PHYSICAL REVIEW B VOLUME 33, NUMBER 2 15 JANUARY 1986

Optical study of complex formation in Ag-doped CdTe

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(Received 3 June 1985)

The thermal instability of substitutional Ag doping on Cd sites in CdTe is studied with optical spectroscopy. For Ag doping levels above 10^{16} cm^{-3} the $\mathrm{Ag_{Cd}}$ concentration decreases gradually during several months while complex defects are formed, as evidenced by the evolution of low-temperature bound-exciton spectra. In particular, such a bound exciton (BE), X_2^{Ag}, at 1.5815 eV has been studied in this work, as a typical example of complex Ag-related defects created in the course of release of Ag from Cd sites. A rich phonon spectrum is found to couple to this BE, as expected for a complex defect involving an interstitial species. Dye-laser-excited photoluminescence excitation (PLE) spectra reveal a single lowest BE state, with an orbitally excited (electron) state 8.6 meV higher. An activation energy of 8.8 meV is also found for the thermal quenching of the X_2^{Ag} PL emission, interpreted as an $1s$-$2s$ rate-limiting excitation of the electron in the BE, in good agreement with PLE data. Zeeman splitting of the 1.5815-eV X_2^{Ag} BE line is consistent with the assumption of an electron-hole pair bound to a neutral "isoelectronic" defect of a symmetry lower than tetrahedral. Further, the local potential of this defect is predominantly hole attractive, while the electron is loosely bound in a shallow donorlike state. The hole is a $m_z = \pm\frac{3}{2}$ state, as expected for an average tensional local strain field. A tentative identification is discussed in terms of a $\mathrm{Ag_{Cd}}$-Ag_i pair, assumed to be produced by the spontaneous release of $\mathrm{Ag_{Cd}}$ into interstitial (i) sites, with a rather high mobility of the Ag_i interstitial also at room temperature. An alternative defect model, a pair of a Cd vacancy and an Ag_i interstitial, cannot presently be excluded, however. A similar thermal instability of $\mathrm{Cu_{Cd}}$ at a slightly higher doping level is found not to produce strong new BE spectra as for the $\mathrm{Ag_{Cd}}$ case.

I. INTRODUCTION

CdTe is a direct-band-gap semiconductor of great future potential for applications in, e.g., optoelectronic devices, due to the relative ease in preparing both n-type and p-type materials with low resistivity, a rather unique feature for II-VI compounds.[1] The material has a band gap of ≈ 1.60 eV at low temperatures,[1] i.e., slightly higher than GaAs and InP, and has similar favorable properties regarding carrier mobilities and luminescence efficiencies.[2] In the past the emphasis on studies of II-VI materials was on the compounds with higher band gaps such as ZnSe, ZnTe, ZnS, and CdS, materials which still offer fundamental difficulties in applications, since so far they cannot be prepared in both n-type and p-type forms with low resistivity.[3]

Only recently more fundamental efforts have been made to explore the defect-related properties of CdTe, relevant for all applications in devices. The most common shallow substitutional acceptors in CdTe have recently been identified and characterized.[3-6] Even in the highest purity material available, contamination with Cu and Ag was always present.[3-6] These Cd-site acceptors are candidates for p-type doping purposes since they can easily be introduced by diffusion in high concentrations in the material.[4,6,7]

A phenomenon that has recently been recognized in CdTe is the apparent lack of stability of these substitutional acceptors even at moderate doping levels ($\geq 10^{16}$ cm^{-3}). One observes that after long-term storage at room temperature (of the order of several months) the fraction of substitutional acceptors decreases dramatically, and instead complexes are formed. This process has been studied in some detail for Ag doping,[8] but has been found to occur for Cu also.[9] The stability of other acceptors has not yet been investigated, to our knowledge. Since these complex phenomena, in general, act to reduce drastically the free-hole concentration in p-type CdTe, they may cause severe problems in devices. It seems therefore important to investigate the basic processes behind such substitutional doping instabilities.

The subject of the present paper deals with this problem. We have undertaken a detailed optical study of the complex formation occurring in Ag-doped CdTe upon room-temperature storage. The ultimate goal is naturally to identify the resulting defects, so that the complexing mechanism for creation of complexes can be modeled. In this paper we shall concentrate on perhaps the most prominent X_2^{Ag} complex defect occurring in the process of reducing the substitutional Ag doping level in CdTe, with a bound-exciton (BE) recombination line at 1.5815 eV at low temperature.[8] (This defect was labeled C_1 in earlier work.) A detailed optical study of this center, including photoluminescence (PL), dye-laser-excited PL excitation spectra (PLE), and Zeeman perturbation spectroscopy, has been undertaken and will be presented in this paper. We are able to conclude, from the detailed properties of the Zeeman splitting of the 1.5815-eV BE line, that the complex defect created is, in fact, of neutral "isoelectronic" character in this case. A tentative model for the identity and the formation of the complex is discussed in terms of a predominant interstitial migration process.

In Sec. II below we describe briefly the procedure of materials preparation and doping, as well as details of the experimental techniques used in the optical measurements. The experimental data are presented in Sec. III, beginning with PL spectra in Sec. III A. Section III B contains a brief account of transmission spectra at 2 K. The phonon coupling to this complex is very complicated and rich in structure, as shown in detail in Sec. III C. Included here is also a careful analysis of the temperature quenching of this bound-exciton line, revealing drastic spectral changes induced by the phonon coupling. The temperature dependence of the PL intensity is discussed in Sec. III D, and gives the activation energy for the electronic thermal quenching process for this BE emission. PLE data for the 1.5815-eV bound-exciton emission taken with tunable dye-laser excitation are displayed and discussed in Sec. III E. Section III F contains the Zeeman data in PL absorption and emission for the 1.5815-eV BE line, interpreted in the context of a complex isoelectronic Ag-related defect.

Section IV contains a more extensive discussion on the two main topics treated in this study, i.e., the electronic structure of a complex isoelectronic center in this material, and the possible identity of this complex. We show in Sec. IV A that the electronic structure observed for this BE is consistent with the Hopfield-Thomas-Lynch (HTL) model[10] usually adopted for neutral (isoelectronic) bound excitons (IBE)'s in semiconductors. In addition, the symmetry of the local crystal field at the defect is found to be lower than tetrahedral. This leads naturally to a simple model for the identity of the complex: a substitutional Ag atom on a Cd site, together with one interstitial Ag, as discussed in Sec. IV B. An alternative model in terms of a Cd-vacancy—Ag-interstitial pair is also discussed.

In Sec. IV C a brief comparison with similar data for Cu-doped CdTe is included, and the possible defect reactions involved are discussed. Finally, in Sec. V we give a brief summary of the basic physical properties revealed for such a model system of a complex IBE, together with suggestions on future work relevant for these problems of defect formation and defect stability in CdTe.

II. SAMPLE PREPARATION AND EXPERIMENTAL PROCEDURE

The base material used in this study was CdTe crystals grown by a modified Bridgman method (B. Schaub, Laboratoire d'Electronique et Technologie del'Informatique, Centre d'Etudes Nucleaires de Grenoble, Grenoble, France. When nominally undoped they were high-purity p-type with a residual acceptor concentration $N_A - N_D = 5\times 10^{14}$ cm^{-3}. The material was provided in polycrystalline slices of thickness about 1 mm. Single crystals of a typical size of 5×5 mm^2 could easily be cleaved from such wafers, and used in further diffusion experiments. Ag was normally introduced by a two-step diffusion procedure with a final diffusion under a Te atmosphere at about 800 °C for several hours, to obtain a reasonably high level of substitutional doping ($\geq 10^{16}$ cm^{-3}) and a low level of initial complex concentration.[5,8] Samples were polished and etched in a 2% Br—methanol solution prior to optical measurements.

Photoluminescence spectra were obtained with excitation by a Kr$^+$-pumped tunable cw dye laser employing an Oxazine 725 dye. For PLE spectra the dye-laser wavelength could be continuously scanned over the region 7400—8200 Å with an energy resolution of about 0.1 meV. The PL signal was detected via a 0.5-m double-grating monochromator with a GaAs photomultiplier and standard lock-in techniques. For Zeeman spectra a superconducting magnet with a maximum field of 4.5 T was available, in which Zeeman spectra were recorded in the Faraday configuration. Also, a 10-T magnet was available, where Zeeman spectra were recorded in the Voigt configuration.

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. Photoluminescence spectra for the Ag-related 1.5815-eV bound-exciton line

In Fig. 1 we show typical PL spectra at 1.6 K for a p-type Ag-doped CdTe sample, measured a few days after preparation (curve a) and after about one year's storage at room temperature (curve b). The most prominent bound-exciton feature in the freshly Ag-doped sample is the A_1^{Ag} line at 1.5885 eV, previously identified as due to recombination of an exciton bound to a substantial neutral Ag$_{\mathrm{Cd}}$ single acceptor.[11] Clearly, upon aging the intensity of this A_1^{Ag} line decreases dramatically, and in curve b it no longer dominates the near-band-gap PL spectrum. The A_1^{Cu} line, which was originally present due to Cu contamination at a concentration lower than the Ag doping, is now actually dominating, since the Cu$_{\mathrm{Cd}}$ acceptors are stable in this concentration range ($<10^{16}$ Cu atoms per cm^3). Two new BE lines occur in Fig. 1(b), as a result of the degraded Ag$_{\mathrm{Cd}}$ concentration, one at 1.5880 eV (here called X_1^{Ag}) and another at 1.5815 eV (X_2^{Ag}). Both these BE lines have a greater intensity than the A_1^{Ag} line at 1.5885 eV. We attribute these new lines to complex defects created in the process of Ag migration out of the substitutional Ag$_{\mathrm{Cd}}$ sites. The identification of X_2^{Ag} as a neutral (isoelectronic) complex is provided by Zeeman data to be reported below. Unfortunately the X_1^{Ag} line at 1.5880 eV never completely dominated the A_1^{Ag} line in our crystals. Zeeman data of this line could therefore not be taken due to interference with the nearby A_1^{Ag} line at 1.5885 eV even at very low magnetic fields. Therefore we have no direct proof of whether the X_1^{Ag} defect is a neutral complex or a complex acceptor.

The energy position of the X_1^{Ag} BE line does not give

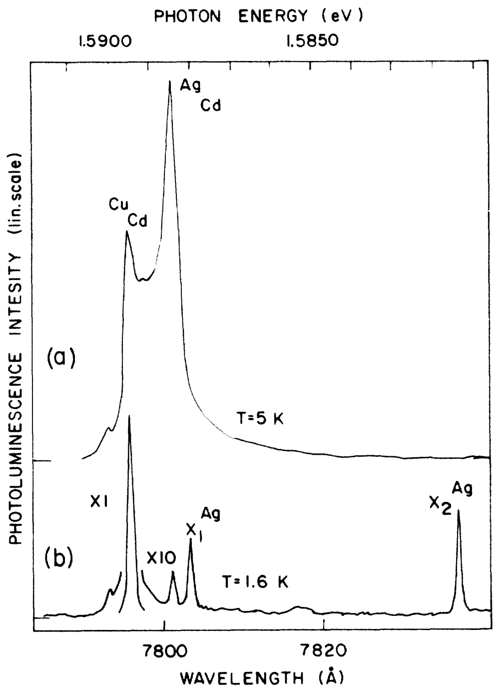

FIG. 1. (a) Photoluminescence spectrum of a Ag-doped CdTe sample measured one day after the Ag diffusion. The Ag_{Cd} line at 1.5885 eV is the bound exciton associated with the substitutional Ag_{Cd} acceptor. The Cu_{Cd} line at 1.5896 eV is due to a similar BE associated with Cu_{Cd} substitutional acceptors, accidentally introduced by contamination during the final Ag diffusion procedure (800 °C, 4 h, Te atmosphere). (b) Similar PL spectrum for the same sample as in *a* measured one year after the diffusion procedure. The sample had been stored at room temperature during this period. The Ag_{Cd} line has decreased in relative importance, while two new lines X_1^{Ag} at 1.5880 eV and X_2^{Ag} at 1.5815 eV appear, due to formation of Ag-related complex defects. Narrower lines in *b* are due to a lower sample temperature in the measurement, as compared to *a*.

any hint regarding these two possibilities, since no "Haynes rule" is valid for the acceptor BE's (ABE's) in these materials.[6] Actually, it has recently been found that the substitutional Au_{Cd} acceptor has a deep ABE line at 1.576 06 eV,[7] even deeper than the X_2^{Ag} IBE. No two-hole spectra are observed upon resonant excitation in the X_1^{Ag} line at 1.5880 eV, which might indicate that this complex defect is also neutral as X_2^{Ag}. It could also be a deep acceptor, however, in which case two-hole spectra are usually very weak, particularly since the radiative PL efficiency was very low in the aged Ag-doped samples. Consequently, we shall restrict our detailed discussion on the physical properties of the Ag-related complexes to X_2^{Ag} ($C1$), which is well isolated from other electronic transitions in the spectrum.

It should be mentioned here that by using a different one-step diffusion technique, aiming directly at a high concentration of complex acceptors, it is possible to create a large number of additional complex defects giving several BE lines in PL spectra between 7800 and 8000 Å. Since the role of such defects in the degradation process of the substitutional Ag_{Cd} acceptor concentration is less obvious, they are excluded from this presentation. It is clear, however, that the substantial reduction of radiative efficiency which always accompanies the transfer from substitutional Ag_{Cd} to Ag-related complexes shown in Fig. 1, can be related to the formation of other nonradiative complexes.

B. Transmission spectra

For a sample thickness of about 0.5 mm or more, good transmission spectra were obtained exhibiting BE features similar to those in the emission spectra. This is shown separately in Fig. 2, where PL emission and absorption (transmission) data are compared for the same sample at 2 K. It is clear from Fig. 2 that the strength of the discrete transitions is very similar in both PL spectra and transmission spectra. This would indicate that X_1^{Ag} and X_2^{Ag} as well as the shallow acceptors A_1^{Ag} and A_1^{Cu} also present in the spectra have similar oscillator strengths. Actually, this observation is similar to our experience of highly Cu-doped ZnTe, where complex IBE and ABE states appear to have similar oscillator strengths as well as lifetimes.[12] This result indicates that Auger processes for ABE recombination are not dominating, a conclusion also found in a recent study of deep ABE spectra in GaAs.[13]

These transmission data are important since they establish the absence of fine structure within the electronic ground state for the X_2^{Ag} BE (as well as for X_1^{Ag}). For an IBE state this means that no strong exchange splitting (electron-hole exchange) occurs, as will be discussed in

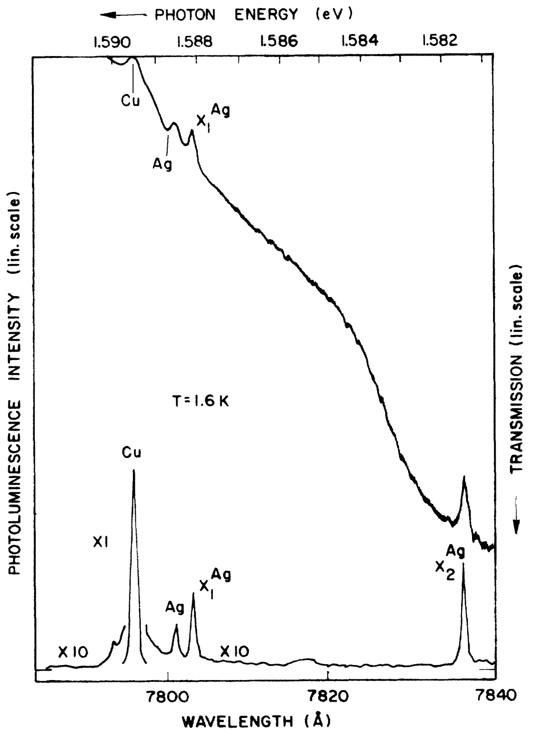

FIG. 2. Comparison between PL emission and absorption (transmission) spectra for the same Ag-doped samples as in Fig. 1, taken after one year of room-temperature storage after the Ag diffusion. The new BE lines X_1^{Ag} and X_2^{Ag} have about the same relative strength in absorption as in emission.

more detail below. We shall also return to the problem of possible single-particle excited states to the X_2^{Ag} IBE in connection with PLE data to be discussed in Sec. III C. The transmission measurements are also very important for Zeeman data, as shown below in Sec. III.

C. Phonon coupling for the 1.7815-eV emission line

The coupling of a defect-related electronic transition to vibrational modes characteristic of the host material as well as of the defect itself is manifested in the phonon wing on the low-energy side of a PL spectrum, and can often give valuable additional information on the defect under study. There are no strong additional electronic transitions directly interfering with the X_2^{Ag} BE spectrum within the one-phonon range below the electronic line at $h\nu = 1.5815$ eV. With excitation near or above 1.5880 eV, however, the phonon replicas of higher BE states overlap the X_2^{Ag} BE spectrum, which makes a detailed study of the phonon coupling to the X_2^{Ag} BE impossible. Fortunately, this problem can be overcome in this case by employing resonant excitation in the X_2^{Ag} BE electronic line at $h\nu = 1.5815$ eV. This way a clean spectrum revealing exclusively the phonons coupling to this particular defect BE is obtained, as shown in Fig. 3(a), and in more detail in Fig. 3(b).

As usual, for shallow BE transitions the LO_Γ phonon ($\hbar\omega = 21.2$ meV) dominates the spectrum with a coupling strength S_{LO} of about 0.2. But, obviously, an appreciable coupling to the acoustical lattice phonons is present, in addition to several rather sharp quasilocalized modes. The phonon energies observed in Fig. 3(b) are summarized in Table I. True local modes above the LO_Γ energy in the one-phonon sideband are possible for impurity atoms of a lighter mass than the host atoms. Since this is actually the case here [both Ag and Cu are lighter than Cd (and Te)], we might expect to see such modes. Actually, a weak feature at 22.7 meV is seen in Fig. 3(b), which we tentatively assign to such a true local mode. The weakness of this mode does not preclude the existence of more true local modes, which are not resolved on the background of the two-phonon part of the spectrum. [Actually, for complex neutral centers in GaP two true local modes were consistently observed.[14–16]] Otherwise the coupling to the very-lowest-energy acoustical modes is indeed strongest and is also manifested by the drastic changes in the electronic line of the spectrum at elevated temperatures (see below). In Fig. 3(c) we also sketched the density of states of the lattice phonon spectrum of CdTe, as obtained from neutron scattering data.[17] Allowing for the larger uncertainty in these neutron scattering values when it comes to evaluating the phonon energies for the high-density-of-states points in the Brillouin zone, we can tentatively identify some of the broader features in the optical one-phonon wing as lattice modes, as indicated in Table I.

The broad band spanned by R_2 and R_3 is thus identified with the high-density-of-states region of the TA spectrum of CdTe in rather good agreement with the neutron scattering data [Fig. 3(c)]. The strong peak R_6 could be a critical point for TA along Σ, and one is tempted to iden-

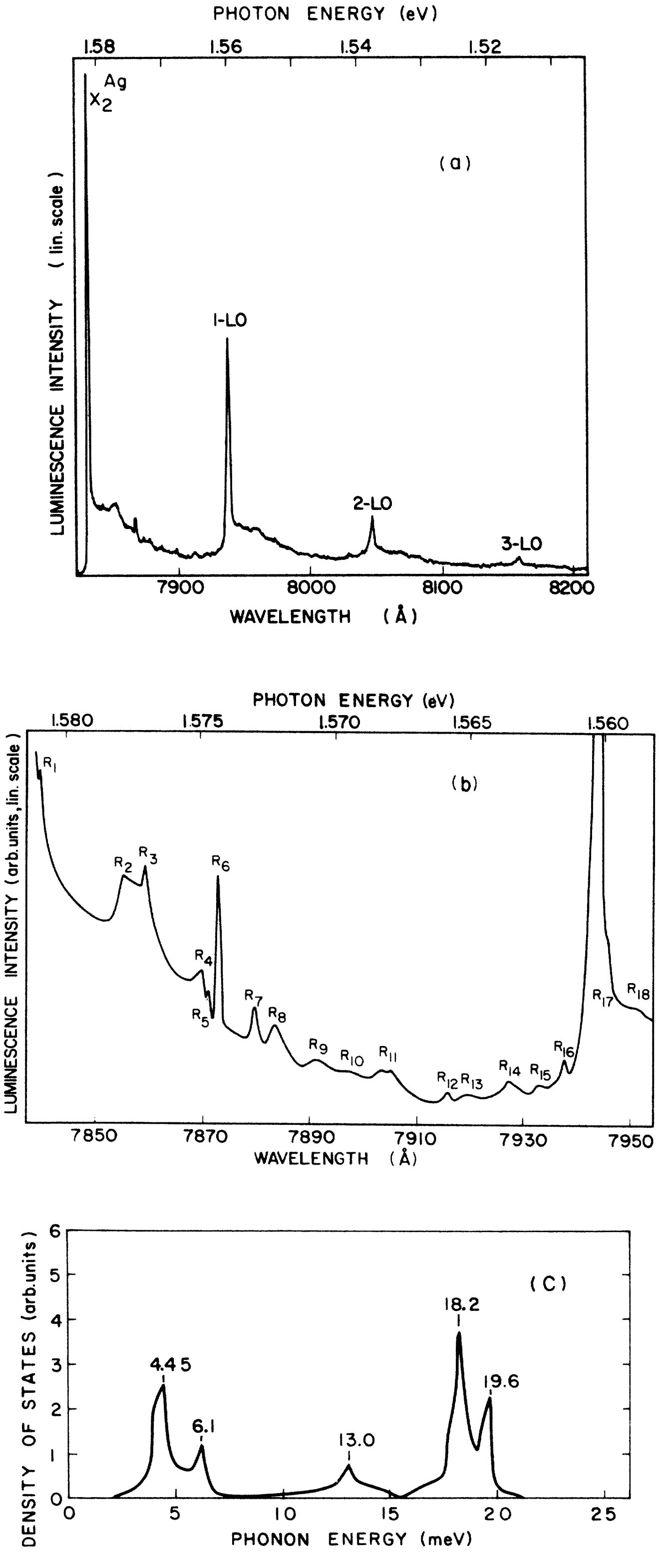

FIG. 3. (a) Photoluminescence spectrum of the X_2^{Ag} emission, showing up to three LO-phonon replicas. (b) The one-phonon range of phonon replicas associated with the X_2^{Ag} electronic line at 1.5815 eV, produced by resonant dye-laser excitation of that line. Discrete replicas are denoted R_1–R_{18}, their energies are listed separately in Table I. (c) One-phonon density of states for CdTe, derived from experimental neutron scattering data (Ref. 17).

TABLE I. Phonon replicas in the X_2^{Ag} bound-exciton PL spectrum. (Question mark indicates uncertainty.)

Notation	Photon energy (eV)	Phonon energy (meV)	Interpretation
X_2^{Ag}	1.581 55		electronic line
R_1	1.580 75	0.8	quasilocalized mode
R_2	1.577 90	3.65	TA_Λ?
R_3	1.577 05	4.5	TA_x?
R_4	1.574 93	6.6	quasilocalized mode
R_5	1.574 67	6.9	quasilocalized mode
R_6	1.574 27	7.3	TA_Σ?
R_7	1.572 97	8.6	quasilocalized mode
R_8	1.572 21	9.35	quasilocalized mode
R_9	1.570 68	10.9	quasilocalized mode
R_{10}	1.569 42	12.1	quasilocalized mode
R_{11}	1.567 94	13.6	LA_L?
R_{12}	1.565 91	15.65	quasilocalized mode
R_{13}	1.565 14	16.4	quasilocalized mode
R_{14}	1.563 60	17.95	optical mode
R_{15}	1.562 50	19.05	optical mode
R_{16}	1.561 48	20.05	quasilocalized mode
R_{17}	1.560 35	21.2	LO_Γ
R_{18}	1.558 88	22.7	local mode

tify R_{11} with the LA_L phonon energy. The rather broad features R_{14} and R_{15} are tentatively assigned to main critical points in the optical band of the spectrum, also in reasonable agreement with the neutron data. It will be possible to test these assignments definitely in the future when similar detailed spectra become available for other low-symmetry defect bound excitons in CdTe.

The additional lines present in the spectrum are either in a low-density-of-states region of the lattice spectrum, or they are quite sharp, indicating that they are defect-related quasilocalized modes. This is true particularly for R_1, R_4, R_5, R_7–R_9, R_{13}, and R_{16}. The appearance of a low-energy mode R_1 at an energy of 0.8 meV is remarkable, but such low-energy modes are common even in other complex spectra in compound semiconductors involving defects containing interstitial species.[15,16] It is not clear whether the sharp peak R_3 is a quasilocalized peak superimposed on the lattice spectrum, or whether it is, in fact, a very sharp critical point in the density of states (TA_x). An argument for the latter interpretation is that the background density of states is quite strong at that energy, which would broaden any quasilocalized mode. The most striking features in the quasilocalized mode structure occur with the modes R_6–R_8, which are fairly strong, but in the case of R_6 and R_7 they are also very sharp. Actually, R_6 has a width (0.15 meV) similar to that of the electronic no-phonon line in all our samples. The low density of states of LA phonons in that energy region can reduce the interaction of the localized vibrations with the surrounding lattice to maintain such sharp phonon modes. R_6 and R_7 are interpreted as such single quasilocalized modes while the broader features R_8 and R_9 could be two-phonon replicas involving R_6 and R_7, respectively, and in addition a low-energy mode of ≈ 2 meV which does not couple directly to the electronic transition. (Similar secondary coupling of quasilocalized modes in BE spectra has been observed in a Cu-related complex in GaP.[18] It has been observed that a quite similar mode structure (but not identical) exists in the phonon wing of X_1^{Ag}, as observed by resonant excitation in the X_1^{Ag} BE line at 1.5880 eV. Apparently such a mode structure is typical for this class of complex defects in CdTe. The most typical quasilocalized mode of the additional peaks in the optical spectrum is R_{16}, resonant with the optical lattice modes. This is not surprising, since defect-related modes in this region are common in BE spectra for many defects, both simple substitutional and complexes.[19]

Unfortunately, no theory has been developed to account for the identity of the observed local and quasilocalized vibrational modes for complex defects involving several atoms, including interstitial species. It is therefore not possible at the moment to predict at which energies certain possible defect-related vibrational modes would occur in the spectrum (if they couple to the electronic transition). It is obvious that a theoretical development of this area would be a very powerful aid in the identification of complex defects from the rich information available in the phonon side bands of such BE electronic transitions as discussed here. At the moment we can only note that the rich structure of quasilocalized modes present in the spectrum is consistent with an identification of the defect as a complex system of more than one impurity atom, allowing several different defect-related vibrational modes, as observed.

D. Temperature dependence of the X_2^{Ag} emission

The behavior of the BE emission spectrum with temperature gives additional information about the phonon coupling, but also on electronic activation energies for the BE state. We have accurately recorded the total BE emission spectrum for X_2^{Ag} at different temperatures ranging from 1.6 up to 25 K, where it is rendered undetectable by thermal quenching. To obtain an accurate measurement of the sample temperature, low excitation-laser power (< 1 mW) was used. It was found that the electronic BE line at 1.5815 eV was broadened already at the very lowest temperature by interaction with low-energy acoustic phonons. This interaction is, in fact, the dominating feature in the development of the spectrum with rising temperature, as can be seen from a collection of such curves in Fig. 4. Only at the very lowest temperature (≈ 4 K) is it possible to observe clearly the quasilocalized modes in the emission spectrum; they rapidly broaden simultaneously with the electronic line, and disappear when this line begins to lose relative intensity, a process which starts to be appreciable as early as below 4 K. This thermal quenching of the no-phonon line relative to the total emission intensity is a simple consequence of linear coupling of the electronic transition to low-energy acoustic (and/or low-energy quasilocalized) phonons,[18] and is unusually evident in this case due to the dominating coupling to the very-low-energy modes.

It is seen in Fig. 4 that the gradual disappearance of the no-phonon line is accompanied by a spreading of its oscil-

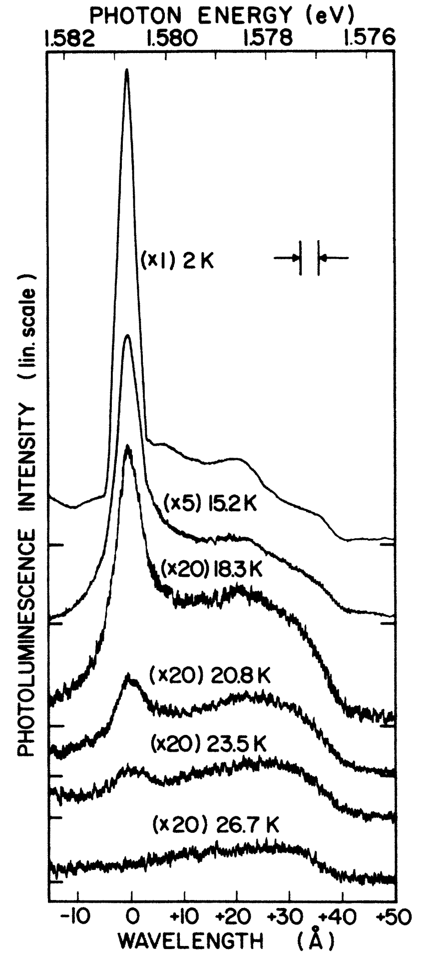

FIG. 4. Temperature dependence of the part of the X_2^{Ag} PL spectrum close to the 1.5815-eV electronic line. These spectra show the drastic changes in the appearance of this electronic line due to linear coupling to low-energy phonons, which finally broadens the line so that it disappears completely above ≈25 K.

lator strength both to higher and lower energies. This is exactly what is predicted by the theory for linear phonon coupling; absorption of phonons of an energy $\hbar\omega$ occurs with a strength proportional to $n(\omega)=(e^{\hbar\omega/kT}-1)^{-1}$ on the high-energy side of the no-phonon line, while emission of phonons occurs with a strength proportional to $1+n(\omega)$ on the low-energy side. This process precedes the general electronic quenching of the total emission so that at the highest temperatures where the spectrum could be measured, the no-phonon line has completely disappeared (together with all its discrete replica). The total emission in this stage (Fig. 4) essentially consists of a broad distorted acoustical wing, and its LO$_{\Gamma}$-phonon replica.

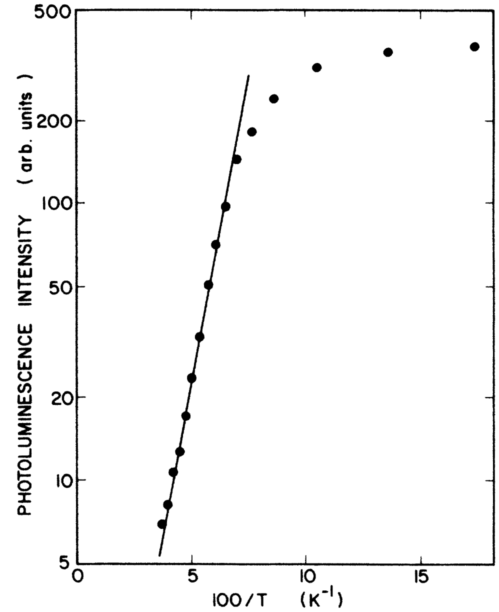

FIG. 5. Temperature dependence of the integrated intensity $I(T)$ of the X_2^{Ag} PL emission, obtained from an evaluation of the area under the total emission envelope at each temperature. A well-defined thermal activation energy of ≈8.8 meV is obtained.

As a result of the important quenching process of the electronic line in this case, it is necessary to evaluate the electronic quenching process by measuring the total area under the PL emission curve for each temperature.[18] We have plotted in Fig. 5 the thermal quenching behavior of the X_2^{Ag} emission, evaluated as the total area under the PL emission curve, truncated at ≈1.567 eV in each case to avoid erroneous contributions from the LO replica of other BE emissions, which could not be avoided here since resonant excitation obviously could not be used. The thermal quenching of the PL intensity $I(T)$ gives a well-defined electronic quenching activation energy of 8.8 ± 0.1 meV according to Fig. 5. Although the results warrant such an accuracy, it has to be acknowledged that systematic errors may be present to some extent in the evaluation of experimental data. Apart from some possible errors in the determination of the actual sample temperature, a certain overlap of the phonon-assisted parts of higher BE emissions, particularly X_1^{Ag}, could not be avoided, and to the extent these emissions may have a different temperature quenching they might slightly distort the data in Fig. 5. We therefore suggest a relaxed accuracy of 8.8 ± 0.5 meV for the activation energy of thermal quenching of the X_2^{Ag} BE emission. The interpretation of this result in terms of the electronic structure of this BE is discussed below in Sec. IV.

E. Excitation spectra for the X_2^{Ag} emission

In general, PLE spectra of BE emissions can give very useful information on excited electronic or vibrational states of the BE, and, in addition, on excitation transfer processes involving other defects than the one giving rise to the BE emission detected. In Fig. 6 we show PLE spectra for the X_2^{Ag} emission, with detection in the no-phonon line at $h\nu_d=1.5815$ eV (curve a), but also with detection at lower energies in the acoustic phonon wing at 1.5781 eV (curve b), and in the one-LO replica at ≈1.560 eV (curve c). Several conclusions follow immediately from the appearance of these spectra. The lowest electronic line at 1.5815 eV related to the X_2^{Ag} bound exciton is a single line as in PL emission, which is important for the discussion of the electronic structure of this BE. Searching for possible electronic excited states of the $X_2^{\rm Ag}$ bound exciton, the first obvious candidate is the rather strong feature X_2^* at ≈ 1.5900 eV, i.e., just above the $A_1^{\rm Cu}$ BE line (which appears as a dip in the spectrum of Fig. 6). This line cannot be identified with any phonon replica of the $X_2^{\rm Ag}$ line at 1.5815 eV, as seen from a comparison with the PL emission spectrum in Fig. 3(b). No line at this energy associated with other shallow states is observed in PL emission, which supports the tentative identification of X_2^* as an electronic excited state related to the $X_2^{\rm Ag}$ BE ground state at 1.5815 eV. In addition, the intensities of X_2^* scale with the $X_2^{\rm Ag}$ line at 1.5815 eV in PLE spectra indicating such a connection. Unfortunately, we had no access to tunable excitation in the Zeeman experiment, so no definite proof of this identification of the X_2^* line can be given at present. The distance of X_2^* to the lowest $X_2^{\rm Ag}$ electronic state is 8.6 meV. Another broadened line, X_2^{**}, 11 meV above the 1.5815-eV $X_2^{\rm Ag}$ line, is also similarly interpreted as an excited electronic state. The expected identity of the lowest excited electronic state for a complex BE would be the $n=2$ orbitally excited state of the electron, if the electron is weakly bound in this IBE state, as is found for the shallow substitutional acceptors in CdTe.[11,20] This requires that $X_2^{\rm Ag}$ have a dominantly hole-attractive central cell, which is reasonable, e.g., if it contains $\rm Ag_{Cd}$ as one part of the complex.

In addition to these tentatively identified electronic excited states related to the 1.5815-eV BE line, sharp lines related to the other known bound-exciton states related to substitutional acceptors and donors in CdTe are also identified in Fig. 6. The rich phonon spectrum seen in PL emission [Fig. 3(b)] is only partly revealed in Fig. 6, due to other overlapping electronic lines discussed above. Several phonon replicas for $X_2^{\rm Ag}$ can be recognized even in absorption, however, as seen in Fig. 6. The phonon energies in PLE absorption differ slightly from what is observed in PL emission, which is not too unusual in similar BE spectra.[18]

Lines which appear as dips in the PLE spectrum are naturally interpreted as a recombination channel competing with $X_2^{\rm Ag}$. This is particularly observed for the creation of donor BE states and free excitons (FE) in Fig. 6. (The PLE spectra were scanned with constant dye-laser intensity.)

F. Magneto-optical data

Magneto-optical data for BE's, in general, give valuable information on the electronic structure of the corresponding defect, and in the case of anisotropy the symmetry of a complex defect can often be deduced. In the present case we do not have a full set of Zeeman data available for the $X_2^{\rm Ag}$ line, but nevertheless very important conclusions can be drawn about the defect. In Fig. 7 we show the $X_2^{\rm Ag}$ no-phonon BE line in transmission, at various values of the magnetic field up to 10 T. Two obvious general conclusions can be drawn from the appearance of the spectra. There is a large diamagnetic shift of the center of gravity of the emission (Fig. 8), $\approx 1.2\times10^{-4}$ meV/K G^2, as compared to 1.32×10^{-4} meV/K G^2, observed for the $\rm Li_{Cd}$ and $\rm Na_{Cd}$ BE's in CdTe.[21] This allows the important conclusion that the electron is bound quite weakly, resembling a shallow donor state.[22] In addition, it is clear that the Zeeman-split BE spectrum in Fig. 7 is composed of a large number of lines; about 12 components can be resolved at 10 T. This can be understood only if we have a superposition of Zeeman spectra from several inequivalent sets of defects, thus providing the confirmation of a complex with a symmetry lower than tetrahedral as responsible for the $X_2^{\rm Ag}$ BE state. The question whether the complex is neutral (isoelectronic) or an acceptor is conveniently settled in transmission Zeeman spectra from the observed absence of thermalization in Fig. 7; even at the highest available field 10 T. Under similar conditions acceptors will give rise to a thermalized BE Zeeman spectrum, due to the splitting of the hole state in the initial state of the BE creation process. This will produce a spectrum where only the high-energy part of the Zeeman-split component is seen at 10 T. On the contrary, from Figs. 7 and 9 the entire Zeeman spectrum is observed,

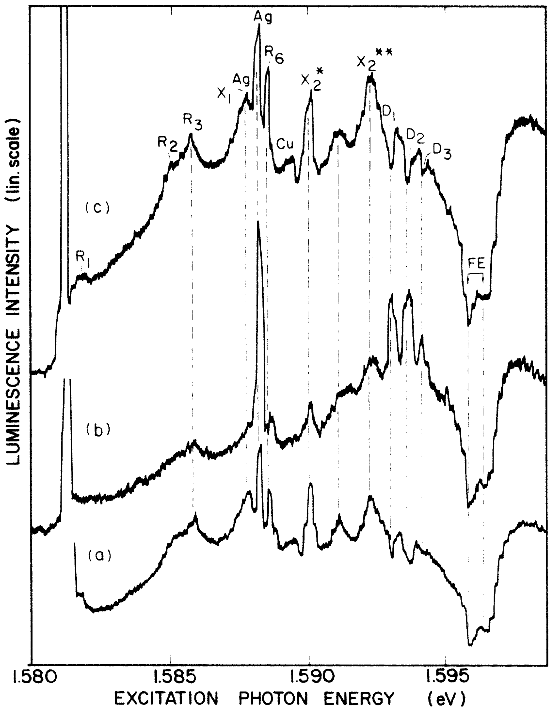

FIG. 6. Photoluminescence excitation spectra for the $X_2^{\rm Ag}$ emission obtained by scanning a tunable dye laser with constant intensity over the photon energy region shown. Curve a is obtained with detection (through a monochromator) in the 1.5815-eV electronic line, curve b with detection in the acoustic one-phonon wing at about 1.5781 eV, while in curve c the detection is set at the one-LO phonon replica of the 1.5815-eV line. Some features in the spectra are not related to the $X_2^{\rm Ag}$ emission, notably the ABE lines from substitutional $\rm Ag_{Cd}$ and $\rm Cu_{Cd}$ at 1.5885 and 1.5996 eV, respectively, and in addition, the weak $X_1^{\rm Ag}$ line at 1.5880 eV, the donor-related lines at $\approx 1.593-1.595$ eV, and the free-exciton doublet ≈ 1.596 eV. A few phonon replicas denoted R_ν are seen, with energies differing only slightly from the $X_2^{\rm Ag}$ PL emission case. Electronic excited states associated with $X_2^{\rm Ag}$ are X_2^* at 8.6 meV above the 1.5815-eV line, and in addition a broad line X_2^{**} about 11 meV above.

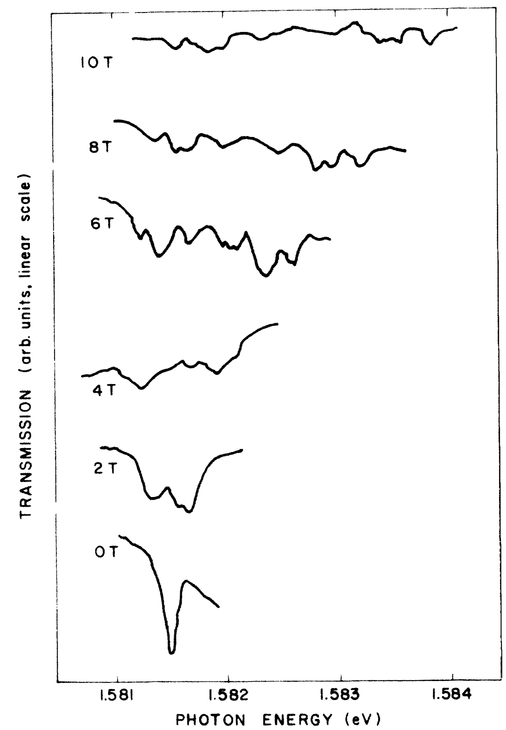

FIG. 7. Transmission spectrum for the X_2^{Ag} 1.5815-eV line in the Voigt configuration, taken for magnetic fields up to 10 T. The full spectrum is observed at all fields, meaning that no thermalization occurs in the ground state of the defect.

from which we can draw the firm conclusion that no spin is present in the initial state of the BE transition in absorption, meaning that the X_2^{Ag} defect is either of neutral isoelectronic character, or an ionized donor or acceptor. If the defect is an ionized center, the observed exciton must be D^+X (exciton bound to ionized donor), since the A^-X complex (exciton bound to ionized acceptor) is not stable in CdTe, where $m_h \gg m_e$. It is very difficult to understand how substitutional $\mathrm{Ag_{Cd}}$ could give rise to a donorlike complex to create a D^+X BE. Therefore it is only reasonable to assume that the X_2^{Ag} defect is of neutral isoelectronic character.

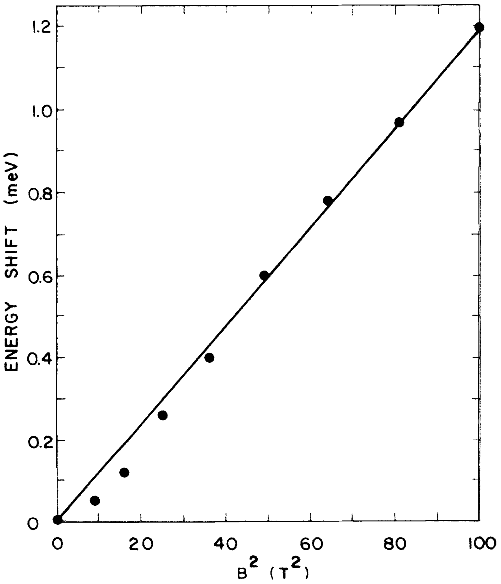

FIG. 8. Quadratic Zeeman shift of the 1.5815-eV PL line structure shown in Fig. 7, for magnetic fields up to 10 T. The value for the shift rate of the spectrum towards higher energy is $\approx 1.2\times10^{-4}$ meV/(K G)^2.

PL spectra at 10 T, on the other hand, show appreciable thermalization. This is expected for a transition from a thermalized Zeeman-split BE state to a spin-free (empty) ground state. This is similar for acceptors and neutral defects, however, and thermalization in PL is often absent due to a short spin-lattice relaxation time. Therefore Zeeman transmission data on BE lines is the only valid optical test for the electrical nature of a defect.

The question of the character of hole states involved in the X_2^{Ag} BE can also be understood from the Zeeman data, in particular from the magnitude of the total splitting of the BE line at 10 T. In a local field lower than tetrahedral, as, e.g., in trigonal symmetry, the bound-hole Γ_8 multiplet is expected to split into two doublets characterized by $m_z=\pm\frac{3}{2}$ and $m_z=\pm\frac{1}{2}$, respectively, where m_z is the projection of the angular momentum on the local defect axis [Fig. 10(a)]. The effective g value for a bound electron-hole pair would be $g_{\mathrm{eff}}^{1/2}=-g_e+K$ for $m_z=\pm\frac{1}{2}$ and $g_{\mathrm{eff}}^{3/2}=-g_e+3K$ for $m_z=\pm\frac{3}{2}$.[23] With use of values appropriate for CdTe, i.e., $g_e\approx-1.77$, $K\approx+0.6$,[11,21,24] the expected numbers are $g_{\mathrm{eff}}^{1/2}=2.37$ and $g_{\mathrm{eff}}^{3/2}=3.57$. The experimental value $g_{\mathrm{eff}}=3.9$ (Fig. 9) suggests that the bound-hole states are of $\pm\frac{3}{2}$ character.

For a local strain field of *tensional sign*, the hole states $m_z=\pm\frac{3}{2}$ will be at lowest energy, which is the case shown in Fig. 10. This seems to require $\mathrm{Ag_{Cd}}$ to be smaller than $\mathrm{Cd_{Cd}}$, which is not unreasonable. Unfortunately, a full rotation in a ⟨110⟩ plane at 10 T was not performed in this case, which means that the exact symmetry of the defects cannot be deduced.

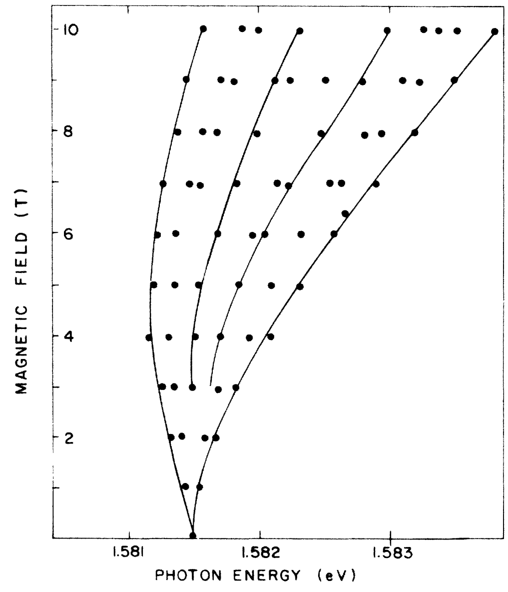

FIG. 9. Synopsis over splitting of the 1.5815-eV PL line with magnetic field up to 10 T. The maximum splitting at 10 T corresponds to an effective g value, $g_{\mathrm{eff}}\approx3.9$.

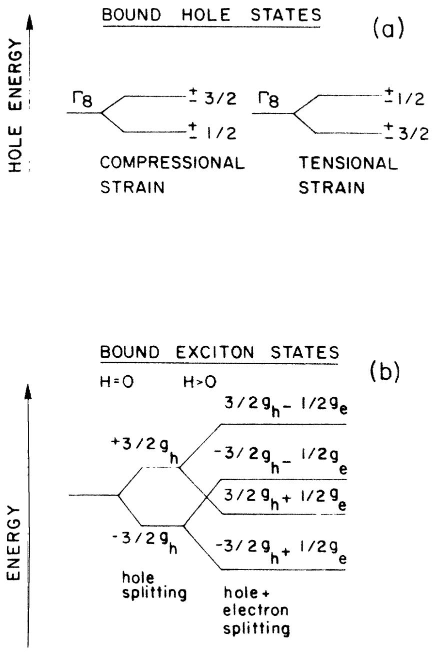

FIG. 10. (a) Schematic picture of splitting of Γ_8-related bound-hole states for a complex defect in CdTe, here assumed to have trigonal symmetry. (b) Schematic picture of Zeeman splitting of an exciton bound to a neutral isoelectronic center. The electron-hole exchange interaction is neglected, and electrons and holes split independently.

IV. DISCUSSION

A. Electronic structure of the X_2^{Ag} bound exciton

The novel basic results from this investigation are connected with the identification of Ag-related complexes formed upon migration of Ag atoms at room temperature, and in addition the electronic and vibrational properties of particles (holes and excitons) bound to such complex defects. The electronic structure of the bound-exciton state is rather simple in the case of a complex IBE, where the exciton hole is more localized than the electron, although still shallow. This situation leads to a negligible electron-hole exchange splitting, mainly due to the very delocalized electron state. In this situation the local low-symmetry stress field at the defect is the dominant perturbation on the electronic bound-exciton states. We consequently arrive at a model for the IBE where the hole is bound by a hole-attractive central-cell potential (partly strain induced), but the BE properties are dominated by the electron, which is apparently bound in a very shallow state. This loose binding of the electron is experimentally manifested in the large diamagnetic shift of the BE, and in the small electronic activation energy of ≈ 8.8 meV of the quenching of the BE emission. It is probable that the 8.6-meV line in the PLE spectrum is a $n=2$ orbitally excited state to the electron in this BE, similar to the case recently observed with an axial ABE in ZnTe.[25] This value of an $n=2$ state is intermediate between the corresponding values for the free exciton ($n=2$ at ≈ 7.6 meV) and the substitutional shallow donors ($n=2$ at ≈ 10.7 meV). We can estimate that the electron is bound by about 12—14 meV in this X_2^{Ag} BE state by comparison with the shallow-donor binding energy of 13.7 meV,[20] which is close to the effective-mass value. With a band gap for CdTe of 1.606 eV,[11] this gives a binding energy of 11—13 meV for the hole in the exciton, i.e., about the same as the electron. This value is rather meaningless to discuss as a binding energy of the hole, since it should not really be referred to the nearest band edge for a particle bound in a localized neutral potential. The slight negative central-cell correction in the electron binding is understandable in view of the repulsive effect of the hole-attractive core (or core sites) of this defect.

The apparent inconsistency of the thermal activation energy of 8.8 meV with an electron binding energy of about 12—14 meV is, in fact, expected in this case. Since the material is rather highly doped ($> 10^{16}$ cm^{-3}) the excited states of the shallow bound electron overlap considerably. This means that photothermal excitation from $n=2$ states to the continuum is expected to occur with relative ease, in which case the $1s$-$2s$ excitation step of the electron is indeed the rate-limiting one. In such a situation the thermal activation energy for liberation of the BE electron (which of course would quench the BE emission) is expected to be close to the corresponding $1s$-$2s$ excitation energy, as observed.

B. Possible defect reactions responsible for the instability of $\mathrm{Ag_{Cd}}$

Since it is established that the isolated $\mathrm{Ag_{Cd}}$ concentration actually decreases during room-temperature storage, two different possible defect reactions have to be considered. Either the $\mathrm{Ag_{Cd}}$ concentration remains the same, and the decrease of *isolated* $\mathrm{Ag_{Cd}}$ is explained by a complex formation of $\mathrm{Ag_{Cd}}$ with other species in the material, which may be mobile at room temperature, or the $\mathrm{Ag_{Cd}}$ site actually is removed by a fundamental instability of $\mathrm{Ag_{Cd}}$. The former alternative obviously requires that the lattice is contaminated with defects other than $\mathrm{Ag_{Cd}}$ in a comparable concentration, which can move to $\mathrm{Ag_{Cd}}$ sites to create neutral complexes to an extent sufficient to reduce the isolated $\mathrm{Ag_{Cd}}$ concentration an order of magnitude.[8] We do not see that there are any such contaminants present in the starting material in sufficient concentration. Cu does enter as a contaminant in the diffusion process, but this cannot explain the $\mathrm{Ag_{Cd}}$ degradation behavior, since the Cu concentration is smaller than the Ag doping, and furthermore the $\mathrm{Cu_{Cd}}$ concentration is approximately stable during the aging process described here. Consequently, we are left with the alternative that isolated $\mathrm{Ag_{Cd}}$ in itself is actually unstable. This means that substitutional $\mathrm{Ag_{Cd}}$ atoms leave their positions spontaneously, producing a Frenckel-type pair of a Cd vacancy (V_{Cd}) and a Ag_i interstitial. The enthalpy of formation of such a defect could be quite low, but it is unknown. Its stability at room temperature is not known either, but if it is stable it is a viable candidate for the identity of X_2^{Ag}. Another possibility is that it is unstable and dissociates into a Ag_i and a V_{Cd}. The isolated V_{Cd} is unstable at room temperature,[26] and will quickly disappear to the surface, or to inclusions or other defects where it can form stable configurations in connection with other defects.

The Ag_i could be rather mobile at room temperature, and find its way to substitutional acceptors (such as Ag_{Cd}), where neutral defects Ag_{Cd}-Ag_i are formed (see below). This could explain the electrical behavior of the aged Ag-doped samples. Furthermore, other additional defect reactions probably occur, creating severe nonradiative defects which dramatically reduce the radiative efficiency of CdTe:Ag during aging.

C. Possible identity of the X_2^{Ag} complex

The identity of the complex neutral defect X_2^{Ag} is an important question, which has not been established in a similar case for any semiconductor. Clearly the classical models of complexes involving vacancies have to be treated with caution, since vacancies are unstable at room temperature in CdTe, and consequently should occur in quite low concentrations in freshly-prepared Ag-doped material. As noted above, pairs of V_{Cd} and Ag_i are probably created during the aging process discussed in this work, and if such a complex is stable at room temperature, it is a realistic candidate for the identity of the X_2^{Ag} complex.

The most realistic alternative is the combination of substitutional and interstitial nearby sites into neutral complexes. A simple possibility is a combination of a substitutional single acceptor (such as Ag_{Cd} or Cu_{Cd} in CdTe) with an interstitial acting as a single donor (such as the group-I species Ag and Cu). This satisfies all bonds in the lattice, assuming that the tetrahedral symmetry is retained, and thus a neutral complex defect is formed. As discussed above, the Ag_{Cd} may partly be released into interstitial positions, where they may be rather mobile even at room temperature, and can form complexes of the nature described when they get close to a Ag_{Cd} (or possibly Cu_{Cd}) position in the lattice. Such complexes are generally not detected in electrical measurements, but may be observed in PL spectra via their BE states, as has recently been found for heavy Ag and Cu doping in ZnSe and ZnTe.[12,27–29]

The tentative assumption of a simple Ag_{Cd}-Ag_i pair as the identity of the X_2^{Ag} defect is a simple and quite reasonable model to explain the optical data. As noted above, the alternative involving a Cu atom (such as Cu_{Cd}-Ag_i) cannot be excluded from the present data, since Cu is always present as a contaminant in our Ag-doped samples. The symmetry of this pair is not evident from the Zeeman data, unfortunately. A simple trigonal (111) symmetry seems to be one obvious possibility. Such a trigonal configuration is seen in the analogous case of a Ag_{Zn}-Ag_i complex in ZnTe.[28] A more remote Ag_i atom would favor the case of a tensional local stress at the defect, however, which also seems to be required from the optical Zeeman data mentioned above. Atomic sizes in crystals are very difficult to predict at the present state, for interstitials as well as for substitutional atoms which do not belong to the same column in the periodic system. It is not unlikely that Ag is slightly smaller than the Cd atom it replaced as Ag_{Cd} (the same argument would hold for Cu_{Cd}). The additional Ag_i in the neighborhood is probably small when its outer electron has been given off to satisfy the local bonding configuration. Therefore, an overall tensional stain may not be unrealistic for a substitutional-interstitial pair in this case.

Clearly for substitutional interstitial neutral complexes in GaP, a compressive stress field has been observed.[15,16,30,31] This is different, however, since in III-V material *two* interstitial group-I atoms are required for a neutral complex with a substitutional group-I atom on a group-III site. provided the tetrahedral bonding is retained. It seems reasonable that three atoms connected to one lattice site in a III-V material would cause a local compressive stress. In II-VI materials, however, only two atoms are involved in the analogous case. We therefore argue that the observation of local strain field of a tensional sign may not be in contradiction with the above substitutional-interstitial pair model for the defect.

Returning to the above-mentioned alternative with a V_{Cd}-Ag_i pair as the identity of the defect, it must be admitted that such an identity could more easily be understood to give rise to the deduced tensional local strain field at the defect. With no independent information on the stability of such vacancy complexes in CdTe at room temperature, this alternative remains a realistic candidate. More detailed work to deduce the symmetry of the defect, and, in addition, radiation treatment to create vacancies in Ag-doped material, will be necessary to decide between these two main models presented for the possible identity of the X_2^{Ag} defect in CdTe.

D. Comparison with Cu-doped CdTe

When Cu is introduced substitutionally on a Cd site in CdTe at a high doping level, a reduction of Cu_{Cd} concentration at room-temperature storage is actually observable (about a factor 2–5 over a period of one year). The process involved could be similar to the case of Ag doping, but interestingly, no new spectral features occur in PL or absorption spectra. This means that no complexes analogous to X_1^{Ag} and X_2^{Ag} are formed. We tentatively explain this different behavior by postulating that the analogous complexes for Cu are actually not stable at room temperature. This means that the Cu atoms that are released from Cd sites upon aging probably go to the Te-rich inclusions always present in the material,[9] or alternatively they leave the crystal to the outer surface.

In any case this problem of instability of substitutional doping for Ag (and Cu) in CdTe is a severe drawback for the use of the elements as acceptor dopants for *p*-type CdTe. It turns out that implantation of group-V elements at Te sites is more promising for practical purposes, since such dopants have a much lower diffusion tendency.[32]

V. SUMMARY

We have presented a detailed spectroscopic study of complex defects resulting from the thermal instability of Ag_{Cd} in CdTe at room-temperature storage. It is noted that defect reactions at room temperature drastically decrease the substitutional Ag_{Cd} concentration (by as much as an order of magnitude during a period of several months). At the same time complex defects are formed as evidenced by the appearance of new bound-exciton spectra in low-temperature optical measurements. Two such different complexes, X_1^{Ag} with a BE line at 1.5880 eV and another line, X_2^{Ag}, at 1.5815 eV, have been particularly studied in this work. Of these two, the X_2^{Ag} spectrum has been studied in great detail, since it is spectrally isolated from the more shallow bound-exciton region around X_1^{Ag}. The latter could not be studied in much detail due to interference with other shallow-acceptor-related spectra very close in energy. Besides these two new defects observed in BE spectra, we believe there are additional deep-level defects created at the same time as X_1^{Ag} and X_2^{Ag}. The deep levels would be mainly responsible for the drastic reduction of radiative efficiency observed from this Ag-doped CdTe material as a result of the room-temperature aging. Detailed spectroscopic information on the X_2^{Ag} spectrum include tunable-dye-laser-excited PL spectra, revealing the electronic line at 1.5815 eV along with a detailed account of phonon coupling to this BE. Temperature dependence of the PL spectrum as well as excitation spectra (PLE) give an activation energy of ≈ 8.8 meV, interpreted as a $1s$-2 one-particle excitation of a shallow electron bound at the X_2^{Ag} defect as the secondary particle. Most importantly, Zeeman data up to 10 T taken in both transmission and luminescence reveal the detailed electronic structure of the defect. The X_2^{Ag} defect is a neutral isoelectronic complex of a symmetry lower than tetrahedral. The hole is bound as a primary particle in a predominantly hole-attractive potential, possibly from $\mathrm{Ag}_{\mathrm{Cd}}$. The magnitude of the effective g factor g_{eff} for the X_2^{Ag} BE strongly indicates that the bound-hole state is characterized by $m_z = \pm\frac{3}{2}$, where m_z is the magnetic quantum number along the defect axis. Such hole states are induced by a tensional average strain field locally at the defect. The $m_z = \pm\frac{1}{2}$ hole states are split off towards higher hole energy by the local axial field, and are in this case probably resonant with the valence band. The electron is found to be essentially in a loosely-bound shallow donorlike state, from the magnitude of the quadratic shift of the Zeeman spectrum for the X_2^{Ag} BE line. This is easily understood if the electron is bound to the defect as a secondary particle, in the Coulomb-like potential of the hole already bound to the (originally neutral) defect.

The X_2^{Ag} defect identity is not revealed from this study, but a simple $\mathrm{Ag}_{\mathrm{Cd}}$-$\mathrm{Ag}_i$ substitutional-interstitial pair is one realistic model, being a neutral complex. The observed instability of $\mathrm{Ag}_{\mathrm{Cd}}$ in CdTe is believed to be connected with a high mobility of interstitial Ag_i forming pairs with $\mathrm{Ag}_{\mathrm{Cd}}$ acceptors. The details of the release of a large number of $\mathrm{Ag}_{\mathrm{Cd}}$ atoms from Cd sites are not presently understood. Therefore, the V_{Cd}-Ag_i complex cannot be excluded as an alternative for the identity of the X_2^{Ag} complex.

Future experimental studies of this interesting phenomenon of substitutional doping instabilities in CdTe should be concentrated on the identification of all complex defects created as a result of room-temperature aging of Ag-doping CdTe. This is presently a very difficult task. In addition, theoretical work, particularly on the activation energy needed to release a Ag atom from a Cd site in CdTe, is necessary to understand the details of this instability.

ACKNOWLEDGMENTS

We acknowledge the expert assistance of L. Revoil in the Ag diffusion of the CdTe samples. Many thanks are due to Ch. Uihlein, H. Krath, and P. L. Liu for assistance in some of the magneto-optical measurements. Useful discussions with N. Magnea and J. L. Pautrat are also acknowledged. One of us (B.M.) is very grateful to the Université Scientifique et Médicale de Grenoble and the Centre d'Etudes Nucléaires de Grenoble for financial assistance during a one-year sabbatical in Grenoble.

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