antiferromagnetic NiO has been detected with a display-type LEED apparatus. (2) Exchange scattering accounts for the intensity of the observed "magnetic" beams.

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[1]C. G. Shull, W. A. Strauser, and E. O. Wollan, Phys. Rev. 83, 333 (1951); J. Singer, Phys. Rev. 104, 929 (1956); W. Roth, Phys. Rev. 110, 1333 (1958); Phys. Rev. 111, 722 (1958).
[2]P. W. Palmberg, Rev. Sci. Instr. 38, 834 (1967).
[3]Crystal obtained from Maubeni'iida Inc., Chicago, Illinois.
[4]P. W. Palmberg, T. N. Rhodin, and C. J. Todd, Appl. Phys. Letters 10, 122 (1967), and 11, 33 (1967).
[5]I. Marklund and S. Anderson, Surface Sci. 5, 197 (1966).
[6]L. A. Vredevoe and R. E. DeWames, to be published.
[7]R. E. DeWames and L. A. Vredevoe, Phys. Rev. Letters 18, 853 (1967).
[8]J. C. Slater, Phys. Rev. 81, 385 (1951).
[9]J. Waller, Z. Physik 38, 635 (1926).
[10]H. L. Cox and R. A. Bonham, J. Chem. Phys. 47, 2599 (1967).

EXCITON STRUCTURE OF TlCl AND TlBr †

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A study of both thick-crystal and thin-film optical absorption data for the thallous halides (CsCl crystal structure) indicates a direct band gap associated with the excitation of the thallous rather than the halide ions. Extremely narrow and very strong exciton lines exhibiting sidebands have been observed in thin films which are relatively free of strain. A very small exciton binding energy, a high polarizability, and large electron-lattice interaction favor this sideband structure which is probably due to coupled exciton-phonon states.

The thallous halides TlCl and TlBr are highly polarizable ionic crystals with characteristic optical absorption which begins in the near-ultraviolet region of the spectrum. A variety of optical data on these interesting materials can be found in the literature,[1-4] and most of this indicates a direct band gap although indirect transitions have also been suggested.[1] Recently two-photon absorption has been reported.[5] Transport experiments[6] on TlCl indicate that both electrons and holes are mobile, and even cyclotron resonance for photocarriers has recently been observed.[7] In this Letter we describe optical measurements at helium temperature on both thick crystals and thin films. Very strong and extremely narrow exciton lines can be observed in thin films of TlCl and TlBr by utilizing a new technique to control the effects of strain. It is found that both TlCl and TlBr have a direct gap with first exciton lines due to excitations centered upon the Tl^+ ions rather than upon the halogen ions as in the alkali and silver halides. Moreover, sidebands, probably due to coupled exciton-phonon states, are observed.[8]

A cryostat and Cary Model 14R spectrophotometer were used to study the absorption edge of thick polished samples of the thallous halides from room down to liquid-helium temperatures. No structure was found in the thick-crystal data, and the edge obeyed Urbach's rule. Entirely similar behavior was observed in crystals of TlBr as well as in TlCl.[9] As the temperature is lowered the edge becomes steeper but this apparent shift of the tail to shorter wavelengths is opposed by the shift of the first exciton peak to longer wavelengths as noted by earlier workers.[1,2] The origin of a positive $(\partial E/\partial T)_p$ for the exciton peak is discussed by Brothers and Lynch[10] who also show that the sign and magnitude of the pressure coefficient is rather similar for both the peak and the tail as would be the case for a direct exciton material with no underlying absorption process toward long wavelengths.

To study the strong optical absorption beyond the tail and edge region, one can use either transmission with thin films or reflection from single crystals. The latter is difficult to carry out with precision since the thallous halides do not readily cleave and highly polished undamaged surfaces are difficult to prepare. We have employed thin films and used the two-thickness subtraction method which corrects for surface re-

flectivity and allows one to determine the absorption constant α.

One of the major problems in thin-film work is the large stresses that are set up due to the deposition of the film and due to differential thermal expansion as the temperature is changed. These stresses result in gross shifts in peak position, associated with a hydrostatic component of the stress; and in the removal of electronic degeneracy associated with noncubic components of the stress. Nonhomogeneity of these effects can also lead to broadening of the lines and further mask the intrinsic linewidths. These effects can be large and any attempt to compare thin-film experiments with theories of line shapes and linewidths must take them into account. Another problem is that the stress effects are thickness dependent as has been quantitatively demonstrated by Ennos.[11]

The films used in the present work were formed on room-temperature substrates of silica (optical flats of Ultrasil), freshly cleaved KCl or KBr, and thin (250-Å) organic substrates of both Formvar and Lucite.[12] The organic substrates were placed unsupported over a hole drilled in a thick polished thallous halide crystal in order to reduce strains upon cooling to liquid-helium temperatures. This technique is very successful and should be applicable to other materials. The samples to be studied were evaporated in a vacuum of 10^{-6} Torr. Thickness was determined during evaporation by a quartz-crystal monitor calibrated by the Tolansky method. Films were transferred to the measuring cryostat in an atmosphere of dry nitrogen.

The thin Lucite substrates mounted over a hole in a crystal were least subject to strain effects and results for these will be discussed first. All of the features which we report have proved to be highly reproducible. Figure 1 shows the absorption coefficient for a relatively strain-free film of TlBr on Lucite measured at 4.7°K. The first exciton peak at 4120 Å or 3.009 eV is shown in more detail in Fig. 2. In TlCl a similar sharp first peak is found at 3642 Å or 3.404 eV. The interesting features here are the extreme narrowness and height as compared with previously reported results. In TlBr at 4.7°K the width at half-maximum is about 5 Å or 3 meV with a maximum absorption of 10^6 cm^{-1}. Earlier workers[1-4] have reported widths around 40 meV and peak absorption coefficients of 10^5 cm^{-1} or less.

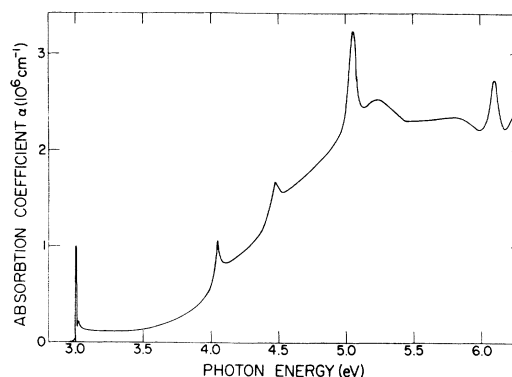In some cases the narrow line shown in Fig. 2

FIG. 1. Absorption coefficient versus photon energy for TlBr on unsupported Lucite at 4.7°K. The first and fourth peaks are associated with transitions on Tl$^+$ and the second and third with transitions on the Br$^-$.

is found to be a doublet with peak separations of about 2 meV. As will become clear, the splitting arises from the lifting of electronic degeneracy by residual strains. The customary halogen doublet[13] (due to spin-orbit interaction) which would be some 50 times larger than the above-mentioned splitting in the chloride and 200 times larger in the bromide is not observed in these spectra in the vicinity of the first peak. This is strong evidence for assigning the initial absorption and band gap to excitation of the $6s^2$ electrons on Tl$^+$ to an excited $6s\,6p$ (^3P) configuration of the same ion. We assume that the ^3P levels of the ion lie well below the ^1P as is the case for the free ion (jj coupling) or the ion as an impurity in an alkali halide. The first exciton peak might then be associated with a spin doublet
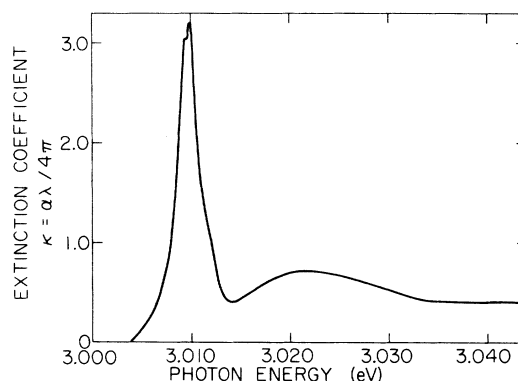

FIG. 2. Extinction coefficients versus photon energy for TlBr on unsupported Lucite at 4.7°K. The structure in the main peak is due to residual stress effects. It is suggested that the sideband results from LO phonon emission modified by the exciton−LO-phonon coupling.

or $\Gamma_6{}^+$ valence band and a fourfold degenerate, including spin, $\Gamma_8{}^-$ conduction band. (The degeneracy of the exciton made up from these band states is slightly lifted by residual uniaxial strain or possibly by dynamic Jahn-Teller effect.)

As one goes to higher energies than the first exciton peak in Fig. 1 three previously reported lines are observed. The two well-resolved peaks at 4.046 and 4.469 eV are almost certainly due to the halogen doublet on the bromine [two lines with appropriately reduced spin-orbit splitting (0.1 eV) are found in TlCl near 5 eV]. The sharp line at 5.04 eV in Fig. 1 may be due to excitation of the thallium to a configuration corresponding to $^1P_1$. The remaining three maxima in the structure above 5.2 eV in Fig. 1 are new features whose interpretation awaits a detailed band calculation.

The most important new feature of the present work is the weak broad band which begins a few meV to the high-energy side of the first exciton line and is best seen in Fig. 2. In both TlBr and TlCl, the sideband peak occurs at (0.82 ± 0.05) $\times \hbar \omega_l$ where $\hbar \omega_l$ (the longitudinal optical phonon energy) is 14.3 meV for TlBr and 21.6 meV for TlCl.[14] Although weak and not well defined, another much broader band is discernable at about twice this energy. The integrated oscillator-strength ratio of the main peak to the first sideband is about 3 to 1 in the bromide and 4.5 to 1 in the chloride measured with respect to the continuum background. Although one might first think this band is due to higher exciton states, the evidence does not bear this out. Most important, the oscillator-strength ratio between this band and the first line is inconsistent with the Elliot theory.[15] Also, in going from the bromide to the chloride which has a higher dielectric constant, one would expect the binding energy and therefore the peak separation to decrease, but in fact the opposite occurs. The spacing scales with the phonon energy. If one assumes that the sideband peak begins at approximately the $n = 2$ line of an exciton series, the strength remaining to the high-energy side is inconsistent with this assumption. Thus in fact the width, strength, and spacing of the sideband from the main peak are difficult to reconcile with this structure being due to higher exciton states. We suggest that this band is associated with a new type of phonon emission process in which the exciton and phonon form a bound state through the exciton-phonon interaction. This coupled state occurs at an energy below $\hbar \omega_l$.[16]

The temperature dependence of the main exciton line in TlBr is very marked. Between nitrogen and helium temperatures there is about a sixfold enhancement in the peak absorption and a corresponding narrowing in the linewidth. The peak position also shifts considerably to short wavelengths with increasing temperature. The spacing between sideband and main exciton line remains constant, however, and the sideband height and width are little affected by changes in temperature. The interpretation of these temperature effects is complicated because of residual stress effects. Above 25°K, however, one can characterize the half-width as increasing linearly with temperature and below 25°K the half-width is less sensitive to temperature.

When the thallous-halide films are deposited upon silica or alkali-halide substrates, the spectra are greatly broadened and weakened. For alkali-halide substrates, the structure in the first peak, which is barely discernable on "strain-free" substrates, becomes very highly resolved. Typically one sees two distinctly different lines, one very sharp with a full width of about 5 Å and the other very broad with a width or roughly 20 Å. The separation between these lines can be as much as 30 Å depending upon the strain. In order to show that such splitting was not specific to the substrate the thallous halide was deposited on a Lucite film mounted over a hole in a copper holder instead of a thallous-halide crystal holder. A splitting similar to but smaller than for the alkali-halide substrates was observed.

Several auxiliary experiments were carried out with the alkali-halide substrates. One involved externally applying a uniaxial stress with the result that a movement of the exciton peak position could be discerned as well as a linear dichroism signal. Such effects were reversible as long as the substrate was not plastically deformed. The birefringence of the strained film was also investigated with polarized light. These various experiments indicate that the structure observed in the main exciton peak is associated with the removal of degeneracy by noncubic components of stress. The noncubic stress at low temperature was reduced by almost a factor of 20 or more in going from the alkali halide or silica substrates to the organic substrates supported on the thallous-halide crystals. Comparison of peak shifts and hydrostatic pressure coefficients[10] indicates that the hydrostatic stresses in some films were equivalent to 2000 atm.

In addition to the foregoing experiments, Faraday-rotation scans on both strained and unstrained films were taken which indicate the strong oscillatorlike nature of the first exciton peak. Further results will be reported elsewhere.

Finally, a few comments should be made on the exciton binding energy in these materials. Even though the first peak is very sharp, an exciton series including $n = 2$ and higher states has not been resolved.[17] The reason for this could be a combination of acoustic-phonon broadening and residual strain effects. If the higher states underlie the first peak, the binding energy would be at most about 6 meV at $4.7°K$. If one estimates the binding energy from the ratio of the area of the first peak to the continuum intensity, one finds a value of the order of 12 meV. It is likely that the binding energy lies within or close to this range. TlCl has a static dielectric constant ϵ_S of 37 and TlBr 35,[14] whereas the optical constants ϵ_∞ are about 5.1 and 5.4, respectively. The observed cyclotron resonances[7,8] for TlCl can reasonably be interpreted as due to an electron polaron mass of $0.53m_e$ and a hole polaron mass of $2.72m_e$ where m_e is the free electron mass. These parameters yield a reduced polaron mass of $\mu = 0.43m_e$ and therefore the $n = 1$ state of a Wannier exciton in TlCl using a hydrogenlike model with polaron masses and static dielectric constant would have a binding energy of $(13.6 \text{ eV}) \times \mu/m_e \epsilon_S^2 = 4.3$ meV. For the same masses TlBr would have an exciton binding energy of 4.8 meV. These compare favorably with the binding energy estimated above and indicate that the use of the high-frequency dielectric constants may not be appropriate even in absorption because of the large radii involved.

The optical absorption in the first exciton band of the thallous halides appears to produce bound polaron states, that is, eigenstates of the electron-phonon system. The important frequency in this regard is not that associated with the energy gap, but the frequency associated with the final particle velocities and lattice frequencies. (A similar conclusion was also reached in interpreting recent experiments for the silver halides and for $n = 2$ and higher exciton states of the alkali halides[7,18] where use of the static dielectric constants and polaron masses appear most appropriate.) In this sense, the first absorption line in the absence of strain can be considered as a zero-phonon line (at least with respect to LO phonons) broadened by acoustic-phonon interactions.

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[1]H. Zinngrebe, Z. Physik 154, 495 (1959). See also W. Martienssen, J. Phys. Chem. Solids 8, 294 (1959).

[2]S. Tutihasi, J. Phys. Chem. Solids 12, 344 (1960).

[3]I. Lefkowitz, R. P. Lowndes, and A. D. Yoffee, J. Phys. Chem. Solids 26, 1171 (1965).

[4]D. C. Hinson and J. R. Stevenson, Phys. Rev. 159, 711 (1967).

[5]M. Matsuoka, J. Phys. Soc. Japan 23, 1028 (1967); M. Matsuoka and T. Yajima, Phys. Letters 23, 54 (1966).

[6]T. Kawai, K. Kobayashi, and H. Fujita, J. Phys. Soc. Japan 21, 453 (1966).

[7]J. Hodby, J. Borders, and F. C. Brown, Phys. Rev. Letters 19, 952 (1967); H. Tamura and T. Masumi, J. Phys. Soc. Japan 23, 1173 (1967).

[8]W. C. Walker, D. M. Roessler, and E. Loh, Phys. Rev. Letters 20, 847 (1968).

[9]The transient photoconductivity of the thick crystals was also measured at low temperature and found to be coincident with the edge. This is not surprising considering the very small exciton binding energy of the thallous halides as discussed below.

[10]A. Brothers and D. Lynch, to be published.

[11]A. Ennos, Appl. Opt. 5, 51 (1966).

[12]The Lucite was dissolved in ethylene dichloride with a trace of Formvar present.

[13]R. S. Knox and N. Inchauspe, Phys. Rev. 116, 1093 (1959).

[14]R. P. Lowndes, Phys. Letters 21, 26 (1966). The LO frequency is calculated from the low-temperature transverse optical and dielectric constant data using $\omega_l = (\epsilon_S/\epsilon_\infty)^{1/2}\omega_t$.

[15]R. J. Elliot, Phys. Rev. 108, 1384 (1957).

[16]A theory of the coupled exciton-phonon state has recently been worked out by Y. Toyozawa and J. Hermanson and will appear soon.

[17]Lefkowitz et al. (Ref. 4) estimate a binding energy as large as 85 meV but the peaks upon which they base this estimate were not reproduced in the present investigations (see Fig. 1).

[18]R. C. Brandt and F. C. Brown, in Localized Excitations in Solids, edited by R. F. Wallis (Plenum Press, Inc., New York, 1968).