EXPERIMENTAL DETECTION OF INTERNAL POLARON STATES ASSOCIATED WITH THE INDIRECT EDGE OF AgBr USING PIEZO-OPTICAL TRANSMISSION*

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(Received 1 September 1967)

This Letter reports evidence from which we conclude that the valence band maximum of AgBr is along the ⟨111⟩ direction. The structure observed in the indirect edge by other authors[1,2] is confirmed and, together with some further structure reported herein, is attributed to excited states of the indirect exciton in which either one or both of the constituting polarons are in the ground or excited state of their respective polarization well or in states in which the center of mass of the exciton has a kinetic energy equal to the LO phonon energy.

These measurements were made possible by the use of an ultrasonic excitation, described previously,[3] that allows us to go to low temperatures (~12°K) without introducing the static stress due to the differential expansion that characterizes the use of piezoelectric transducers. The alternating strains were $\sim 10^{-6}$ and the frequencies of oscillation ranged from ~50 to 100 KHz depending on the sample's dimension and orientation. The static strains in our high-purity samples were $\lesssim 10^{-9}$. Relative changes of absorption $\sim 10^{-6}$ can be observed with signal-to-noise ratio about 1.

A general feature of the signal corresponding to the modulation of the optical transmission, at both 12 and 77°K, is that the signals obtained with light polarized parallel and perpendicular to the direction of the exciting force have opposite signs; on this "background" are superposed positive and negative peaks attributed to singularities in the density of states. The "background," on the other hand, is attributed to the intermediate states that contribute to the indirect edge. A similar effect exists in the indirect edge of Ge where the initial state has Γ_{25} symmetry while the intermediate state is at Γ_2'. This case was studied both by Engeler, Garfinkel, and Tieman[4] and by Adler and Erlbach.[5]

The data of Fig. 1 refer to a sample made to vibrate in its fundamental extensional mode by an exciting force applied along [111]. The largest peak in Fig. 1(a) at 2.6950 ± 0.0003 eV is assigned, in agreement with Ref. 1, to an indirect transition in which an LA phonon, whose energy is 7.5 ± 0.5 meV, is emitted and the final state is the lowest exciton state in which the lattice polarization corresponds to the new equilibrium configuration. This peak has an opposite sign with respect to the background, in Fig. 1(b), while it has the same sign when observed with light of both polarizations, when the exciting force is in the [100] direction. In the case when the force is applied along [110] this peak is only observed clearly with light polarized perpendicular to the applied force and is almost absent when the direction of polarization is parallel to the applied force. When the applied force is along [100] the polarization of the light is in a (110) plane; when the force is along [110] it is in a (001) plane.

These observations, together with the observation that the conduction-band minimum of AgBr is spherical,[6-8] indicate that the degeneracy of the valence-band maxima is not split by a [100] compression; the maxima are therefore along ⟨111⟩ in agreement with Bassani, Knox, and Fowler[9] and Scop.[10] Another peak is observed at 2.6985 ± 0.0005 eV which has the same sign with respect to the general background when the force is applied in any of the principal crystalline directions indicating that it is a nondegenerate state. We attribute the peaks at 2.6950 and 2.6985 eV to the $n = 1$ state of the exciton split by valley-orbit interaction produced by the interaction of the carriers with each other's polarization. From group-theoretical consideration[9,11] splitting of our exciton into an orbital triplet and a singlet is expected. The corresponding states when the phonon is absorbed rather than emitted are seen in Fig. 1(a) at 2.680 and 2.685 eV.

At 2.705 and 2.7114 ± 0.0005 eV in Fig. 1(a) we observe another pair of peaks that can also be observed when the applied force is along [100] or [110]. The 2.7114-eV peak is attributed to the formation of a free electron-hole polaron pair; the binding energy of the exciton is therefore 16.4 meV. Brandt[12] observed a peak (23.8 meV) of induced optical absorption attributable to the ionization of an electron trap filled by exceptionally long-lived photocarriers[13] (lifetime of minutes). The above result,

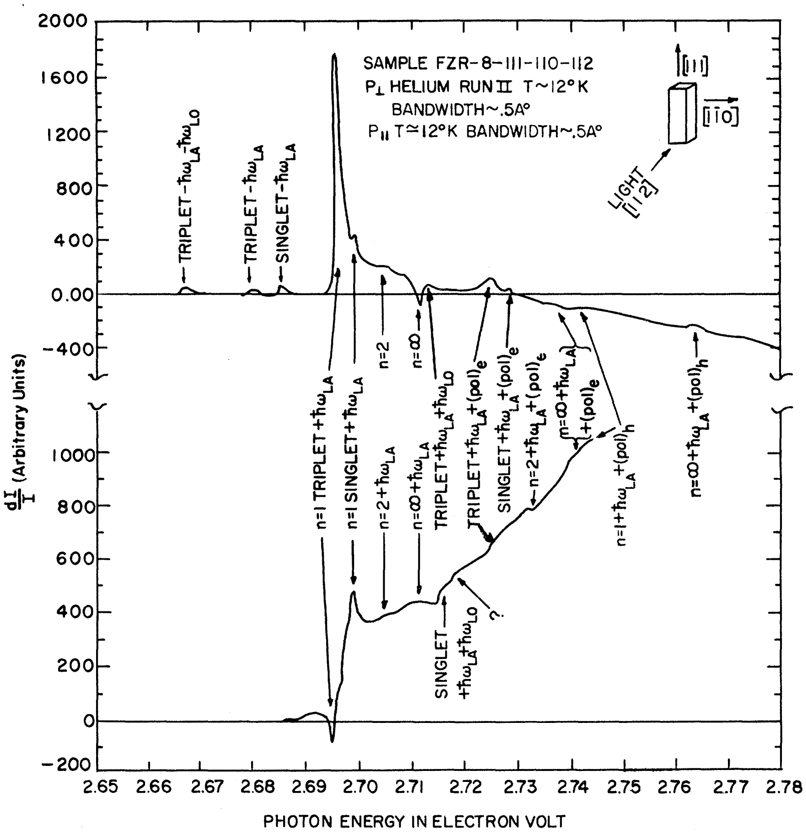

FIG. 1. AgBr sample stressed along [111], optical bandwidth 0.5 Å, frequency of vibration 59 230 Hz. Upper curve, polarization of the light along [1$\bar{1}$0]; lower curve, along [111]. Temperature ~12°K. Signal in arbitrary units. Light incident along [11$\bar{2}$].

associated with our evaluation of the exciton binding energy (16.4 meV), permits us to evaluate the ratio of electron and hole bare masses (0.46), the hole coupling constant ($\alpha_h = 2.5$), and the depth of the ground state of the hole in its polaron well (45 meV). Lynch[14] observed that in hydrostatically compressed AgBr the binding energy of the direct exciton varies in a way opposite to that of the band gap. In the case of the indirect exciton the same effect will give rise to a piezo-optical signal whose polarity is opposite to that of the orbital singlet state. The 2.705-eV peak is instead attributed to the formation of an exciton in the $n = 2$ state. The binding energy of this state (6.4 meV) is larger than what would be obtained by scaling Brandt's result[15] (3.8 meV) by the ratio of the reduced and electron bare masses; this is not astonishing since we are presumably observing a $2S$ state while Brandt observes a $2P$ state. The cubic field in the vicinity of the hole (or impurity) and the valley-orbit interaction will split the $2P_{\pm}$, $2P_0$, and $2S$ states.[16]

Some of the exciton states are repeated again displaced by $\hbar\omega = 17.6$ meV towards higher energies. When the exciting force is along [111] [Fig. 1(a)], [100], or [110] and the polarization of the light is perpendicular to the applied force, a peak is observed at 2.7126 ± 0.0005 eV, while when the polarization of the light is parallel to the exciting force applied along [111] [Fig. 1(b)] or [110] a peak is observed at 2.715 ± 0.001 eV: They are attributed, respectively, to the formation of triplet or singlet excitons whose center of mass has a kinetic energy equal to $\hbar\omega$. Both Feynman et al.[17] and Velicky[18] concluded that there should be a singularity in the density of states when the polaron kinetic energy is equal to the LO phonon energy; Johnson and Larsen[19] observed it for excitons in InSb. The same final state can be obtained if the exciton absorbs an energy $\hbar\omega$ from the lattice rather than from the electromagnetic field; the corresponding peak at 2.666 ± 0.001 eV is seen in Fig. 1(a). The value of the LO phonon energy so determined is in excellent agreement[20-22] with that obtained from other sources.

The exciton states observed between 2.6950 and 2.7114 eV are reproduced when either the electron or the hole is excited to the edge of its polarization well.[23,24] With the exciting force in either [111], [100], or [110] and the polarization of the light perpendicular to it, the $n=1$ triplet state is seen (2.725 ± 0.001 eV) while with light polarized parallel to the exciting force the $n=1$ singlet is observed at 2.728 ± 0.001 eV. The peaks at 2.736 and 2.740 eV are assigned to the $n=2$ and $n=\infty$ states of this exciton series in which only the electron is excited to the edge of its well. Using Feynman's[17,25] theoretical results and the value of the electron-lattice coupling constant (1.67) obtained from transport measurements,[20] we calculate that the energy of the ground state of the polaron in its well is 30 meV below the continuum; our data indicate instead 30.2 meV. The constant difference between the states of this exciton ladder and the corresponding ones attributed to the usual indirect exciton gives further support to this assignment.

The exciton states corresponding to the case when the hole polaron is excited should appear starting 45 meV above the 2.6950 peak. The $n=1$ states are observed between 2.745 and 2.750 eV and the $n=\infty$ at 2.765 eV. The $n=1$ state of the exciton when both the electron and hole polarons are excited to the edges of their wells is observed at 2.818 eV. The peaks at 2.772 eV [Fig. 1(a)] and 2.718 eV [Fig. 1(b)] are not identified.

We may briefly return to the "background" signal mentioned above. Two intermediate states are expected to give the largest contribution to the indirect transition[9,10,26]: an $L_{2'}$ state of the conduction band and a Γ_{15} state of the valence band. Uniaxial stress along [100] does not remove the degeneracy between the four $L_{2'}$ states: If this state would have an overwhelming importance in the transition, the piezo-optical signal should not depend on the direction of polarization of the light. If the most important intermediate state has L_{15} symmetry instead, no uniaxial stress will produce the same changes of optical absorption when observed with light polarized parallel and perpendicular to the stress. In the case of a [100] exciting force the "background" signal has a different dependence on photon energy when observed with light of different polarizations; we conclude therefore that the Γ_{15} state of the valence band is the most important

Table I. Summary of experimental data.

	This experiment	Other data
LA phonon	7.5 ± 0.5 meV	8.05 meV[b]
Exciton binding energy	16.4 ± 0.5 meV	$23.8(\mu/m_e)$ meV[a,c]
Singlet-triplet separation	3.5 ± 0.5 meV	
Binding energy of the $n=2$ state of the exciton (2S?)	6.4 ± 1 meV	$3.8(\mu/m_e)$ meV[d]
LO phonon	17.6 ± 0.5 meV	17.4 ± 0.5 meV[e-g]
m_h/m_e	2.18 ± 0.2	
m_h^*/m_e^*	2.87 ± 0.2	
α_e	1.69	1.67 ± 0.03[h] 1.69[i]
α_h	2.5 ± 0.3	
Electron polaron state	30.2 ± 0.5 meV	30 ± 1 meV[d,h,j]
Hole polaron state	52 ± 5 meV	45 meV[k]

[a]μ is the reduced mass of the exciton. The result of Buimistrov's (Ref. 15) calculation should be corrected for the low-temperature value of the dielectric constant (Ref. 7).

[b]Ref. 1.
[c]Ref. 14.
[d]Ref. 13.
[e]Ref. 20.
[f]Ref. 21.
[g]Ref. 22.
[h]Ref. 20.
[i]Ref. 7.
[j]Ref. 25.
[k]Calculated from exciton binding energy.

intermediate state for these optical transitions.

The conclusions of this Letter regarding the energy levels of excitons and polarons are summarized in Table I.

The author is grateful to Professor A. K. Ramdas, Professor P. Fisher, Professor S. Rodriguez, Professor F. C. Brown, and Dr. R. Lobo for enlightening discussions. The help of Mr. A. Perregaux in setting up the experimental equipment is acknowledged. The author wishes to warmly thank Dr. F. Moser and Dr. R. S. VanHeyningen of the Kodak Research Laboratories for the pure AgBr precipitate from which some of the crystals for this study were grown and Dr. J. E. Luvalle of the Research Laboratory, Fairchild Space and Defense System, for an ingot of zone-refined AgBr from which other crystals used in this experiment were cut. The author is grateful to Dr. F. C. Brown and Dr. R. C. Brandt for informing him of their results prior to publication.

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*Work supported in part by the Advanced Research Projects Agency and the National Science Foundation.

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