tion, for which helicons can propagate. In evaluating $\xi_+(z)$ we have neglected the change in dispersion of both the helicons and phonons caused by helicon-phonon coupling.

[13] If we take $\tau \approx 10^{-10}$ sec, $a \approx 1.25$ corresponds roughly to the low-frequency slow shear wave of Ref. 3. The curves seem qualitatively similar to the data of Ref. 3.

[14] No discussion of this point is given in Ref. 3, so it is difficult to make more than a qualitative comparison with the experimental data presented there.

# DOUBLE-DONOR-ACCEPTOR PAIR LINES AND THE CHEMICAL IDENTIFICATION OF THE $I_1$ LINES IN CdS

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We report a new type of pair-line spectrum, namely, the recombination of a double neutral donor with a shallow neutral acceptor. An isotope shift in this pair-line spectrum proves that the acceptor is lithium. This identification, together with the results of chemical doping experiments, provides strong evidence that the $I_1$ lines in CdS are due to Li and Na.

During the last ten years the edge emission in CdS and other II-VI semiconductors has been intensively studied. It has been established that the low-temperature edge emission consists primarily of bound exciton,[1,2] pair recombination,[3,4] and free-to-bound transitions[3-5] involving shallow donors and acceptors. During this time very little progress has been made in establishing the chemical nature of the shallow donors and acceptors. While a few emission lines due to particular donors have been identified, it is known that many of the group III*A* and VII*A* impurities form substitutional donors in CdS[6,4] and that most or all donors in CdS have very similar properties, such as a binding energy of about 33 meV.[7] The situation is quite different for the acceptors. Only two prominent $I_1$ lines (excitons bound to shallow neutral acceptors) have been observed in CdS. To distinguish these two $I_1$ lines, we will call the one at 4888.53 Å $I_{1a}$ and the one at 4888.20 Å $I_{1b}$. The chemical nature of the acceptors responsible for these $I_1$ lines has been a mystery up to now, although several authors have suggested[4,8] that they are Cd-vacancy–donor complexes, but on the basis of weak evidence. From the Zeeman experiments of Thomas and Hopfield,[1] all we know for sure is that the acceptors have high symmetry and that, therefore, they must be either substitutional or interstitial impurities or complexes aligned along the *c* axis. The binding energies of these two acceptors is determined from the position of the distant pair band to be about 165 meV.[4,9]

In this Letter we report a new type of pair-line spectrum due to the recombination of a double neutral donor (two electrons bound to a charge of $+2e$) and a shallow neutral acceptor. The shallow acceptor is identified as Li from an isotope shift associated with these pair lines. This identification, together with chemical doping experiments and the existing knowledge about deep acceptors, provides strong evidence that $I_{1a}$ and $I_{1b}$ are due, respectively, to Li and Na acceptors on a Cd site.

The pair-line spectrum is shown in Fig. 1. There are a series of sharp lines which converge at low energies in the same manner as ordinary donor-acceptor pairs. These lines have a different magnetic behavior than ordinary donor-acceptor pair lines in CdS. Normal pair-line transitions have a coupled electron and hole in the excited state and no paramagnetism in the ground state.[9] By contrast these pair-line transitions (Fig. 1) behave as if they have a single uncoupled hole in the excited state and a single uncoupled electron in the ground state. We were able to show that the paramagnetic hole is in the excited state by observing the thermalization of the pair-line Zeeman pattern in absorption. There were three pair-line transitions between $I_1$ and $I_2$ which were intense enough to observe in absorption. We believe a pair-line spectrum with these magnetic properties can arise only from the recombination of a neutral double donor and an ordinary neutral acceptor.

Each pair line was accompanied by a second weaker line shifted to lower energy (Fig. 1). The second line is due to a naturally abundant isotope of either the donor or the acceptor impurity. The isotope shift was $0.19 \pm 0.01$ meV for the more distant pair lines and decreased to zero for the pair lines near the $I_1$ line and at higher

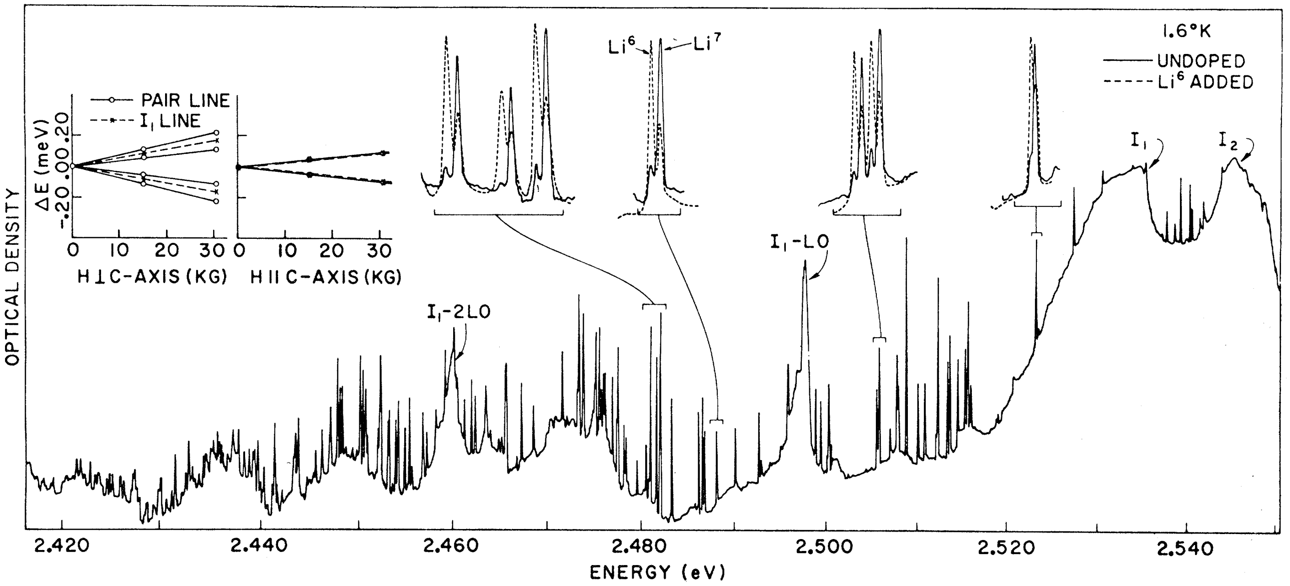

FIG. 1. The pair-line spectrum, the $I_1$ line (actually $I_{1a}$), and the $I_1$ LO phonon replicas; inserts show the isotope shifts of several pair lines and Zeeman splittings of a typical pair line and of the $I_1$ line.

energy. From photomultiplier measurements of the ratio of the two lines, we found the abundance of the less abundant isotope to be about (8 ± 1.5)%. The only atoms with two common isotopes near this ratio are Li, K, and Ne. Both Li and K are possible substitutional acceptors on the Cd site. A series of chemical doping experiments (discussed later) showed that Li is incorporated in CdS, but K is not. We then confirmed that the acceptor was Li by observing the pair spectrum in samples doped with $Li^6$ (Fig. 1).

Double donors may arise from S vacancies, Cd interstitials, or group-IV impurities. We have produced this pair spectrum by growing undoped platelets (or platelets lightly doped with $Li^6$) by sublimation and annealing the crystals immediately after growth with a small pressure of Cd. These conditions favor S vacancies or Cd interstitials. While we have not been able to analyze the pair-line spectrum in detail, it appears to have the features expected of a type-II spectrum[9] (one in which the donor and acceptor are on different sites). Thus we tentatively identify the double donor as an S vacancy.

The pair-line spectrum is much more intense than ordinary donor-acceptor pair-line spectra previously observed in CdS,[9] yet we could find no distant pair peak accompanying this spectrum. These facts are explainable if we assume that the pairs are not randomly distributed but have migrated to relatively close separations. The distant pair-line energies are given by

$$E = E_{\text{gap}} - E_A - E_D + e^2\{\epsilon_\perp \epsilon_\parallel [x^2 + y^2 + (\epsilon_\perp/\epsilon_\parallel) z^2]\}^{-1/2}. \qquad (1)$$

The 98th pair line, corresponding to a separation of 17.2 Å and a Coulomb energy of 93.1 meV, occurs near 2.448 eV. Assuming that Eq. (1) is valid for this separation, we conclude $E_A + E_D = 228 \pm 10$ meV. $E_D$ is the energy required to remove one electron from a double neutral donor. In analogy with the problem of atomic helium,[10] this energy should be about 1.8 times the hydrogenic donor binding energy, or about 60 meV. Using the value of $E_A + E_D$, we conclude that $E_A(\text{Li}) = 168 \pm 10$ meV.

The hole $g$ value for $H \perp c$ axis, $g_\perp$, is zero for isolated shallow acceptors in CdS. For most donor-acceptor pairs, the symmetry of the acceptor site is lowered by the presence of the donor. We expect this perturbation to mix the low-lying $1s\Gamma_7$ excited state into the $1s\Gamma_9$ ground state. In first order, this mixing causes $g_\perp$ to be nonzero, but does not alter $g_\parallel$.[9] As expected, $g_\perp$ was often nonzero for the pair lines and when $g_\perp$ was small, the pair lines (except for the very close pairs) had exactly the same value of $g_\parallel$ as for the acceptor giving rise to the $I_1$ line. The splittings of a typical pair line are compared with the $I_1$ line in Fig. 1.

A strong $I_{1a}$ line accompanied the pair spectrum. $I_{1a}$ is always found in our undoped CdS platelets. The Li pair spectrum was found in undoped crystals. Doping with 95% enriched $Li^6$ only increased the $Li^6/Li^7$ ratio to 2:1. This indicates that Li is probably a common contaminant of undoped CdS crystals.

Since the two $I_1$ lines are so similar it is very likely that they are both due to alkali atoms. In fact, it was surprising at first that there were only two $I_1$ lines when there are five alkali atoms. An attempt was made to dope CdS crystals during growth by sublimation with Li, Na, K, Rb, and Cs. Both the broadening of the luminescence lines by doping, and spectrochemical analysis, indicated that only Li and Na appeared to dope the crystal. These results confirmed previously published studies showing that Li and Na are readily incorporated in CdS[6, 11, 12] while K is not.[12, 13] The covalent radii of Li, Na, K, Rb, Cs, and Cd are, respectively, 1.34, 1.54, 1.96, 2.11, 2.25, and 1.48.[14] Only Li and Na are close to Cd in size. K, Rb, and Cs are apparently too big to be incorporated substitutionally. Li-doped crystals gave only the $I_{1a}$ line, while the $I_1$ luminescence of the Na-doped crystals was dominated by $I_{1b}$. From these doping experiments, from the correlation of $I_{1a}$ and the pair lines, and from the fact that the Li acceptor has the correct binding energy and $g$ value, we conclude that $I_{1a}$ is due to Li and that $I_{1b}$ is due to Na.

This assignment is consistent with the existing knowledge about acceptors in II-VI compounds. The experiment of Handelman and Thomas,[8] showing that the $I_1$ lines are destroyed by annealing in excess Cd, is understandable, since such treatment will force impurities substituted for Cd out of these sites. ESR studies by Holton et al.[15] have shown P and As to be deep acceptors in ZnSe. Tell[16] has recently provided optical evidence that these acceptors are about 1 eV deep in CdS. The Cd-vacancy–donor complexes suggested as shallow acceptors by Thomas, Dingle, and Cuthbert[4] are similar to the Zn-vacancy–donor complexes shown by ESR to be deep acceptors in ZnS and ZnSe.[17] ESR experiments of Kasai[18] and Shirmer[19] have shown Li to be a fairly deep acceptor in ZnO. This does not contradict our assignment of Li as a shallow acceptor (binding energy ≈ 165 meV) in CdS, since no edge emission due to shallow acceptors, analogous to the green edge emission in CdS, occurs in ZnO.[20]

Hopfield[21] has suggested that acceptors on Cd sites are likely to be shallower than acceptors on S sites because in more ionic semiconductors, such as CdS, the holes will reside primarily on the negative-ion sites and therefore central cell corrections for acceptors substituting for positive ions will be small.

Our identification of Li and Na as the shallow acceptors can provide a possible explanation of why CdS and similar II-VI compounds cannot be made to have $p$-type conductivity: It may be that the formation of these acceptors is accompanied by the simultaneous entry of Li or Na into interstitial sites to form compensating donors.

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