Configuration of Li acceptor in ZnSe determined by infrared magnetoabsorption measurements

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Based on the experimental results of the infrared magnetoabsorption measurements, we propose that a Li acceptor is displaced from its proper substitutional site in ZnSe. Infrared absorption spectra in magnetic fields reveal additional splitting of acceptor levels that cannot be understood in the framework of cubic symmetry. The splitting is caused by the symmetry lowering induced by the displacement of the Li atom. The splitting of the $1S_{3/2}$ ground state is estimated to be 2.9 meV. The $2P_{3/2}$, $2S_{3/2}$, and $2P_{5/2}(\Gamma_8)$ states split into two states, and the magnitude of the splitting is estimated to be 5.5, 5.3, and 5.6 meV, respectively.

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Impurities in bulk semiconductors occupy the substitutional or interstitial sites. The displacements of the impurity atoms from the proper substitutional sites in some kinds of semiconductors have been reported and explained according to Jahn-Teller effect. Skolnick *et al.* have observed infrared absorption of Co^{2+} in InP in magnetic fields and concluded that the impurity has the C_{3v} axial symmetry caused by dynamic Jahn-Teller effect.[1] Murakami *et al.* have reported the off-center substitutional impurity in Si doped with nitrogen.[2] The nitrogen atom in Si is trigonally distorted with C_{3v} symmetry about the [111] axis and it was explained by the pseudo-Jahn-Teller effect. In this work we will present the infrared absorption spectra of ZnSe in magnetic fields and discuss the possibility of the displacement of the residual Li acceptor, i.e., the off-center Li atom, in ZnSe.

Lithium in ZnSe is an amphoteric impurity, i.e., it acts as an acceptor on a substitutional site or as a donor on an interstitial site. The substitutional acceptor with the ionization energy of ~110 meV has been well studied through photoluminescence measurements.[3] We have observed infrared absorption peaks on residual Li acceptors in ZnSe and assigned them by assuming T_d symmetry for Li acceptors.[4,5] A distinguished peak related to the lowest energy at 72.80 meV was identified with the transition of $1S_{3/2}$-$2P_{3/2}$ with reference to the results of photoluminescence by Tews *et al.*[3] The above notations follow ones by Baldereschi and Lipari.[6] There are three $2P$ states with different total angular momenta, $2P_{1/2}$, $2P_{5/2}$, and $2P_{3/2}$ for an acceptor in spherical environment in the case when the hole belongs to the valence band with the angular momentum of 3/2. The $2P_{5/2}$ state splits into two states, $2P_{5/2}(\Gamma_8)$ and $2P_{5/2}(\Gamma_7)$ by cubic symmetry. The most intensive doublet peaks were assigned to $1S_{3/2}$-$2P_{5/2}(\Gamma_8)$ and $1S_{3/2}$-$2P_{5/2}(\Gamma_7)$ that have been observed as the strongest peaks for Ge.[6] They are named as *D* and *C* lines after the notation of Fisher and Fan, respectively.[7]

With reference to the calculation by Baldereschi and Lipari, we could estimate Luttinger parameters from the peak energies of this doublet and the heavy-hole mass along [111] direction obtained from microwave cyclotron resonance.[5,8] The obtained Luttinger parameters explain well the small anisotropy of heavy-hole mass observed in cyclotron resonance.[8] Some of the other peaks are related to LO-phonon emission because of a strong electron LO-phonon coupling in II–VI compound semiconductors. There were still some unidentified peaks with an apparent energy difference of 6.2 meV from the well-defined ones. As an origin for these peaks we had proposed earlier a model of simultaneous excitation of a donor and an acceptor.[9] The above-mentioned small energy difference was assumed to be that of $1S$-$2S$ transition of interstitial Li donor. The data presented in this paper, however, contradict the simultaneous excitation model in some respects. Accordingly we propose a different model of the off-center substitutional Li acceptor in ZnSe.

The sample that we used in this study was a bulk ZnSe grown by a solid-growth method. A magnetic field was applied along [111] crystallographic axis in Faraday configuration. The infrared light from a Fourier transform infrared spectrometer (Bomem DA8) was guided to the sample at 4.7 K with brass optical pipes and metal mirrors. The transmitted light was led to an MCT (HgCdTe) detector with optical pipes. The data were analyzed by using the Fourier transform technique so as to remove the oscillations due to the interference effect of light reflected at the surfaces.

Figure 1 shows the absorption spectra of residual Li acceptors in ZnSe with and without magnetic fields. Almost all the lines shift to the higher energy side with increasing magnetic fields. The peak energies are plotted against magnetic fields in Fig. 2.

Splitting of the peak was not observed for the majority of peaks. Table I summarizes the peak shifts ΔE at 15 T and their tentative assignments. These peaks can be classified into four groups according to the amount of peak shifts in magnetic fields. Their final states are $2S$, $2P$, $3P$, and $4P$ in small to large order of the peak shifts. We observed seven peaks related to $2P$ state, and one of them at the lowest energy was identified as $1S_{3/2}$-$2P_{3/2}$. The peak at 102.95 meV was assigned to $1S_{3/2}$-$2P^{LO}_{3/2}$ which is the transition to $2P_{3/2}$ excited state accompanied by an LO-phonon emission with energy of 30.2 meV. The other five peaks are related to $2P_{3/2}$ or $2P_{5/2}$ state because $2P_{1/2}$ state has very small ion-

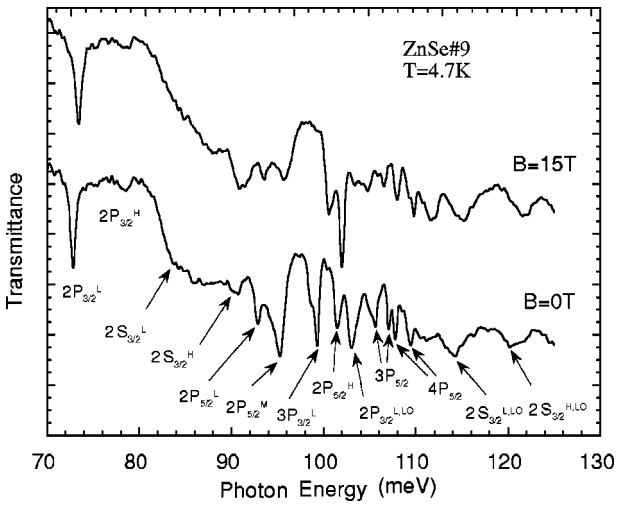

FIG. 1. Overview spectra of infrared absorption of Li acceptors in ZnSe with and without magnetic fields. The labels indicate the final states and the associated LO phonon.

ization energy, and the absorption peak related to this state could not be observed in this experiment.

The existence of six $2P$ states contradicts the cubic symmetry, where the $2P_{5/2}$ state splits into two states of $2P_{5/2}(\Gamma_8)$ and $2P_{5/2}(\Gamma_7)$. In order to explain our experimental results we assume the symmetry lowers because of the off-center position of the Li acceptor. In this case we exclude the idea of simultaneous excitation of a shallow donor for optical transition of Li acceptor. If the Li atom is displaced to [111] or [100] direction, the primary T_d symmetry is lowered to C_{3v} or D_{2d}.[10] The Γ_8 state splits into two states for C_{3v} or D_{2d} symmetry, and we name these states H and L as shown in Fig. 3. The $2P_{5/2}(\Gamma_7)$ state does not split in the lowered symmetry, and it is denoted by $2P^M_{5/2}$. As a result, the $2P_{5/2}$ state splits into three states, $2P^H_{5/2}$, $2P^M_{5/2}$, and $2P^L_{5/2}$ states. The $1S_{3/2}$ ground state also splits into two states, $1S^H_{3/2}$ and $1S^L_{3/2}$, in C_{3v} or D_{2d} symmetry.

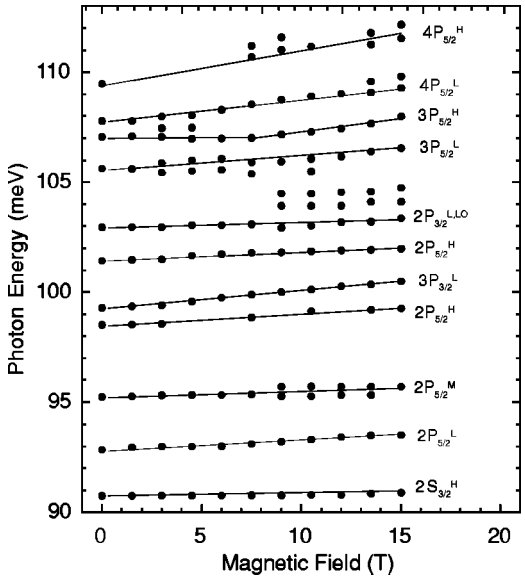

FIG. 2. Energies of the absorption peaks are plotted against magnetic fields.

TABLE I. Peak shift at 15T and assignments of the transitions.

Photon energy (meV)	ΔE(meV)	Transitions
72.8	0.63	$1S^H_{3/2}$-$2P^L_{3/2}$
78.3	0.61	$1S^H_{3/2}$-$2P^H_{3/2}$
82.6		$1S^H_{3/2}$-$2S^L_{3/2}$
90.75	0.14	$1S^L_{3/2}$-$2S^H_{3/2}$
92.85	0.66	$1S^H_{3/2}$-$2P^L_{5/2}$
95.24	0.46	$1S^H_{3/2}$-$2P^M_{5/2}$
98.53	0.74	$1S^H_{3/2}$-$2P^H_{5/2}$
99.30	1.21	$1S^H_{3/2}$-$3P^L_{3/2}$
101.44	0.55	$1S^L_{3/2}$-$2P^H_{5/2}$
102.95	0.41	$1S^H_{3/2}$-$2P^{L,LO}_{3/2}$
105.62	0.94	$1S^H_{3/2}$-$2P^L_{5/2}$
107.07	0.93	$1S^H_{3/2}$-$3P^H_{5/2}$
107.78	2.03	$1S^H_{3/2}$-$4P^L_{5/2}$
109.48	2.06	$1S^H_{3/2}$-$4P^H_{5/2}$

The peak of 101.44 meV at zero magnetic field grows with increasing magnetic fields and has the highest intensity at maximum magnetic field of 15 T in this experiment. It means that this peak corresponds to the transition from the ground state with the larger effective g value. The electron population in this ground state should rapidly increase as the energy separation of this state and the upper-lying excited states becomes large with increasing magnetic fields. As the temperature is raised, the intensity of this peak swiftly decreases as shown in Fig. 4. We conclude thus that the initial state of this peak should be the lowest one as shown in Fig. 3. We assign the peak at 101.44 meV to $1S^L_{3/2}$-$2P^H_{5/2}$. The initial state of the other peaks related to $2P_{5/2}$ is no doubt different from that of 101.44 meV peak because their peak intensities show their dependence on magnetic fields in the different ways. We assigned them to the transitions from $1S^H_{3/2}$ to $2P^L_{5/2}$, $2P^M_{5/2}$, and $2P^H_{5/2}$ in the order in which the transition energy increases. The final states should be the same for the peaks at 101.4 and 95.2 meV, because their

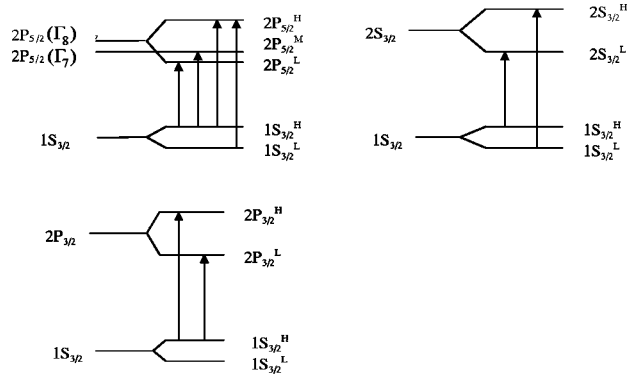

FIG. 3. Energy diagrams of the transitions to $2P_{5/2}$.

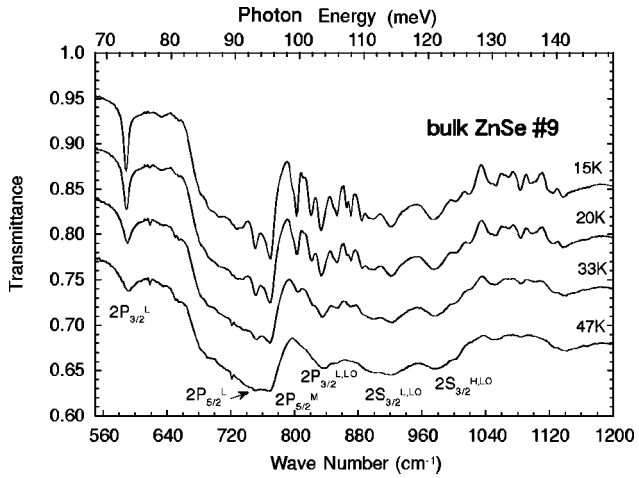

FIG. 4. Infrared absorption spectra of Li acceptor in ZnSe at various temperatures.

energy difference is equal to the splitting of the ground state of 2.9 meV. The splitting of $2P_{5/2}(\Gamma_8)$ state in the lowered symmetry, i.e., the energy difference between $2P^L_{5/2}$ and $2P^H_{5/2}$, is about 5.6 meV.

In C_{3v} or D_{2d} symmetry, the $2P_{3/2}$ state also splits into two states, $2P^L_{3/2}$ and $2P^H_{3/2}$. The temperature dependence of absorption intensity indicates that the transition comes from the $1S^H_{3/2}$ state. The peak is assigned to $1S^H_{3/2}$-$2P^L_{3/2}$. There is a possibility that a small peak observed at 78.3 meV corresponds to $1S^H_{3/2}$-$2P^H_{3/2}$ transition. If it is true, the splitting of $2P_{3/2}$ state is estimated to be 5.5 meV.

The peaks that shift about 1 meV at 15 T are assigned to the $3P$ state, and their detailed notations are $3P^L_{3/2}$, $3P^L_{5/2}$, and $3P^H_{5/2}$ in the order in which the energy increases. In the same manner, two peaks that shift about 2 meV at 15 T are assigned to $4P^L_{5/2}$ and $4P^H_{5/2}$.

As for the S state, we assign the peak of 90.75 meV at zero magnetic field to $2S_{3/2}$. But Tews *et al.* have observed a peak at 82.6 meV and identified it as $2S_{3/2}$.[3] We suppose that $2S_{3/2}$ state splits into two states, and the peaks at 90.75 meV and 82.6 meV correspond to $1S^L_{3/2}$-$2S^H_{3/2}$ and $1S^H_{3/2}$-$2S^L_{3/2}$, respectively, because the intensity of the peak at 90.75 meV increases with increasing magnetic fields. In the present experiment the peak at 82.6 meV was hardly observed. The splitting of $2S_{3/2}$ state, i.e., the energy difference between $2S^L_{3/2}$ and $2S^H_{3/2}$ is about 5.3 meV, which is close to that of the $2P_{3/2}$ and $2P_{5/2}$ states. The LO-phonon replicas of these lines are observed at 114 and 121 meV, respectively. In our previous paper, we assigned them to the transition including excitation of Ga donors. The splitting of the LO-phonon coupled state was estimated to be 6.2 meV according to the analysis of Piao *et al.*[11] This value is less than the splitting of the fundamental lines by 1.95 meV. The reason may come from the effect due to dispersion of the LO phonon available for Fano resonance, where the transition should satisfy the energy and momentum conservation. The energy and momentum of the LO phonon concerning the resonance is closely related to the dispersion of the valence band. Therefore, the accurate band parameter will be decided by this observation if the dispersion characteristics of the LO phonon are clear.

We cannot decide the direction of the displacement of a Li atom. The application of the magnetic field to other crystallographic directions enables us to clarify the symmetry of the Li acceptor. The displacement may be caused by the dynamic Jahn-Teller effect observed in Co^{2+} in InP or N in Si. The other possibility is the influence of interstitial Li donors, which are presumably located in the neighborhood of Li acceptors. This is speculated from the donor-acceptor recombination in photoluminescence measurements.

In conclusion, we observed the infrared absorption of undoped ZnSe in magnetic fields. Residual Li acceptors are responsible for the absorption lines. The peak shifts in magnetic fields clearly show that the final states related to these transitions are $2S$, $2P$, $3P$, and $4P$. The splitting of the states induced by the magnetic field that cannot be understood by the cubic symmetry of Li acceptor suggests symmetry lowering due to the off-center configuration of Li acceptor. Temperature dependence of the spectra supports the model of the displacement on the Li atom.

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