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57

Physics of Highly Excited States in Solids

Edited by M. Ueta and Y. Nishina

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57

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FOREWORD

The Oji Seminar on "Physics of Highly Excited States in Solids" was held from Sept. 9 to 13, 1975, in Tomakomai, Hokkaido, Japan. The Seminar was held under the auspices of the Japan Society for the Promotion of Science by the fund donated by the Fujihara Foundation of Science upon contributions from the Paper Companies of Oji, Jujo, Honshu and others in commemoration of the centennial of the production of western style papers by the old Oji Group in Japan.

It was attended by 65 participants from 9 countries of America, Asia, Australia and Europe. The present volume contains the invited lectures and original/review papers contributed by 36 research individuals and their co-workers. The contents of the volume are grouped under the following headings:

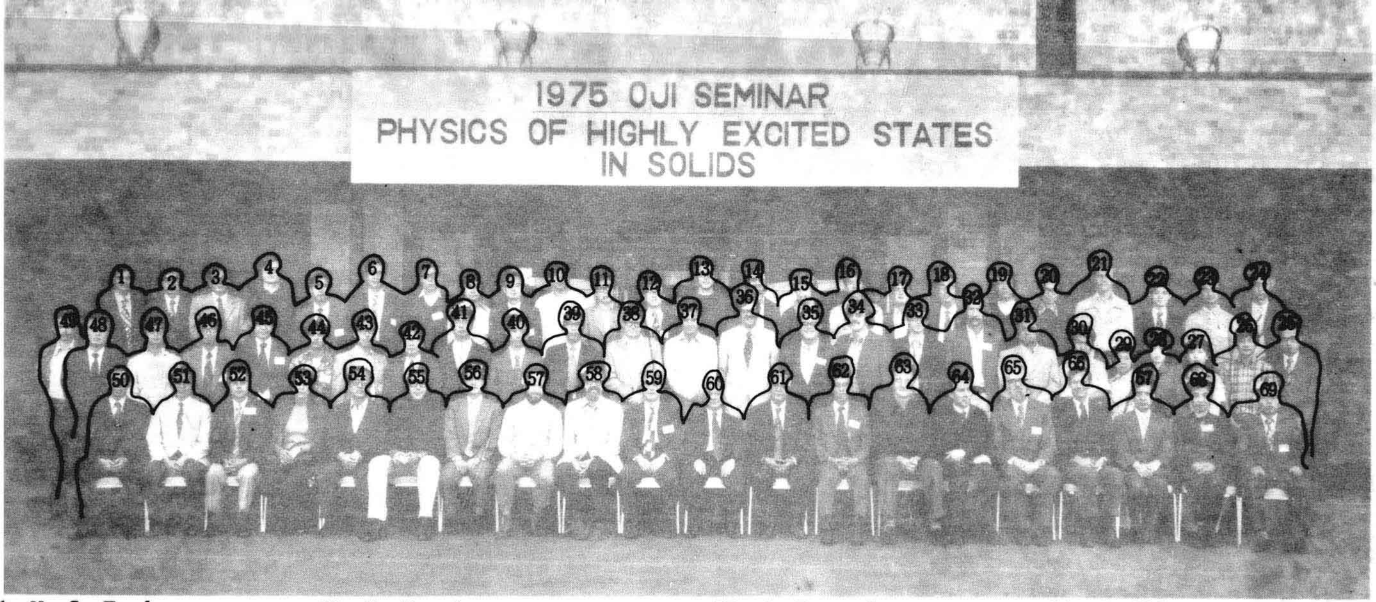
Excitonic Molecules
Excitonic Condensation
Phase Transition
Electron-Hole Drops
Light Scattering
Stimulated Photoluminescence
Nonlinear Optics.

Many interesting events of the Seminar took place in the active discussions following each presentation and throughout the free hours after scheduled sessions as well, when the personal contacts could be blended with beverages of various origins. The informality of this seminar, however, made it difficult to keep the written forms of communications which brought up many important points of the above-mentioned subjects to the attention of the audiences and even contributors themselves.

Each contribution was refereed by two members of the participants whose enduring assistance was deeply acknowledged by the Organizing Committee.

July 1976

Masayasu Ueta, Editor
Yuichiro Nishina, Co-editor



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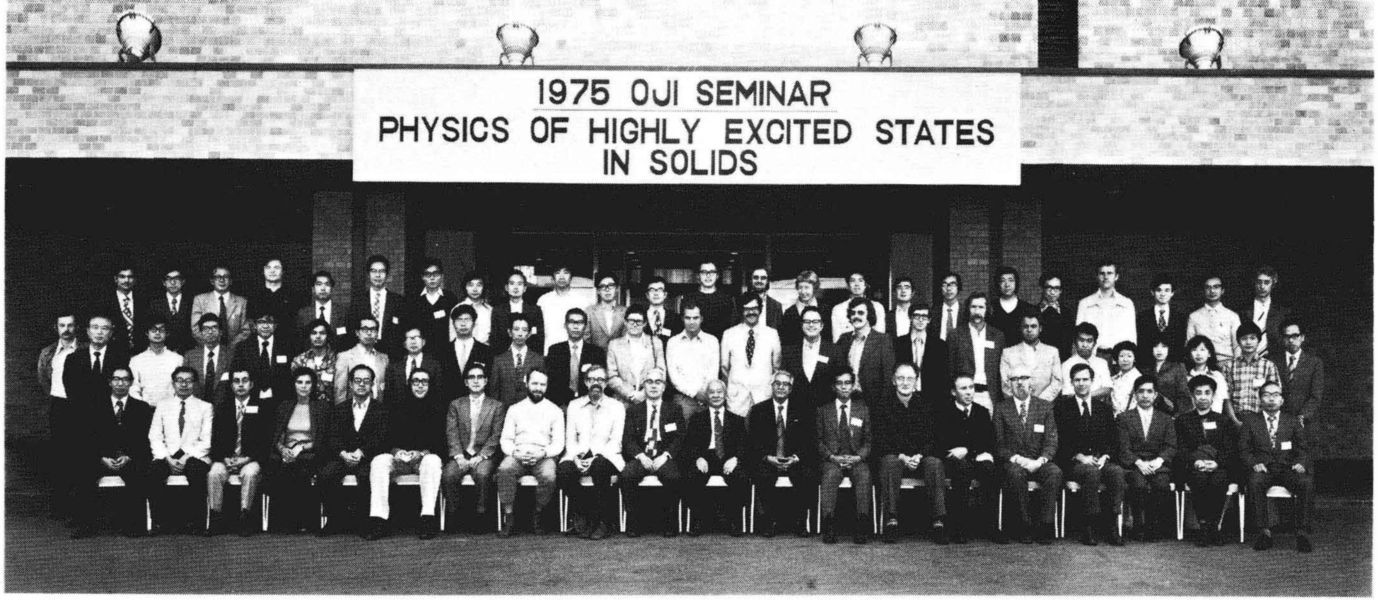
1975 OJI SEMINAR
PHYSICS OF HIGHLY EXCITED STATES
IN SOLIDS

CONTENTS

EXCITONIC MOLECULES

EXCITONIC CONDENSATION

PHASE TRANSITION

ELECTRON-HOLE DROPS

LIGHT SCATTERING

STIMULATED PHOTOLUMINESCENCE

NONLINEAR OPTICS

TWO-PHOTON GENERATION OF EXCITONIC MOLECULES IN CuCl AND CuBr

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ABSTRACT

Radiative recombination of excitonic molecules in CuCl and CuBr is reviewed. The emission consists of M_L and M_T bands in CuCl and of M_L, M_T and M_f bands in CuBr. These bands correspond to the recoil of an exciton into the longitudinal, transverse and triplet states, respectively. When excitonic molecules are generated indirectly by the excitation of crystals into the band-to-band region, the line shape of the bands is explained by considering that excitonic molecules are in Maxwell-Boltzmann distribution. Excitonic molecules are found to be generated directly by the giant two-photon absorption. In this case, extremely sharp emission lines appear at the high energy edges of each M band, which are attributed to the Bose condensation of excitonic molecules. The two-photon resonance Raman scattering is discussed in connection with the emission from the Bose condensed state.

I. INTRODUCTION

1.1 Excitonic Molecule

There are two main interaction products between excitons in highly excited semiconductors; an excitonic molecule and electron-hole metallic phase. The former is found in cuprous halides and probably in CdS and CdSe and the latter in Ge and Si. The Wannier exciton is analogous to the hydrogen atom so that excitonic molecules have been expected to be formed since 1958 by Lampert[1] and Moskalenko.[2] From the theoretical work[3] dealing the binding energy of the excitonic molecule, it was considered to be unstable in crystals having the electron and hole effective mass ratio, M_e/M_h, ranging between 0.2 and 0.4. Therefore, experimental work to find the excitonic molecule was directed to crystals such as CuCl having $M_e/M_h < 0.2$ and Ge or Si in which $M_e/M_h > 0.7$.

In 1966, Haynes[4] found a superlinear emission band at 1.08 eV in Si and considered it as the radiative annihilation of an excitonic molecule with leaving a free electron and hole pair behind. In Ge, a similar emission band was later found at 0.708 ev.[5] These emission bands are now attributed to the electron-hole drops, other than the excitonic molecules.

In CuCl crystals, a new emission band was found by ruby laser excitation and it was assigned as due to the excitonic molecule by Grun *et al.*[6] and by Goto *et al.*[7], because the emission intensity increased in proportion to the square of the excitation density and the energy separation of the emission band from the free exciton band, ~40 meV, was reasonable for the binding energy of the excitonic molecule expected from the theoretical work. Here an excitonic molecule was assumed to be annihilated radiatively with an exciton left behind.

In highly excited states, a number of elementary interactions between exciton-exciton and exciton-free charge carriers lead to superlinear emissions, the photon energies of which depend on the interaction mechanisms. Therefore, the observation of the square dependence of emission intensity upon excitation power and the energy position of the emission band are not enough to decide uniquely the elementary processes responsible for the emissions.

The first reliable proof of the existence of excitonic molecules was given by Souma *et al.*[8] in zone refined CuCl through the line shape analysis of a new superlinear emission band, called M band, which appeared when the crystal was illuminated by a giant ruby laser at 4.2 K. A similar emission band attributed to excitonic molecules has been found also in CuBr.[9] After theoretical work concerning the binding energy of an excitonic molecule by Akimoto and Hanamura[10] which showed that the excitonic molecule could be formed in crystals, having any values of M_e/M_h, new emission bands similar to the asymmetric M band in CuCl and CuBr, were found by Shionoya's group successively in

CdS,[11] CdSe[12] and ZnO,[13] and they were attributed to the radiative annihilation of excitonic molecules. On the other hand, a somewhat different assignment has been made by another group that they are attributed to the stimulation of acoustic side bands of bound excitons.[14] However, the experiment on the stress effect in CdS, carried out by Segawa and Namba,[15] seems to give a confirmation of the molecule. The complex band structure, anisotropy of electron and hole masses, some difficulty of purification and small binding energies make the exciton molecule emission complex in II-VI compounds. Different exciton complexes found in different groups might have their emission bands in nearly the same energy positions.

1.2 Bose Condensation of Excitons and Excitonic Molecules

The boson-like nature of excitons and excitonic molecules has been the basis for the discussions[16] on how their statistics manifests themselves in the phase change at low temperature. The first experimental report on a narrow emission line showing the Bose condensation of excitons has been done by Akopyan *et al.*[17] in CdSe excited by the second harmonics of a neodymium laser at 4.2K. The conclusion of the Bose condensation was based on the consideration that excitons in CdSe are repulsive to each other and satisfy the necessary conditions for the Bose condensation. However as described above, excitons are attractive to form excitonic molecules. Thus, the Bose condensation of single excitons in CdSe becomes to be unexpected. In fact, the narrow line reported by Akopyan *et al.* has not been observed by other researchers. Czaja and Schwerdtfeger[18] are the second reporter of the Bose condensation of indirect excitons in AgBr at 1.6 K. They found a narrow emission line near K=0 in the TA phonon-assisted exciton band. Together with the very low threshold temperature for the appearance of the emission line, the Bose condensation has been concluded.[19]

On the Bose condensation of excitonic molecules, Kuroda *et al.*[20]

reported an emission line on the high energy edge of the emission band of the excitonic molecule in CdSe, and attributed it to the Bose condensation of the excitonic molecule at K=0. However, Johnston and Shaklee[21] have claimed on the conclusion of Kuroda *et al.*, and assigned the narrow emission to a bound exciton complex involving a neutral donor. Thus, the Bose condensation of excitonic molecules has not been clarified yet. In the experiments above mentioned, crystals were excited into their band-to-band region and excitonic molecules are formed secondarily through the interactions between excitons generated by the recombination of hot electrons and holes. Therefore, the temperature of the excitonic molecules will not be low enough to condense as confirmed by Souma *et al.*[8]

Hanamura[22] has recently shown theoretically that excitonic molecules can be generated directly by the giant two-photon excitation with using photons, of which energy is given by

$$h\nu = E_{ex} - \frac{1}{2} E_m^b \tag{1}$$

where E_{ex} stands for the exciton energy and E_m^b the binding energy of an excitonic molecule. Furthermore, the Bose condensed molecules are expected to be created coherently with using a laser excitation. Hanamura has further shown that the absorption coefficient for the two-photon generation of excitonic molecule given by (1) depends on the photon density, and it amounts to the order of $\sim 10^5$/cm with using the photon density, of 10^{15} photons/cm^2. Gale and Mycyrowicz[23] have confirmed the two-photon generation of excitonic molecules in CuCl by observing that the absorption coefficient for the two-photon absorption increases rapidly, when the incident photon energy approaches that given by (1) and the extrapolated absorption coefficient at the peak will be the same as that for the one-photon absorption in the exciton band, $\sim 10^5$/cm, with photon density of 10^{17}/cm^2.

We could confirm also the efficient generation of the excitonic molecules by the two-photon excitation in CuCl as well as in CuBr. Moreover, the emission band has been found to show extremely sharp lines at the high energy edges of the M_L and M_T bands, which is considered to show the Bose condensation of the excitonic molecule at $K\sim 0$.

In this paper, we present experimental results in cuprous halides carried out in our laboratory on the emission bands originating from excitonic molecules in their thermal equilibrium and Bose condensed states.

II. EXPERIMENTAL RESULTS AND DISCUSSIONS

2.1 Emission of Excitonic Molecules of Maxwell Distribution in CuCl and CuBr Crystals near 4.2 K

Cuprous halides have the zincblende crystal structure, and an exciton consists of a Γ_6 electron and a Γ_7 or Γ_8 hole. The exciton absorption bands[24,25] in CuCl and CuBr crystals, called Z_3 and $Z_{1,2}$, are well separated from the continuous band due to the band-to-band transition, and thus the binding energy of the exciton is rather large, 190meV for CuCl and ~120meV for CuBr.

The M band due to the excitonic molecule was found[8] to have an asymmetric line shape as mentioned before, and this was explained to reflect the Maxwell-Boltzmann distribution of the kinetic energy of excitonic molecule. The line shape was expressed by

$$I(E) \propto E^{1/2} \exp(-E/kT), \qquad (2)$$

where E is measured towards the low photon energy side. The emission is concluded to arise from the transitions between energy levels of excitonic molecule and single exciton as shown in Fig.1. Namely, an excitonic molecule is concluded to be annihilated radiatively with leaving an exciton behind. From the energy separation of the peak from the high energy edge, which is equal to 1/2kT, the temperature of the excitonic molecule was shown to be 26 K which was higher than the lattice temperature in Souma's experimental condition; the crystal was illuminated by a Giant Ruby laser with ~50 MW/cm^2. By assuming the above conclusion of the M-emission mechanism correct, the binding energy of the molecule is determined from the energy separation between the free exciton band and the high energy edge of the M band to be 34 meV in CuCl[8] and 26 meV in CuBr.[9]

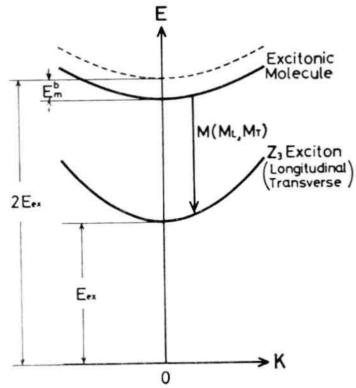

Fig.1. Schematic representation of energy levels of exciton and excitonic molecule.

The remaining exciton can be in either longitudinal or transverse states. With reflecting this fact, the M band was found by Koda's group[26] to consist of two bands, called M_L and M_T bands. The energy separation between them was in fact equal to that of the L-T splitting of the exciton, being 5.4 meV.[27] The longitudinal state is singlet and the transverse state is doubly degenerate, so that the M_T intensity must be twice as much as the M_L intensity. However, as shown in Fig. 2, the intensity ratio is a function of excitation density, and with increasing excitation density, the M_L band becomes much stronger than the M_T band. Grun *et al.* [28] have shown the intensity ratio of 2 is observed in a wide range of excitation density. For the dependence of the M_L and M_T band-intensities upon excitation density, an opinion has been proposed that the two M bands come from the different rotational levels of the molecule.[29]

In CuBr, the M band was previously found to consist of two bands, M_1 and M_2, and they were previously assigned as the recoil of an exciton into the transverse and triplet states,[9] respectively. However in a

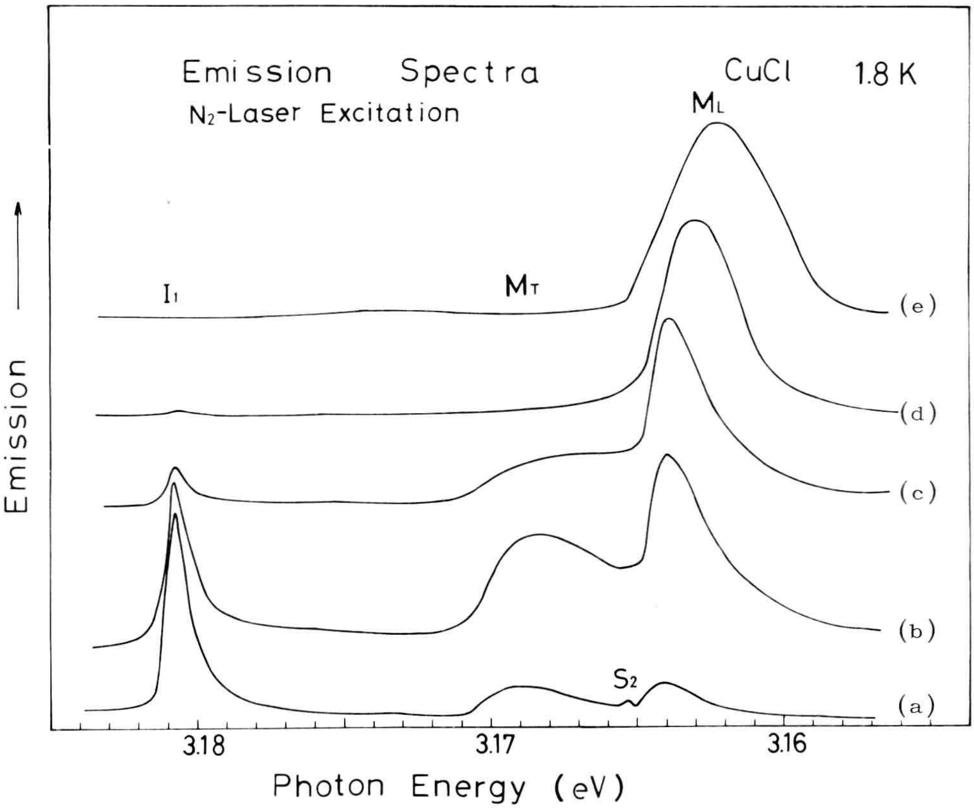

Fig.2. The variation of emission spectrum of excitonic molecule with the power of exciting N_2-laser in CuCl. Excitation intensity increases from (a) toward (e).

recent work, they have been clearly assigned to the M_L and M_T as in CuCl, because the energy separation between two bands coincides also with the L-T splitting of the exciton, 11.2 meV, which is determined from the Kramers-Kronig analysis of a reflection spectrum. Therefore, the two bands in CuCl are considered to be due to the recoil of an exciton into the L and T states, rather than to be attributed to the rotational structure.

2.2 Line Shape of the M Band

Figure 3 shows a typical M emission spectrum of CuCl[30] excited into the band-to-band region with using a N_2 laser. The spectrum is