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# Relaxation processes and characteristics of the luminescence spectra of ZnTe and $Zn_xCd_{1-x}Te$ crystals

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An investigation was made of the features of the luminescence spectra ZnTe and $Zn_xCd_{1-x}Te$ crystals at low rates of resonant pumping with sources of half-width $\Delta\Omega$ much smaller than the natural exciton-level width $\gamma$. An analysis of the polarization and energy correlations between the structure of the observed emission spectra and the excitation photons yielded information on the longitudinal and transverse relaxation times. The problem of the relationship between resonance Raman scattering and luminescence was considered from the point of view of the relaxation theory. It was found that for $\Delta\Omega<\gamma$ there was a possibility of a change from the resonance Raman scattering to the usual thermalized luminescence via various stages of hot luminescence.

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## 1. INTRODUCTION

In studies of radiative recombination in crystals under resonance excitation conditions much attention is usually given to the question of the relationship between resonance Raman scattering and hot and ordinary luminescence.[1,2] Recently, this relationship has become particularly important because its studies may solve one of the most difficult problems in the physics of interacting excitons, which is the experimental realization of the Bose–Einstein condensation.

If we follow the Heitler theory of resonance fluorescence,[3] we find that luminescence can be obtained only if we use a source whose excitation band is of half-width $\Delta\Omega>\gamma$, where $\gamma$ is the natural width of an electron (exciton, biexciton) level. In the opposite case, i.e., for $\Delta\Omega<\gamma$, the structure of the spectra should be governed by the light scattering processes. Nagasawa *et al.*[4] investigated only the correlation between the luminescence spectra and the excitation photons from a tunable laser, and they concluded that this behavior was exhibited by their CuCl crystals in the case of two-photon resonance excitation of the biexciton energy band.

However, the validity of the Heitler results[3] in the case of an exciton system is not self-evident and these results may be even incorrect because in solids there is a possibility of going over from light scattering processes to luminescence for any nonzero value of $\Delta\Omega$ smaller than $\gamma$ and this can occur as follows. During a time interval $\gamma^{-1}$ there exist scattering complexes for which the absorption and luminescence processes are, in principle, indistinguishable.[5] The luminescence appearing before the completion of the relaxation processes is known as the hot luminescence. The ordinary luminescence is the radiation which appears after the relaxation is complete. It thus follows from Toyozawa's

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theory[5] that recording of the luminescence spectra with a time resolution of a fraction of a picosecond after various time intervals from the excitation should show that the nature of the observed luminescence depends on the stage reached by the relaxation processes. Direct measurements with this type of time resolution are very difficult to perform. However, this difficulty may be bypassed if the following circumstance is taken into account. Toyozawa[5] shows that information on the stage of a relaxation process can be deduced from an analysis of the polarization correlation between the luminescence spectra and excitation photons. A polarization correlation appears because radiative transitions may occur before the completion of the transverse and longitudinal relaxation processes, which essentially represent the absorption of the excitation energy. Therefore, the luminescence and absorption processes are correlated in time and the properties of the observed spectra depend on the properties of the excitation photons. Consequently, if a polarized excitation source is used, the luminescence photons may be correlated with the absorbed excitation photons both in respect of the energy and polarization. It should be noted that in studies of luminescence it is implicitly assumed that the absorption and luminescence processes are independent, i.e., that luminescence appears after absorption.

Naturally, in an analysis of the polarization correlation we have to select radiative transitions with times much shorter than the relaxation times [for example, processes accompanied by the emission of longitudinal optical (LO) phonons for which the time $\tau_{LO}$ is $\sim 10^{-13}$ $-10^{-12}$ sec]. If we then use photons whose energy $E_{exc}$ exceeds by various amounts the energy corresponding to the bottom of the exciton band and if we analyze the properties of the luminescence bands after the emission of various numbers of the LO phonons, we can obtain information on the progress of the relaxation processes and observe a transition from Raman scattering to luminescence.

We shall describe an investigation of the linear polarization correlation of the luminescence spectra of cubic ZnTe and $Zn_xCD_{1-x}Te$ crystals with the excitation sources. We shall use the results to draw conclusions on the relaxation times and the nature of the observed luminescence.

## 2. EXPERIMENTAL METHOD AND RESULTS

We investigated the characteristics of the low-temperature luminescence spectra of cubic ZnTe and $Zn_xCd_{1-x}Te$ crystals in the range of their exciton states. The excitation was provided by various linearly polarized argon ($Ar^+$) and helium-cadmium (He-Cd) lasers, i.e., of the gas lasers for which $\Delta\Omega$ was known to be smaller than $\gamma$. The measurements were carried out at a relatively low excitation flux density $R_{exc}$ ($10^{19}$ photons$\cdot$cm$^{-2}\cdot$sec$^{-1}$) but for various differences between the energy of the excitation photons $E_{exc}$ and the exciton ground state $E_{A_{n=1}}$ (these differences will be denoted by $\Delta E_{exc}$). The investigated spectra were recorded photographically using a PGS-2 diffraction spectrograph and they were also studied photoelectrically using the synchronous detection method. The degree of linear polarization of the luminescence was calculated from the ratio $(I_{\parallel}-I_{\perp})/(I_{\parallel}+I_{\perp})$, where $I_{\parallel}$ and $I_{\perp}$ were the intensities of the luminescence bands in the geometry in which the plane of polarization of the polarizer $E_p$ was parallel or perpendicular to the plane of polarization of the excitation radiation $E_L$ provided by the lasers.

We shall first consider the main features of the structure of the luminescence spectra of cubic ZnTe crystals obtained for $R_{exc} \approx 10^{19}$ photons$\cdot$cm$^{-2}\cdot$sec$^{-1}$ at $T = 4.2$ °K, observed for various values of $\Delta E_{exc}$. The latter were varied from 0.4271 to 0.0293 eV, i.e., from $16.4E_{LO}$ to $1.1E_{LO}$, where $E_{LO}$ is the energy of the LO phonons. We obtained the microphotograms of the appropriate luminescence spectra (Fig. 1). It was found that for $\Delta E_{exc} = 16.4E_{LO}$ (He-Cd laser, $\lambda_{exc} = 4416$ Å) and $\Delta E_{exc} = 12.3E_{LO}$ ($Ar^+$ laser, $\lambda_{exc} = 4579$ Å) the structure of the spectra was identical (points in Fig. 1a). For both values of $\Delta E_{exc}$ there were several luminescence bands whose intensity maxima were located at $\lambda = 5202$ Å ($M_u$), 5219 Å ($I_1$), 5229 Å ($I_2$), and 5249 Å ($I_3$). The first of them, denoted by $M_u$, was in the direct vicinity of the ground exciton state and was due to the luminescence of the upper polariton branch.[6] The next two bands ($I_1$ and $I_2$) were due to the radiative recombination of exciton-impurity complexes, i.e., of excitons localized at neutral acceptors and donors, respectively. The nature of the third exciton-impurity complex (corresponding to the line $I_3$) was not identified. In agreement with the cubic structure of the investigated crystals, there was no significant polarization of any of the luminescence bands for both values of $\Delta E_{exc}$.

For $\Delta E_{exc} = 6.1E_{LO}$ ($Ar^+$ laser, $\lambda_{exc} = 4880$ Å) there was still no polarization of the luminescence bands. In general, the spectrum was similar to those described above. The observed changes (represented by triangles

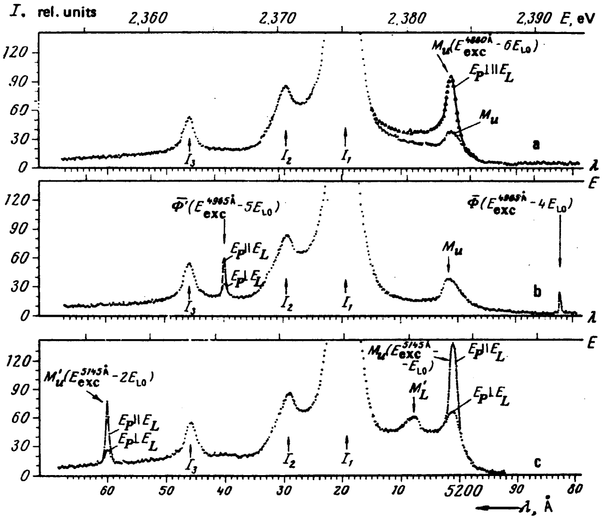

FIG. 1. Microphotograms of the luminescence spectra of ZnTe crystals obtained at excitation rates $R_{exc} \approx 10^{19}$ photons$\cdot$cm$^{-2}\cdot$sec$^{-1}$ at $T = 4.2$ °K for different values of $\Delta E_{exc}$: a) $16.4E_{LO}$, $12.3E_{LO}$, $6.1E_{LO}$; b) $4.5E_{LO}$; c) $1.1E_{LO}$.

in Fig. 1a) were limited to a considerable rise of the band $M_u$ and a considerable reduction in the asymmetry of its shape.

A further reduction in $\Delta E_{\text{exc}}$ resulted in the appearance of certain features in the luminescence spectra. For example, for $\Delta E_{\text{exc}} = 4.5E_{\text{LO}}$ (Ar⁺ laser, $\lambda_{\text{exc}} = 4965$ Å), we observed two additional bands: $\bar{\Phi}(\lambda = 5182$ Å) and $\bar{\Phi}'(\lambda = 5240$ Å) located on the long-wavelength side of the excitation band and separated exactly by $4E_{\text{LO}}$ and $5E_{\text{LO}}$ (Fig. 1b). The luminescence band $\bar{\Phi}$ corresponded to an energy higher and the band $\bar{\Phi}'$ to an energy lower than the bottom of the exciton band $E_{A_{n=1}}$. Both $\bar{\Phi}$ and $\bar{\Phi}'$ were polarized in the plane of polarization of the laser providing the excitation (the degree of the linear polarization was 0.32 and 0.20, respectively).

For $\Delta E_{\text{exc}} = 1.1E_{\text{LO}}$ (Ar⁺ laser, $\lambda_{\text{exc}} = 5145$ Å) there was luminescence also from the lower polariton branch originating from its bottleneck region (denoted by $M_L'$ in Fig. 1c). The intensity of the $M_u$ band then increased strongly again and its asymmetry became much less compared with the excitation which was not in resonance with $E_{\text{LO}}$ (for example, $\lambda_{\text{exc}}$ 4579 Å). In addition, at an energy $E_{\text{LO}}$ on the long-wavelength side from $M_u$, there appeared a new band $M_u'(\lambda = 5260$ Å), which was located below $E_{A_{n=1}}$. Both the $M_u$ and $M_u'$ bands were polarized in the plane of polarization of the laser radiation. The degree of their linear polarization was 0.70 and 0.66, respectively.

Among the above results the most interesting were the cases of $\Delta E_{\text{exc}}$ amounting to $6.1E_{\text{LO}}$ and $1.1E_{\text{LO}}$, i.e., when an approximately integral number of the LO phonons made it possible to reach directly the exciton resonance region. Therefore, we studied the evolution of the structure of the luminescence spectra in these two cases during smooth departure from resonance as a result of variation of $E_{A_{n=1}}$ with temperature. We obtained microphotograms of the following spectra (Fig. 2): a) the reflection and luminescence spectra for the same value of $R_{\text{exc}} = 10^{19}$ photons·cm⁻²·sec⁻¹ at $T = 40$ °K, for which $\Delta E_{\text{exc}}$ was b) $6.6E_{\text{LO}}$ (Ar⁺ laser, $\lambda_{\text{exc}} = 4880$ Å) and c) $1.6E_{\text{LO}}$ (Ar⁺ laser, $\lambda_{\text{exc}} = 5145$ Å). The results indicated that at this temperature the intensity of the line $I_1$ due to exciton–impurity complexes decreased considerably compared with the intensity of this band at $T = 4.2$ °K. The exciton–impurity bands $I_2$ and $I_3$ disappeared completely. Within the exciton reflection band we observed luminescence due to the lower and upper polariton branches (bands $M_l$ and $M_u$ in Figs. 2b and 2c). The region of the upper polariton branch displayed the $M_u$ band itself with the characteristic asymmetry profile and also the unpolarized band $\tilde{\Phi}$, which was located on the long-wavelength side of $\lambda_{\text{exc}} = 4880$ Å always by an amount equal to $6E_{\text{LO}}$, i.e., its spectral position remained unchanged when $E_{A_{n=1}}$ was varied. It should be noted that the band $\tilde{\Phi}$ was found at energies greater than $E_{A_{n=1}}$. Below $E_{A_{n=1}}$ there was no additional structure which would be energy-correlated with $\lambda_{\text{exc}}$. A complex structure was also observed in the exciton resonance region for $\lambda_{\text{exc}} = 5145$ Å. However, in this case the band $\bar{\Phi}$ was polarized in the plane of polarization of the laser excitation radiation (the degree of polarization was 0.70). It should be stressed that the band $\bar{\Phi}$ was located on the long-wavelength side of $E_{\text{exc}}$ and separated from the latter by an amount exactly equal to $1E_{\text{LO}}$, and that its spectral position remained unchanged for a variation of $E_{A_{n=1}}$ similar to that which occurred in the case of the $\tilde{\Phi}$ band.

It should be noted that for $\lambda_{\text{exc}} = 5145$ Å at $T = 40$ °K in addition to the $\bar{\Phi}$ band at energies below $E_{A_{n=1}}$, there were also two polarized bands $\bar{\Phi}'$ ($\lambda = 5260$ Å) and $\bar{\Phi}''$ ($\lambda = 5319$ Å). The energy positions of all three bands $\bar{\Phi}$, $\bar{\Phi}'$, and $\bar{\Phi}''$ remained unchanged when the temperature increased and they obeyed exactly the relationship $E_{\text{exc}} - nE_{\text{LO}}$ with $n = 1, 2$, or 3. The half-widths of these bands reflected the instrumental function of the spectrograph used. This was the reason for their common behavior.

We determined the temperature dependences of the intensities of the bands $\tilde{\Phi}$ for $\lambda_{\text{exc}} = 4880$ Å, $\bar{\Phi}$ for $\lambda_{\text{exc}} = 5145$ Å, and $M_u$ for ZnTe crystals subjected to a constant excitation rate $R_{\text{exc}} = 10^{19}$ photons·cm⁻²·sec⁻¹ (Fig. 3). All the intensities were normalized to the intensities of the corresponding bands at $T = 4.2$ °K, which were taken as unity.

The use of $\text{Zn}_x\text{Cd}_{1-x}\text{Te}$ mixed crystals made it possible to vary the band gap $E_g$ and the energy of the exciton ground state $E_{A_{n=1}}$ by altering the composition $x$. For this reason we carried out a similar investigation on $\text{Zn}_{0.94}\text{Cd}_{0.06}\text{Te}$ cubic crystals at $T = 4.2$ °K at the same excitation rate of $R_{\text{exc}} = 10^{19}$ photons·cm⁻²·sec⁻¹.

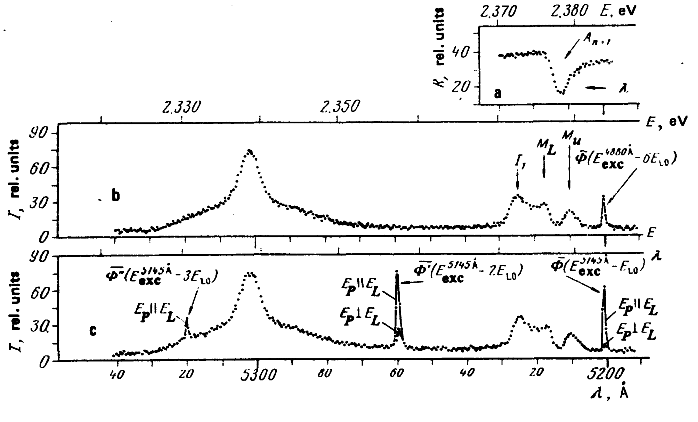

FIG. 2. Microphotograms of the reflection and luminescence spectra of ZnTe crystals at $T = 40$ °K for $R_{\text{exc}} \approx 10^{19}$ photons·cm⁻²·sec⁻¹ for different values of $\Delta E_{\text{exc}}$: a) reflection spectra; b) luminescence spectra for $6.6E_{\text{LO}}$; c) luminescence spectra for $1.6E_{\text{LO}}$.

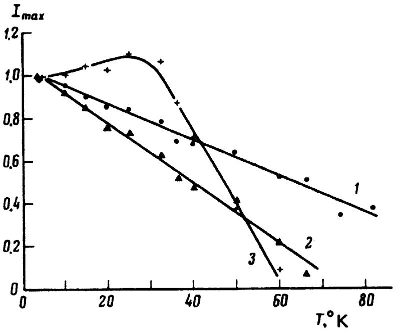

FIG. 3. Temperature dependences of the intensities $I_{\max}$ at the band maxima: 1) $\bar{\Phi}$; 2) $\tilde{\Phi}$; 3) $M_u$ (normalized to $T = 4.21$ °K).

This made it possible to increase the range of values of $\Delta E_{\text{exc}}$ and to consider also the features of the luminescence spectra at $\Delta E_{\text{exc}} = 2.2E_{\text{LO}}, 5.6E_{\text{LO}}, 7.2E_{\text{LO}}, 9.7E_{\text{LO}}$, and $17.5E_{\text{LO}}$. The microphotograms of the spectra of these crystals were basically similar to those given above and they simply supplemented the results obtained for the ZnTe crystals. In fact, at $\Delta E_{\text{exc}} = 2.2E_{\text{LO}}$ and $5.6E_{\text{LO}}$ the luminescence spectra of $\text{Zn}_{0.94}\text{Cd}_{0.06}\text{Te}$ included not only lines due to exciton-impurity complexes, lower polariton branch, and upper polariton branch, but also polarized $\bar{\Phi}$ bands, and for $\Delta E_{\text{exc}} = 7.2E_{\text{LO}}$ the unpolarized band $\tilde{\Phi}$. For $\Delta E_{\text{exc}} = 9.7E_{\text{LO}}$ and $17.5E_{\text{LO}}$ the observed spectra were identical in respect of the structure and all the luminescence bands were unpolarized.

The features of the polarization correlation of the luminescence spectra are presented in a systematic manner in Table I for all values of $\Delta E_{\text{exc}}$.

## 3. DISCUSSION OF RESULTS

It is clear from our results that at a constant excitation rate of $R_{\text{exc}} \approx 10^{19}$ photons · cm$^{-2}$ · sec$^{-1}$, created by a source with $\Delta\Omega \ll \gamma$, variation of $\Delta E_{\text{exc}}$ from $1.1E_{\text{LO}}$ to $(9-10)E_{\text{LO}}$ generates the intrinsic luminescence of the ZnTe and $\text{Zn}_{0.94}\text{Cd}_{0.06}\text{Te}$ crystals independent of the properties of the excitation photons (bands $M_u, I_1, I_2$, and $I_3$), as well as other bands $\Phi$ ($\bar{\Phi}$ and $\tilde{\Phi}$) whose energy positions are always, and the polarizations sometimes (in a certain range of $\Delta E_{\text{exc}}$), correlated with the excitation radiation. The pure luminescence origin of the first group of bands is self-evident but the nature of the second group requires separate consideration. In this connection it must be stressed that the complete explanation of the $\Phi$ bands meets with a number of difficulties if we adopt the model postulating luminescence of "hot" excitons.[7] In fact, according to this model there should be no luminescence band with $n = 1$. However, this band appears clearly in the spectra of ZnTe crystals for $\lambda_{\text{exc}} = 5145$ Å. It is particularly important to note that in the case of ZnTe crystals at $T = 40$ °K for $\lambda_{\text{exc}} = 5145$ Å there are simultaneously bands with $n = 1, 2$, and 3 and the last of them, i.e., $\bar{\Phi}''$, is located considerably lower than $E_{A\,n=1}$ (by about 60 meV). This circumstance effectively excludes the possibility of its interpretation as the "hot" exciton luminescence or any other luminescence process because there are no exciton states in the energy range $E \ll E_{A\,n=1}$.

TABLE I. Characteristics of luminescence spectra of crystals for all values of $\Delta E_{\text{exc}}$.

| $\Delta E_{\text{exc}}$ (in units of $E_{\text{LO}}$) | | |
|---|---|---|
| 1.1-1.6, 2.2, 4.6 | 6.1-6.6, 7.2, 8.6 | 9.7, 12.3, 16.4, 17.5 |
| Correlation of luminescence with excitation photons | | Luminescence independent of properties of excitation photons |
| phase and energy<br>$\tau_{\text{rad}} < \tau_{\text{tr}}, \tau_{\text{rad}} < \tau_{\text{lg}}$ | energy alone<br>$\tau_{\text{tr}} < \tau_{\text{rad}} < \tau_{\text{lg}}$ | $\tau_{\text{rad}} > \tau_{\text{tr}}, \tau_{\text{rad}} > \tau_{\text{lg}}$ |
| scattering ≈ strongly unthermalized hot luminescence | partly thermalized hot luminescence | ordinary totally thermalized luminescence |
| absorption and luminescence processes mutually related | | independent absorption and luminescence processes |

It seems to us that the results obtained should be analyzed on the basis of ideas put forward by Toyozawa.[5] According to these ideas, the energy and polarization correlations with the excitation photons are typical of secondary unthermalized radiation which appears during time intervals shorter than the longitudinal ($\tau_{\text{lg}}$) and transverse ($\tau_{\text{tr}}$) relaxation times representing in fact the absorption of the excitation energy. Here, $\tau_{\text{lg}}$ represents the energy and $\tau_{\text{tr}}$ the phase (polarization) times of the correlation between the pump photons and the electron excitations created in a crystal.

In this connection it should be noted that by reducing $\Delta E_{\text{exc}}$ we have reduced primarily the transition times of electron excitations to their lowest energy states, from which radiative transitions mainly take place. If we assume that the LO phonon emission time $\tau_{\text{LO}}$ is less than $\tau_{\text{tr}}$ and $\tau_{\text{lg}}$, the nature of the observed spectra and the properties of the $\Phi$ bands obtained for various values of $\Delta E_{\text{exc}}$ should reflect the features of the radiative processes at various stages of the relaxation. Consequently, an analysis of the polarization properties of the $\Phi$ bands demonstrates the possibility of going over from the ordinary thermalized luminescence to stimulated Raman scattering through various stages of the hot luminescence. Such a transition occurs partly under our conditions. In fact, it is clear from Table I that the variation of $\Delta E_{\text{exc}}$ from $17.5E_{\text{LO}}$ to $(9-10)E_{\text{LO}}$ does not affect the structure or energy positions of any of the luminescence bands. Moreover, they are all unpolarized, as expected for cubic ZnTe crystals. These factors are direct evidence of their pure luminescence origin. Under these conditions the absorption and subsequent reemission processes are separated in time by intervals $\tau > \tau_{\text{lg}}$, $\tau > \tau_{\text{tr}}$, i.e., by intervals during which all the longitudinal and transverse relaxation processes are readily completed. Therefore, the absorption and emission are independent processes and it is natural to expect the loss of the energy and phase (polarization) coupling between the emitted radiation and the excitation photons.

In the range $6E_{\text{LO}} < \Delta E_{\text{exc}} < 9E_{\text{LO}}$ the spectra have bands $\tilde{\Phi}$, whose energy positions are correlated with the pump photons. They are always located above the bottom of the exciton energy band and, like the pure luminescence bands, are unpolarized. Their appearance is due to the excess populations of the intermediate states with electron excitations, for which the transverse relaxation process is completed but not the longitudinal one. This is why there is a correlation between the energy positions of the $\tilde{\Phi}$ and the pump photons. Therefore, the $\tilde{\Phi}$ bands may be classified as representing partly thermalized hot luminescence, which appears at the later stages of the relaxation processes.

The bands $\tilde{\Phi}$ observed in the range $\Delta E_{\text{exc}} < 6E_{\text{LO}}$ are characterized by the energy and phase (polarization) coupling with the pump photons. This circumstance demonstrates that a reduction in $\Delta E_{\text{exc}}$ reduces also the transition times of the electron excitations to their lowest energy states. Therefore, radiative transitions accompanied by the emission of the LO phonons occur before the completion of the longitudinal and transverse relaxation processes. Consequently, the $\bar{\Phi}$ bands reflect to a greater degree the properties of the pump photons and not the pure intrinsic luminescence of the ZnTe crystals. In principle, they can be regarded as strongly nonthermalized hot luminescence. However, under these conditions we also observe the bands $\overline{\Phi'}$ and $\overline{\Phi''}$ located much below $E_{A n=1}$, where there are no exciton states. These bands can only be due to resonance Raman scattering. Therefore, the appearance of the polarization in the $\bar{\Phi}$ bands should be interpreted by assuming that the strongly unthermalized hot luminescence acquires features typical of the resonance Raman scattering, i.e., it should contain the luminescence component and the component due to the Raman scattering. It is the second component that gives rise to the $\overline{\Phi'}$ and $\overline{\Phi''}$ bands.

The increase in the degree of polarization of the $\bar{\Phi}$ bands on reduction of $\Delta E_{\text{exc}}$ from $4.5E_{\text{LO}}$ to $1.1E_{\text{LO}}$ shows that the relative contribution of the scattering component increases. Therefore, the bands with $n=1$, 2, and 3, and also possibly the bands with $n=4$ or 5, can be regarded as the resonance Raman scattering bands.

If the loss of the polarization of the $\Phi$ bands for $\Delta E_{\text{exc}}$ beyond $6E_{\text{LO}}$ does indeed reflect a transition from resonance Raman scattering to luminescence, the luminescence component should exhibit thermal quenching. We can consider this point by analyzing the results shown in Fig. 3, which demonstrate that an increase in temperature from 4.2 °K to 70 °K reduces considerably the intensity of the $\Phi$ bands at both values of $\lambda_{\text{exc}}$ (lines 1 and 2). This may be due to two factors: 1) a reduction in the detuning from resonance as a result of variation of $E_{A n=1}$ with temperature; 2) thermal quenching of the luminescence. Since between 6LO and 1LO phonons results in approach to $E_{A n=1}$ with practically the same accuracy (≈1 Å) and since the energy positions of the $\bar{\Phi}$ and $\tilde{\Phi}$ bands at both $\lambda_{\text{exc}}$ do not vary with rising temperature, the influence of the detuning on their intensities is the same. Consequently, the difference between the slopes of lines 1 and 2 indicates more effective thermal quenching of the intensity of the unpolarized $\tilde{\Phi}$ band even if we assume that it occurs also in the case of the $\bar{\Phi}$ band. Therefore, the $\tilde{\Phi}$ band is closer to luminescence than $\bar{\Phi}$. In fact, curve 3 reflects the temperature dependence of the intensity of the pure luminescence band $M_u$. It is clear from Fig. 3 that up to 30 °K the intensity of this band rises somewhat. This is clearly due to the effective thermal dissociation of electron–impurity complexes in this temperature range. The concentration of free excitons should, therefore, rise initially, compensating the thermal reduction in the intensity of the $M_u$ band. After the dissociation of the electron–impurity complexes, i.e., in the temperature range $T > 30$ °K, the rate of reduction of the intensity of the $M_u$ band is considerably greater than the rate of reduction of the intensities of the $\bar{\Phi}$ and $\tilde{\Phi}$ bands. This is easily explained by the fact that the pure luminescence is completely thermalized and should be sensitive to an increase in the efficiency of nonradiative processes. The position of the $\Phi$ bands is related only to a reduction in the excess of the excitation energy by the emission of the LO phonons. It is very characteristic that the slope of line 2 is greater than that of line 1 but it is less than that of curve 3. This is to be expected because line 2 represents the thermal reduction in the intensity of the partly thermalized hot luminescence whose properties are closer to those of the pure luminescence than to the Raman scattering. Therefore, the slope of the corresponding dependence should be intermediate between the cases of the completely thermalized luminescence (curve 3) and the Raman scattering, i.e., maximally unthermalized, radiation (line 1).

If we consider the $\bar{\Phi}$ bands representing the Raman scattering, we can also explain other features of the observed spectra. In particular, in the case of the Raman scattering the one-phonon process, i.e., the process accompanied by the emission of one LO phonon, is—in principle—forbidden by the law of conservation of momentum. However, this restriction can be lifted by the size resonance effects[8] and also by the contribution of impurities and acoustic phonons to the scattering processes.[9] Therefore, the one-phonon scattering band (with $n=1$) appears clearly in the luminescence spectra of ZnTe crystals for $\lambda_{\text{exc}} = 5145$ Å. Moreover, we can now account for the presence of the $\overline{\Phi''}$ band which is located well below $E_{A n=1}$ (by 60 meV). In fact, in spite of the fact that the emission of two LO phonons we reached the region where there are no exciton states, further reduction in the energy occurs as a result of the scattering by the LO phonons exclusively because of the Raman component.

## 4. CONCLUSIONS

The results obtained demonstrate that the use of an excitation source with $\Delta\Omega \ll \gamma$ produces spectra whose structure are governed by the relaxation processes. In the case of ZnTe and $\mathrm{Zn}_x\mathrm{Cd}_{1-x}\mathrm{Te}$ crystals subjected to excitation at a rate $R_{\text{exc}} \approx 10^{19}$ photons · cm$^{-2}$ · sec$^{-1}$ the transverse relaxation time $\tau_{\text{tr}}$ is ~$6\tau_{\text{LO}}$ and the longitudinal relaxation time $\tau_{\text{lg}}$ is ~$(9-10)\tau_{\text{LO}}$, i.e., $\tau_{\text{tr}} < \tau_{\text{lg}}$. If the radiative transitions occur during the interval $\tau_{\text{rad}} < \tau_{\text{tr}}$, strongly unthermalized hot luminescence with the characteristics of resonance Raman scattering is observed. In the range $\tau_{tr} < \tau_{rad} < \tau_{1g}$ the emitted radiation is the partly thermalized hot luminescence, whose properties approach that of the ordinary luminescence. The completely thermalized luminescence appears in the $\Delta\Omega \ll \gamma$ case only after the relaxation processes are completed. Thus, the hot luminescence is an intermediate type of radiation on transition from resonance Raman scattering to luminescence.

We shall conclude by noting that our polarization analysis of the relaxation processes applies to relatively low rates of excitation when the frequency of the exciton–exciton collisions $\nu_{e-e}$ ($10^8$ sec$^{-1}$) is less than the frequency of the exciton–phonon collisions $\nu_{e-ph}$, which is $(6-8) \times 10^{10}$ sec$^{-1}$. Therefore, the main mechanism of the excitation energy dissipation is the interaction between excitons and phonons. At high rates of excitation the exciton–exciton interaction processes may alter considerably the relaxation and the nature of the emitted radiation.

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# Analogs of superfluid currents for spins and electron-hole pairs

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States analogous to those with superfluid currents in an ordinary superfluid can exist in a Bose-condensed electron-hole liquid as well as an easy-plane antiferromagnet. For easy-plane antiferromagnets these states are metastable helicoidal structures with an antiferromagnetic vector that rotates inside the easy plane. These structures are investigated with the aid of the usual phenomenological theory based on the Landau-Lifshitz equations to which some dissipative terms are added. The metastable helicoidal structures can be produced by injecting spins into the antiferromagnet. This gives rise to magnetization far from the point of injection, a manifestation of a real spin transport in these states. For a band antiferromagnet, the stationary phenomenological equations are the Ginzburg-Landau equations, which are derived by using an excitonic-state model with extrema that do not coincide in *k*-space.

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## INTRODUCTION

Bose condensation of electron-hole pairs in a solid leads to the appearance of a complex order parameter $\Delta = |\Delta| e^{i\varphi}$,[1] and for this reason the possible existence, in analogy with ordinary superfluids, of nondissipative currents proportional to $\nabla\varphi$ (supercurrents) has been under discussion for quite some time.[2-8] It has been established that this analogy must not be drawn too far. First, a current of electrons and holes transports neither mass nor energy, thereby excluding a large number of traditional methods of producing and observing supercurrents. Second, the electron and hole conservation law is satisfied at best only approximately, since interband transitions take place. These, as shown by Guseĭnov and Keldysh, lift the phase degeneracy of the order parameter and make the existence of stationary spatially homogeneous supercurrents impossible. There can exist, however, stationary states with finite supercurrents, which are inhomogeneous along the supercurrent direction. They were investigated with the aid of the Ginzburg-Landau (GL) equations for a semimetal with band extrema that coincide in **k**-space,[6] as well as for a system of spatially separated electrons and holes.[7] It was shown in [6] that such inhomogeneous states are metastable so long as the processes that fix the phase are weak enough. A generalization of the results of [6] to the case when the pair-forming electrons and holes pertain to extrema that do not coincide in **k**-space and the wave function of the electron-hole pairs is triplet in spin is briefly reported in [8]. In analogy with the *A*-phase of superfluid He$^3$ [9] one can speak here of two Bose condensates of pairs with spin projections +1 and –1 on the wave vector of the spin-density wave (SDW) that is produced in this case.[3] If both condensates have equal superfluid velocity, then a current of electron-hole pairs exists, and if their velocities are equal but opposite, then a

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