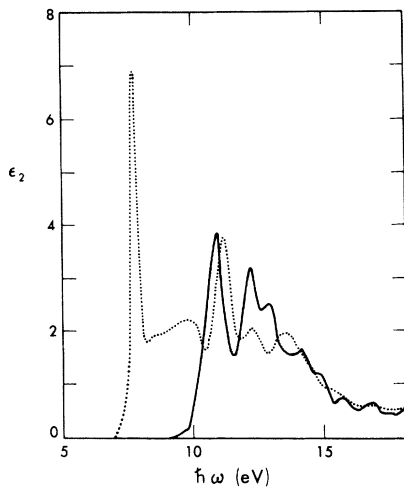


FIG. 2. Comparison of the calculated (solid curve) and the experimental $\epsilon_2(\omega)$.

ture are given in Table I. The energies of the main peaks are in good agreement with experiment, but the heights of the peaks are not. Relative heights are consistent with experiment, and we have used an overall scale factor of 0.6 in the calculated $\epsilon_2(\omega)$ to make the main peak at 11.1 eV agree with the corresponding experimental value. Because of this scale factor and the cut-off in energy at 18 eV, the sum rule for the theoretical curve is obviously not obeyed.

The exciton appearing at 7.73 eV (300°K) and the structure near the fundamental gap have also been observed by Baldini and Bosacchi.⁵ This exciton structure, which is well separated from the band edge, has been examined at low temperatures, and the spin-orbit splitting and higher order lines in the exciton series have been observed.^{2,5} The experimental results of Refs. 2 and 5 are in excellent agreement. The exciton structure is not included in the theoretical $\epsilon_2(\omega)$

and hence this curve begins with $\Gamma_{15} - \Gamma_1$ transitions at 8.97 eV. The exciton is associated with this edge.

The next structure in the curve arises from transitions along the [111] direction, i.e., contributions arising from $L_3 - L_2'$ transitions at 9.86 eV and coming from $\Lambda_3 - \Lambda_1$ transitions at 10.29 eV. The magnitude of this structure differs greatly between experiment and theory as it does in MgO,^{3,4} GaAs,⁶ and other zinc-blende compounds.⁷ The origin of this discrepancy is not known at present, but final-state electron-hole interactions and the inadequacy of pseudo-wave functions to give reliable oscillator strengths have been suggested⁴ for MgO. The MgO and NaCl spectra do differ in this region. In the latter case part of the $L-\Lambda$ structure is masked by the prominent $\Sigma-\Delta-X$ peak around 11.0 eV in both the experimental and theoretical curves.

In the zinc-blende structures and in MgO the largest interband peak in the optical spectrum comes from transitions along Σ and Δ . In addition, this structure has shoulders arising from transitions near X . The same type of structure is found in NaCl around 11.0 eV (see Table I). In the case of NaCl the X_3 level is lower than in the other crystals. This lowering of X_3 does not affect the optical structure greatly in this region and it is difficult to determine the energy of the $X_5' - X_3$ splitting exactly. We have recently computed the spectrum of KCl and our preliminary results indicate that X_3 is even lower in this crystal and an exciton is associated with this edge.

Because of the lowering of the upper conduction bands in NaCl the wide dip in ϵ_2 around 14.5 eV in MgO is absent in the corresponding 11.0- to 12.0-eV region in NaCl. Transitions between the fourth and sixth bands begin in the 12.0-eV

Table I. Identification of prominent optical structures and comparison of the energies (in eV) between the calculated and the measured $\epsilon_2(\omega)$.

Prominent interband transitions	Energy (theory) (eV)	Energy (experiment) (eV)
$\Gamma_{15} \rightarrow \Gamma_1$	8.97	8.97
$L_3 \rightarrow L_2'$	9.86	9.5 ± 0.3
$\Lambda_3 \rightarrow \Lambda_1$	10.29	10 ± 0.3
$X_5' \rightarrow X_3$	10.34	
$X_5' \rightarrow X_1$	10.42	10.5
$\Delta_5 \rightarrow \Delta_1$	11.07	11 ± 0.2
$\Sigma_4 \rightarrow \Sigma_1$	11.32	11.4 ± 0.2
$L_3 \rightarrow L_3'$	12.25	12.25 (peak)
$\Gamma_{15} \rightarrow \Gamma_{25}'$	12.68	13.2

energy range and the peak at 12.25 eV arises from $L_3 - L_3'$ transitions.

In conclusion the EPM calculation allows an identification of most of the optical structure in NaCl and confirms many of the assignments made by Roessler and Walker² who used the MgO band structure as a prototype. The theoretical $\epsilon_2(\omega)$ gives the positions in energies and the shapes of the optical structure in agreement with experiment, but the magnitudes of the peaks are not in good agreement with experiment.

We would like to thank Professor W. C. Walker and Dr. D. M. Roessler for sending us their results prior to publication and for helpful discussions. A complete critical-point analysis and $\epsilon_2(\omega)$ with constant matrix will be given in the forthcoming paper.

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LINEAR STARK EFFECT OF ELECTRO-OPTICALLY ALIGNED F_A CENTERS*

Franz Rosenberger and Fritz Lüty

Physics Department, University of Utah, Salt Lake City, Utah

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Using selective optical excitation under high dc fields, F_A centers were aligned with respect to their optical-absorption tensors and microscopic inversion asymmetry. This ordering process removes the macroscopic inversion symmetry of the crystal, allowing the measurement of first-order electro-optical effects in the F_A absorption. The analysis of the linear Stark effect provides information about size and sign of the dipole-moment difference between ground and excited F_A states.

Many color centers consisting of a complex of two or more lattice site defects lack microscopic inversion symmetry. For the simplest case, two neighboring nonidentical point defects, the complex can be called a "defect dipole," with a vector indicating its orientation. The application of an electric field parallel to the defect dipole should produce a first-order change in the optical transitions of the defect because of the difference in electric dipole moment Δp of its ground and excited state.¹ For a macroscopic system of defect dipoles, however, this first-order effect cancels (for all absorption bands which are broad compared with the Stark shift) because of the existence of equal amounts of defect dipoles in opposite directions; only a much smaller second-order effect remains.¹

We consider the F_A center [an F center with a (100) neighboring foreign cation] as the simplest example of a defect dipole with C_{4v} symmetry.^{2,3} Partial alignment among the six equivalent defect-dipole states (x), (\bar{x}), (y), (\bar{y}), (z), (\bar{z}) can be achieved by irradiation with (100) polarized light, inducing for the selectively excited centers reor-

ientation jumps into one of the equivalent neighboring configurations [Fig. 1(a)]. This process achieves at most a full ordering of the absorption tensors ("optical alignment") with equal amounts of dipoles in opposite directions [e.g., the states x and \bar{x}] in Fig. 1(a)].

The application of a dc electric field will produce a polarization of the center (particularly a displacement of the Li^+ ion) which should remove the equality of reorientation jumps during optical alignment. As illustrated in Fig. 1(b) this may for instance increase the jump rate of process A and decrease that of process B , thus producing an excess of dipole states x vs \bar{x} . This electro-optically aligned defect-dipole system should therefore reveal a first-order Stark effect proportional to the population difference $N(x) - N(\bar{x})$.

This behavior has been verified for F_A centers in KCl:Li and KBr:Li (additively colored and optically $F \rightarrow F_A$ converted). In the experiment we start with an optically aligned F_A -center system, the defect dipoles being in the y and \bar{y} states [Fig. 1(b)]. By a proper (100) polarized-light excitation, these centers are reoriented into the x