between Γ_7^+ and Γ_8^+ in Fig. 2(a).

In a previous theoretical analysis of the effects of band structure on the energy distribution of field-emitted electrons,[14] it was shown that the tunneling probability from a localized d band would be ~10^{-2} that of the tunneling from a s band. Physically this resulted from the additional confinement of the d-wave function by the centrifugal potential barrier. The d-wave functions are contracted about the ion core and do not extend into the vacuum as far as the free-electron (s-band) wave function. We expect that the tunneling from localized d-associated surface states would be similar to narrow d bands, but if surface states are occupied, then in order to preserve charge neutrality in the unit cells of the last layer or two of the metal a charge redistribution must occur.[3] Consequently the density of s-band electrons at the surface would be decreased, increasing the ratio of the tunneling probability from the surface state relative to the free electrons. The large enhancement factor for the surface states [Fig. 2(b)] relative to the contribution from the d band ($\epsilon = -0.78$ eV) supports this argument.

Tentatively we would expect the presence of surface states and their removal upon adsorption to affect the work function in a manner not previously included in any analysis.

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Anomalous Exciton Spectra in Uniaxially Deformed CuCl: Experimental Evidence for the Effect of the Stress-Induced k-Linear Term

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Anomalous exciton spectra have been observed in uniaxially deformed CuCl. The observed features, which cannot be accounted for by the previous theory, were successfully interpreted by the effect of the stress-induced k-linear terms in the energy band of CuCl, as very recently proposed by Sakoda and Onodera. Experimental evidences for this interpretation are presented.

Among several experimental means for investigating exciton states in semiconductors, the effect of uniaxial stress has been recently attracting considerable interest, mainly in view of obtaining information on the stress and spin-exchange coupling effect.[1] For the parabolic exciton at the Γ point, a general theory has been recently presented by Langer et al.[2] taking stress-exchange effect into account for cubic zinc blende and hexagonal wurtzite semiconductors. In this Letter, however, we report a new phenomenon we have observed in zinc blende CuCl, which cannot be explained by the previous theory. Essential points of the experimental results are presented here along with their interpretation in terms of the stress-induced k-linear term, very recently theoretically investigated by Sakoda and Onodera.

The uniaxial stress measurements have been made on reflection spectra of CuCl single crystals at 1.8°K. Oriented samples having parallelepiped shape of about $4\times3\times3$ mm were cut and polished from single-crystal blocks of CuCl grown by the Bridgman method.[3] Polished surfaces of the sample were chemically etched by concentrated hydrochloric acid. The pressure apparatus used in this experiment was essentially the same as described in Ref. 2. The reflection spectra for the nearly normal incident light were measured photoelectrically by a 3.4-m Jarrell-Ash spectrograph having an inverse dispersion of 0.24 nm/mm. Measurements were performed on several different geometries, including $P \parallel [001]$ (for $k \parallel [110]$ and $k \parallel [100]$), $P \parallel [110]$, $P \parallel [111]$, and $P \parallel [11\bar{2}]$. Here P is the applied stress, while k is the wave vector of the incident light.

Before presenting the experimental results, we shall make a brief summary on the excitons in the zinc blende CuCl. The free excitons in CuCl are formed by an electron in the Γ_6 conduction band and a hole in the valence bands which are composed of the upper Γ_7 ($j=\frac{1}{2}$) band and the lower Γ_8 ($j=\frac{3}{2}$) band. The negative spin-orbit splitting of these valence bands is ascribed to a large amount of mixture of the $3d$ orbitals of Cu.[4,5] The exciton states associated with these energy bands are the Γ_5 (optically allowed) and the Γ_2 (forbidden) excitons for the Γ_6-electron$-\Gamma_7$-hole pair, and are the Γ_5 (allowed) and the Γ_3, Γ_4 (both forbidden) excitons for the Γ_6-electron$-\Gamma_8$-hole pair. Customarily the former Γ_5 exciton is called the Z_3 exciton while the latter Γ_5 exciton the $Z_{1,2}$ exciton, following the nomenclature of Cardona.[4] The observed stress-induced change of the reflection spectra should be related to the behaviors of these excitons in the deformed CuCl.

Instead of showing the whole experimental results we have observed for the various geometries described above, we shall confine ourselves in this paper to report a peculiar phenomenon we found in the exciton spectra in the uniaxially deformed CuCl. The most typical result representatively demonstrating this feature is the case of $P \parallel [001]$ and $k \parallel [110]$, shown in Fig. 1. At $P=0$, double-reflection anomalies exist at about 3.205 and 3.272 eV which correspond to the Z_3 and $Z_{1,2}$ excitons, respectively. By applying stress in this geometry, these spectra show remarkable change, the main features of which are summarized as follows:

(1) With small stress, a sharp reflection peak, denoted as I_1' in Fig. 1, appears for $E \parallel P$ at the high-energy side of the Z_3 exciton. Its position coincides within experimental accuracy with the reported energy of the longitudinal exciton associated with the Z_3 exciton.[6] With increasing stress, this peak developes to an unusually strong reflection anomaly as seen in Fig. 1.

(2) A weak but distinct reflection peak I_1'' was found to appear for $E \perp P$ on the low-energy side of the Z_3 exciton. The energy of this peak coincides with the position of the triplet Γ_2 exciton reported by Staude.[6]

(3) The original Z_3 peak shows a slight splitting into two components polarized with $E \parallel P$ and $E \perp P$, respectively.

(4) The $Z_{1,2}$ exciton splits into two components, I_2^1 and I_2^2, polarized with $E \parallel P$ and $E \perp P$, respectively.

(5) A new structure I_2' becomes observable for $E \perp P$ on the low-energy side of the $Z_{1,2}$ exciton. This structure occurs at about 60-meV higher energy than the I_1'' peak, which is attributed to the Γ_2 exciton. This energy separation

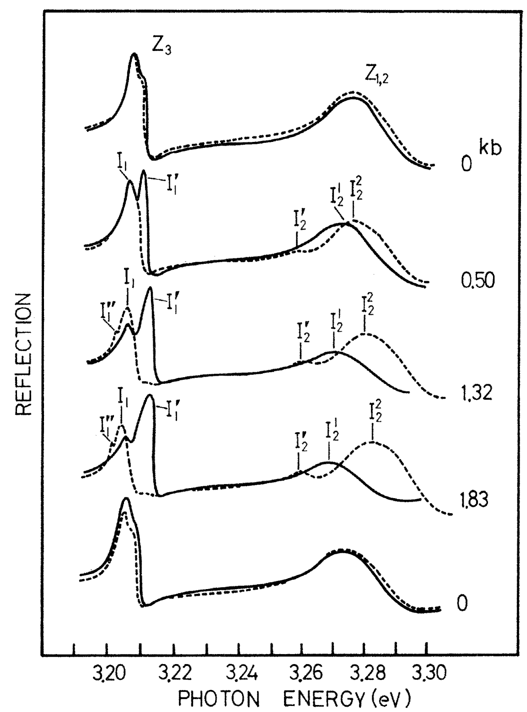

FIG. 1. Stress-induced change of the exciton reflection spectra of CuCl for $P \parallel [001]$ and $k \parallel [110]$. Solid and broken lines represent the polarized components with with $E \parallel P$ and $E \perp P$, respectively. I_1 and $I_2^{1,2}$ are the structures associated with the Z_3 and $Z_{1,2}$ excitons, respectively, while structures I_1', I_1'', and I_2' are stress-induced reflection anomalies. The bottom curves represent spectra after release of the applied pressure.

is equal to the spin-orbit–splitting energy of the valence band of CuCl. Since the separation between the two triplet excitons, Γ_2 ($^3P_0$) and $\Gamma_{3,4}$ ($^3P_2$), is determined by the spin-orbit interaction of the hole irrespective of the spin-exchange energy, it would be natural for us to attribute this structure to the Γ_4 triplet exciton associated with the $Z_{1,2}$ exciton. This assignment is also confirmed by the theoretical consideration described later. When applied pressure was released, the whole spectra were found to return to the original spectra at $P=0$, as shown in Fig. 1.

As for the interpretation of these results, splitting of the $Z_{1,2}$ exciton is evidently attributable to the splitting of the orbitally degenerate Γ_8 valence band. Also, the stress-induced appearance of the normally forbidden triplet Γ_4 exciton is explainable by the deformation-induced mixing of the Γ_4 exciton with the $E \perp P$ component of the $Z_{1,2}$ exciton. These features are quite similar to the case of the A excitons in zinc blende ZnSe and ZnS as observed by Langer et al.[2] On the other hand, a slight splitting of the Z_3 exciton can be accounted for as well by the previously known effect of the stress-exchange coupling for the Z_3 exciton. Thus all of these features [(3)-(5)] are qualitatively well understood in the framework of the usual exciton matrix formalism hitherto applied to the stress effect of excitons with $k=0$.

However, when we try to interpret the first two features described above, we encounter serious difficulty. Especially with regard to the most striking feature of the present results, namely, the surprisingly strong reflection anomaly which appears at the longitudinal mode of the Z_3 exciton, the usual theory seems to become completely inapplicable. One possible cause for finding a reflection anomaly on the high-energy side of an exciton is the effect of spatial dispersion as demonstrated by Hopfield and Thomas.[7] However, the present phenomenon is evidently originating from a different mechanism, since the surface condition is not essential in the present case. Also the strong polarization and (as described later) k-vector–dependent anisotropy of structure is hardly explained by the spatial dispersion effect.

The remaining possibility is the stress-induced mixing of the longitudinal and transverse excitons in the deformed crystal, but as long as we consider the problem at $k=0$, this is also inapplicable to the present case simply for the reason that the uniaxial distortion along the [001] axis never mixes these two modes. For distortion along the [001] axis, the excitons can be still classified as a purely longitudinal or purely transverse mode at $k=0$, even in a deformed lattice. Therefore, the longitudinal exciton should be unobservable, in contradiction to the observed result. Also, the usual exciton matrix fails to predict the appearance of the Γ_2 triplet exciton with stress. Consequently, we have to conclude that we are dealing with a new phenomenon where some higher-order effect is playing an essential role.

The only possible answer to this problem seems to be an effect of the finite k vector of the exciton. Longitudinal-transverse mixing due to the finiteness of the k vector has been discussed for wurtzite ZnO by Hopfield and Thomas.[8] Also the effect of the finite k vector, combined with a k-linear term of the energy band, has been demonstrated by Mahan and Hopfield[9] to exhibit an additional reflection anomaly on the B exciton in CdS. It was considered that such an effect arising from the finiteness of the k vector was likely to play an important role in the anomalous exciton spectra of the CuCl observed here.

This speculation has been given a theoretical foundation very recently by Sakoda and Onodera.[10] Although the relevant energy bands, i.e., the Γ_6-conduction and the Γ_7-valence bands for the Z_3 exciton, possess no k-linear term in cubic zinc blende CuCl, the external stress will split them at the off-Γ points, giving rise to the stress-induced k-linear terms in these energy bands near the Γ point. Sakoda and Onodera investigated the effect of such a stress-dependent k-linear term for excitons with finite k vectors. The qualitative conclusions of their treatments pertaining to the Z_3 exciton under the [001] stress are summarized as follows:

(1) For $k \parallel [110]$, the longitudinal Z_3 exciton can indeed mix with the $E \parallel P$ component of the transverse Z_3 exciton by virtue of the stress-induced k-linear term. Therefore, the mixed mode should become optically active for $E \parallel P$, in agreement with the experimental result.

(2) By increasing stress along the [001] axis and for $k \parallel [110]$, energies of these two branches, one mainly transverse and the other longitudinal, cross, giving rise to a clamping effect near the crossing point due to the coupling by the stress-induced k-linear term. As a result, the natures of the two branches are interchanged beyond this crossing point, a dominantly transverse mode

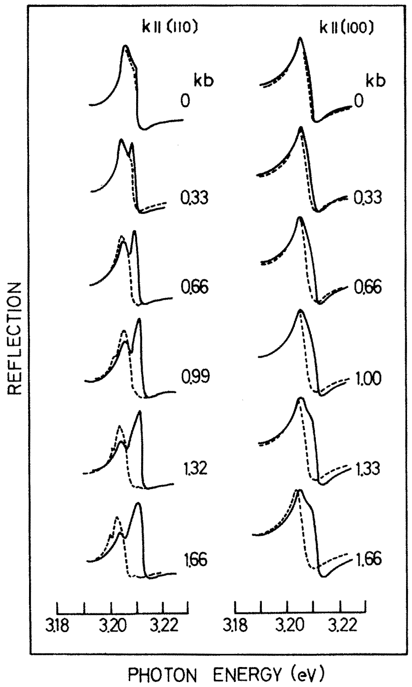

FIG. 2. Stress-induced change of reflection spectra due to the Z_3 exciton in CuCl, the left half for $P \parallel [001]$ and $k \parallel [110]$, and the right half for $P \parallel [001]$ and $k \parallel [100]$. The solid and broken lines represent the polarized components with $E \parallel P$ and $E \perp P$, respectively.

appearing at higher energy and a dominantly longitudinal one at lower energy.

(3) The stress-induced k-linear term is also responsible for the mixing of the $E \perp P$ component of the transverse Z_3 exciton and the Γ_2 triplet exciton. Thus, it is predicted that the Γ_2 triplet exciton should become observable for $E \perp P$, again in accordance with the experiment.

All of these theoretical results by Sakoda and Onodera could explain the observed features quite well. Especially, it should be emphasized that anomalous increase of intensity of the stress-induced reflection anomaly I_1' could be qualitatively understood by the clamping effect between the interacting longitudinal and transverse modes of the Z_3 exciton. Their theory has been found also to be valid for experimental results observed in other geometries than $P \parallel [001]$. Yet the most direct evidence for this interpretation will be found in the case of $P \parallel [001]$ and $k \parallel [100]$. In this geometry, the theory predicts that the k-linear term only mixes the longitudinal Z_3 exciton with the optically forbidden Γ_2 triplet exciton, therefore the reflection anomaly due to the mixed mode should be absent for $k \parallel [100]$ in contrast to the case of $k \parallel [110]$. The experimental results are shown in Fig. 2. We can immediately notice that the corresponding structure is much smaller for $k \parallel [100]$ than the anomaly observed for $k \parallel [110]$. Considering the accuracy of the optical alignment (estimated to be about 5°) in the present experiment, the appearance of a weak shoulderlike structure for $k \parallel [100]$ would be safely attributed to a slight misalignment of the experimental geometry. We believe that this result should be regarded as definite evidence for the effect of the stress-induced k-linear term on the anomalous exciton spectra in uniaxially deformed CuCl, as proposed by Sakoda and Onodera.

A fuller account of the experimental results as well as their quantitative analysis in terms of the Sakoda-Onodera theory will be reported shortly.

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