DEFORMATION POTENTIALS FOR EXCITONS IN CsI†

D. W. Lynch and A. D. Brothers*
Institute for Atomic Research and Department of Physics, Iowa State University, Ames, Iowa 50010
(Received 21 June 1968)

The shifts of the first two exciton peaks with hydrostatic pressure have been measured in CsI films at 78°K and found to be linear. The deformation potentials deduced are −2.10 eV and +2.10 eV, respectively. These results confirm Onodera's assignment of the two peaks to excitons derived from bands of different symmetry. The data indicate that above 7 kbar the conduction bands cross and the Γ_{12} level lies below the Γ_1 (Onodera's assignment).

The band structures of several alkali halides with the NaCl structure have now been calculated.[1-3] The valence-band maximum is at the center of the zone and has Γ_{15} symmetry (split by spin-orbit interaction). The conduction-band minimum has Γ_1 symmetry and the corresponding wave functions are largely composed of s-like ionic functions on both cations and anions. Just above this Γ_1 minimum (1.3 eV above in KI,[3] ~2.2 eV in KCl[1]) there are two more conduction-band states of symmetry Γ_{12} in KI and $\Gamma_{25'}$ in KCl derived largely from d states on the K^+ ion. The corresponding states are far higher in energy in NaCl,[4] for the Na^+ $3d$ levels lie too high. Indeed the Γ_{12} and $\Gamma_{25'}$ levels in NaCl are primarily halogen ion states. The band through Γ_1 goes to the edge of the zone at X, where it yields an X_1 level several eV above the Γ_1 minimum in NaCl, KCl, and KI. The band through $\Gamma_{25'}$ decreases in energy toward X, giving an X_3 energy minimum only about 1 eV above the Γ_1 minimum in KI and KCl.

Onodera and Toyozawa[5] and Baldini and Bosacchi[6] have shown that the exciton spectra in many alkali halides can be explained as arising from two Wannier exciton series originating from the spin-orbit split Γ_{15} valence band and terminating with excitons containing Γ_1 electrons. There are three more Wannier series (only one if spin-orbit effects are small) originating from spin-orbit split valence bands at X and terminating with excitons containing X_3 electrons, except in sodium and lithium salts which presumably have no low-lying X_3 minimum. At higher photon energies, excitons containing Γ_{12} and $\Gamma_{25'}$ electrons should contribute to the spectrum.

Onodera[7] recently calculated the band structure of CsI (Fig. 1). The original calculation was revised to fit the lowest energy exciton peaks. In contrast to KI there is no conduction-band minimum at X, but a Γ_{12} minimum is practically degenerate with the Γ_1 minimum. The exciton spectrum of CsI is unusual in that after the first peak there is a very sharp doublet.[8-10] Upon cooling, the first peak shifts to higher energy while the doublet shifts very slightly, if at all. Onodera assigns this doublet to excitons associated with the Γ_{12} minimum, whose wave functions are largely Cs^+ $5d$ functions.[11] We have measured the shift of the peak position of this doublet and of the first peak as a function of hydrostatic pressure.

Films of CsI about 1000 Å thick were evaporated on quartz substrates. The substrates were mounted in a sapphire-windowed pressure cell using helium as a pressure fluid, and cooled to 78°K to sharpen the exciton peaks. Absorption spectra were taken on a Cary 14R spectrophotometer. The resolution was poor because of high absorbance in the films, substrate, and optical system but was adequate for the purpose at hand.

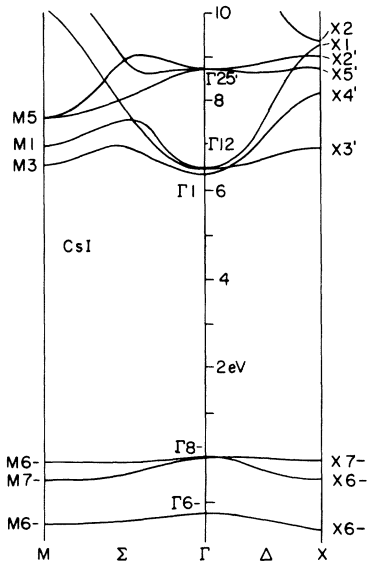

FIG. 1. Band structure of CsI according to Onodera (Ref. 7).

Figure 2 shows the exciton peaks at two pressures. Note that the doublet is not resolved. Spectra were taken for two films at a series of pressures to 3.4 kbar. Plots of exciton peak position versus pressure were straight lines with slopes $(\partial E/\partial P)_T$ of $+16.4\times10^{-6}$ eV/bar for the $\Gamma_8-\Gamma_1$ $n=1$ exciton and -16.5×10^{-6} eV/bar for the $\Gamma_8-\Gamma_{12}$ $n=1$ doublet. At zero pressure these peaks occured at 5.78 eV and 6.01 eV, respectively. The peak positions vary with film thickness; so exact agreement with the positions of the peaks of Ref. 9 is not expected. By using elastic constants[12] these slopes can be converted to deformation potentials of −2.10 eV ($\Gamma_8-\Gamma_1$) and +2.10 eV ($\Gamma_8-\Gamma_{12}$). The deformation potential for the $\Gamma_8-\Gamma_1$ transition is similar in both sign and magnitude to those for the corresponding transition in KI,[13] KBr,[13] AgCl,[14] and AgBr[14] (all NaCl structure) but not that of the first exciton transition, probably at Γ, in TlCl[14] and TlBr.[14] In the latter case, however, the symmetries of the states at the band edges may not be Γ_8- and Γ_1.

These measurements cannot determine at which point in the Brillouin zone the transition is occurring, unless band-structure calculations are made for several values of lattice parameter. Hence the $M_6-\rightarrow M_3$ transition or a transition at X (not likely from Fig. 1) cannot be ruled out. However, the great difference in deformation potentials for the two exciton peaks is good evidence that the excitons are derived from conduction bands of different symmetry.

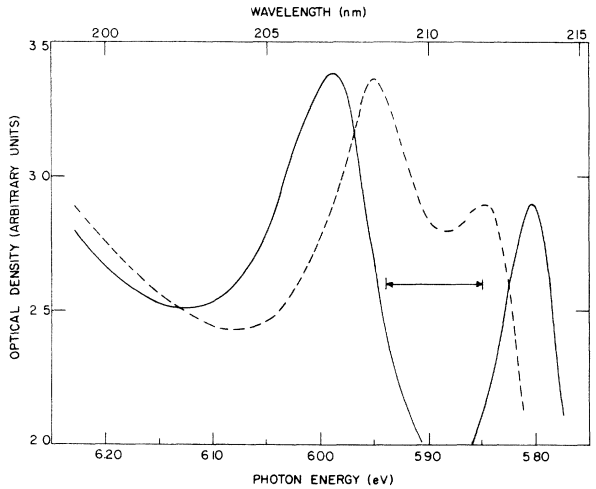

FIG. 2. Absorption spectrum of CsI film at 78°K at 1.05 kbar (solid line) and 3.38 kbar (dotted line). The arrow indicates the spectral band pass.

At a pressure of about 7 kbar, the Γ_1 and Γ_{12} excitons should occur at the same energy. At higher pressures, the lowest minimum should be the d-like Γ_{12}, not the usual s-like Γ_1. This should cause a change in a number of electronic properties.

Knof and Maisch[15] have measured the shift of the peak of the F-band absorption in CsI, taking most of their data above 10 kbar. Thus their data were taken on F centers for which the conduction-band minimum had Γ_{12} symmetry. We measured the shift of the F band in additively colored CsI at 78°K from 1 to 3 kbar, taking several points which fell on a straight line of slope $(\partial E/\partial P)_T=+11\times10^{-6}$ eV/bar. This is a higher slope than that found by Knof and Maisch, but the two values agree within an estimated combined limit of error of 20%. Not much difference in these coefficients is expected, for the F center levels involved here are, to first order, those of a free electron in a potential well, and the detailed nature of the conduction band is probably not important.

This work was stimulated by a preprint of Ref. 7 kindly supplied by Dr. Onodera to whom we are grateful.

---

†Work was performed at the Ames Laboratory of the U. S. Atomic Energy Commission.

*Present address: Department of Physics, St. Benedict's College, Atchison, Kan. 66002.

[1]S. Oyama and T. Miyakawa, J. Phys. Soc. Japan 21, 868 (1966).

[2]P. D. DeCicco, Phys. Rev. 153, 931 (1967).

[3]Y. Onodera, M. Okazaki, and T. Inui, J. Phys. Soc. Japan 21, 2229 (1966).

[4]T. D. Clark and K. L. Kliewer, Phys. Letters, 27A, 167 (1968).

[5]Y. Onodera and Y. Toyozawa, J. Phys. Soc. Japan 22, 833 (1967).

[6]G. Baldini and G. Bosacchi, Phys. Rev. 166, 863 (1968).

[7]Y. Onodera, to be published.

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

[9]J. E. Eby, K. J. Teegarden, and D. B. Dutton, Phys. Rev. 116, 1099 (1959).

[10]K. Teegarden and G. Baldini, Phys. Rev. 155, 896 (1967).

[11]A doublet occurs because the Γ_{12} minimum is not parabolic and a "triplet" exciton can be formed by an electric dipole transition. See Ref. 7.

[12]D. I. Bolef and M. Menes, Bull. Am. Phys. Soc., 427 (1959).

[13]V. Gerhardt and E. Mohler, Phys. Status Solidi 18, K45 (1966).

[14]A. D. Brothers and D. W. Lynch, Phys. Rev. (to be published).

[15]H. Knof and W. G. Maisch, J. Phys. Chem. Solids, 24 1625 (1963).

FLUX JUMP SIZE DISTRIBUTION IN LOW-κ TYPE-II SUPERCONDUCTORS

C. Heiden*†
Department of Physics, University of California, Berkeley, California

and

G. I. Rochlin‡
Department of Physics and Inorganic Materials Research Division,
Lawrence Radiation Laboratory, University of California, Berkeley, California

(Received 3 June 1968)

The size distribution of noncatastrophic flux jumps in cylindrical specimens of Pb+2 at.%-In alloys in an axial, homogeneous, linearly swept magnetic field has been measured as a function of field at 4.2°K and found to approximate the form $N(\varphi)=N(0)\times\exp(-\varphi/\bar{\varphi})$, where the mean bundle size $\bar{\varphi}$ was of the order of $10^2\varphi_0$ to $10^4\varphi_0$. The fraction of the entering flux participating in the jumps was found to have a field dependence similar to that of $\bar{\varphi}$. When surface superconductivity was present, the jumping persisted up to H_{c3}.

It is well known that the magnetic flux entering or leaving a solid cylindrical specimen of a type-II superconductor in an external, time-varying, axial magnetic field may do so by means of "flux bundles" composed of many individual fluxoids. Previous papers[1-3] dealing with flux penetration have reported primarily the occurrence of giant jumps of the order $10^8\varphi_0$ ($\varphi_0\equiv$ elemental fluxoid $\approx 2\times10^{-7}$ G cm^2), which arise from thermal runaway.[4]

We wish to report the measurement of the size distribution of flux jumps over the range $\sim10\varphi_0$ to $\sim10^4\varphi_0$ as a function of magnetic field for low-κ ($\approx$1.5) specimens of Pb+2 at.% In at 4.2°K; these specimens have an H_{c2} of 980 Oe and an H_{c1} of ~400 Oe at this temperature.

The specimens were in the form of circular cylinders approximately 60 mm long and 1.2 mm in diameter. They were prepared from 99.999%-pure metals by melting for several hours in a vacuum of 10^{-6} Torr, quenching in liquid nitrogen, and cold drawing through a die. They were then chemically polished and stored at 77°K to prevent annealing until used. The samples to be measured were placed in a homogeneous, axial magnetic field generated by a compensated copper solenoid. Flux jumps were measured with a small, tightly wound, 3600-turn pickup coil as the field was swept. Figure 1(a) is a schematic diagram of our apparatus. The flux jumps appeared as a set of irregularly shaped voltage pulses induced by flux bundles suddenly entering or leaving the sample, superimposed on a smoothly varying "dc" voltage due to flux entry via other mechanisms. These pulses were first electronically integrated and then converted into a narrow pulse whose height was proportional to the number of fluxoids in the bundle.[5] The size distribution of the bundles was then obtained directly by means of a 400-channel pulse-height analyzer. In order to accumulate good statistics over any narrow region of magnetic field, the field was swept up and down linearly from a small initial value below H_{c1} to fields above H_{c2}. Since the magnetization loops were closed, we could repeatedly take data over any convenient narrow field interval by using a gate to block the analyzer in all but the preselected region. Our basic sweep rate was 10 Oe/sec; the data were not altered by raising this rate to as high as 100 Oe/sec. The lack of dH/dt dependence indicates that thermal relaxation effects due to the heating produced by a flux jump played no significant role in our distributions.

The results of a typical run are shown in Fig. 1(b). The size distribution asymptotically approaches the form

$$N(\varphi)=N(0)e^{-\varphi/\bar{\varphi}} \tag{1}$$

which defines the mean bundle size $\bar{\varphi}$ for each curve. The two distributions shown in Fig. 1(b) were taken on the same sample at different values of H. In all cases, we observed deviations from a true exponential behavior at low values of φ. Some of this deviation can be explained by