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ADP013083

TITLE: Oriented Silver Halide Nanocrystals Embedded in Crystalline Alkali Halide Matrix as Studied by EPR and ODMR

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ADP013002 thru ADP013146

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Oriented silver halide nanocrystals embedded in crystalline alkali halide matrix as studied by EPR and ODMR

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Abstract. Shallow electron centers, self-trapped holes and self-trapped excitons in small AgCl crystals embedded in KCl matrix were investigated by optical spectroscopy, optically detected magnetic resonance (ODMR), and electron paramagnetic resonance (EPR) techniques. These investigations showed that single AgCl microcrystals are formed in KCl crystalline matrix with their lattice symmetry axes oriented parallel to the axes of the host lattice. Multi-quantum ODMR spectroscopy was used for the investigation of the effect of confinement on singlet-to-triplet splitting of self-trapped excitons and on the parameters of shallow electron centers.

Introduction

Semiconductor and solid-state physics nowadays appears to be the physics of systems with the reduced dimensionality. The fabrication of single or periodic potential wells by simply combining two materials of different bandgap energies and having spatial dimensions confining the motion of electrons and holes, results in many impressive possibilities for engineering of the new properties of solid-state structures.

It has long been known that in alkali halide crystals doped with silver halides the silver ions Ag^+ substitute for alkali ions and both single Ag^+ ions and pairs of silver ions can be observed. Under ultra-violet (UV) light or x-ray irradiation a number of different silver-related defects can be formed: Ag atoms in cationic and anionic positions, Ag^- in anionic position, Ag^{2+} ions, Ag atoms near anionic vacancies (laser active A_F centers), silver pairs Ag_2^+ [1, 2]. Along with Ag-related point defects oriented silver halide nanocrystals (down to 5 nm) embedded in crystalline alkali halides matrix can be produced in the process of the growth of single crystals of alkali halides heavily doped with silver halides [3]. The bandgap energies of KCl and AgCl are 7.8 eV and 3.1 eV, respectively. Thus AgCl nanocrystals can be considered as a system of quantum dots (QD).

Silver halides have some unique features and occupy a particular position in solid state physics because their properties can be considered as of borderline nature between ionic and covalent bonding, that is they are located close to the boundary corresponding to the critical value of ionicity 0.785, namely 0.856 for AgCl and 0.850 for AgBr [4]. Silver halides play an important role in the photographic industry, since it is one of the few materials in which the process of latent image formation takes place. In order to get better understanding of this process, it is important to learn more about the intrinsic properties of the material particularly when one goes from the present micrometer (~ 10 μm) world to the nanometer (~ 10 nm) world where materials are known to behave quite differently because of quantum effects.

Under UV light irradiation of AgCl an electron is excited from the valence band into the conduction band and a hole is left in the valence band, which is subjected to self-trap, to form the self-trapped hole (STH) Ag^{2+} . Free electrons can be captured by some

Coulombic core and form shallow electron (SE) centers. A STH can capture an electron from the conduction band in a very delocalized hydrogen-like $1s$ orbital forming the self-trapped exciton (STE). STE, STH and SE were successfully studied by ODMR (see [5] and references therein). It was shown that STE in AgCl consist of a very diffuse electron (with the Bohr radius of $15.1 \pm 0.6 \text{ \AA}$) attracted by a strongly localized STH [6].

One of the basic problems which could not be solved during last 50 years, in spite of a big progress in application of silver halides in photography, was the identification of the structure of the intrinsic shallow electron centers which are believed to play an important role in the latent image formation process. The first direct determination of the wave function distribution of the intrinsic shallow electron center in AgCl was reported in [7]. It was shown that the wavefunction of SE is very diffuse and is spread over a radius of nearly 4 nm. A microscopic model was suggested in which an electron was shallowly trapped by two adjacent silver ions on a single cationic site (split-interstitial silver pair).

In the present paper, we report the study of shallow electron centers, self-trapped holes and self-trapped excitons in small AgCl crystals embedded in KCl matrix applying optical spectroscopy, optically detected magnetic resonance (ODMR), and electron paramagnetic resonance (EPR) techniques.

1. Results and discussion

KCl: AgCl monocrystals were grown by the Stockbarger method and contained 1 to 3% of AgCl. Two types of samples were available: crystals with a natural abundance of the Ag isotopes and ^{109}Ag -enriched crystals. Optical absorption and EPR were studied with commercial apparatus. 35 GHz ODMR was detected at 1.7 K by monitoring luminescence excited with a Deuterium arc lamp.

Figure 1 shows ODMR spectra recorded by monitoring the emission intensity in two samples which were cut from different parts of KCl: AgCl (2%) crystals. The microwaves were chopped at 80 Hz and a lock-in amplifier was used to detect microwave-induced variations of the luminescence intensity. The upper spectrum (1), which was measured in a sample with higher Ag concentration, is similar to the ODMR of bulk AgCl. Anisotropic resonance signals of STH and STE and an isotropic line of SE centers are observed as indicated by arrows. Since STH's are Jahn-Teller distorted along one of three $\langle 100 \rangle$ axes, three type of centers exist. The lines indicated by \uparrow belong to the centers with the distortion axes oriented parallel to the magnetic fields B , whereas the lines indicated by \downarrow result from the two centres with the axes perpendicular to B . The same applies for the triplet state of STE, because the central hole of the STE is virtually identical to the isolated STH. In the latter case two lines are observed for each of possible center orientations because of zero-field (fine structure) splitting which is characterized by a parameter D . $D = -710 \text{ MHz}$ for bulk AgCl. The g -factors of SE centers and STH and also the fine structure splitting D of STE determined from the ODMR spectrum 1 of KCl:AgCl (Fig. 1) are close to those of bulk AgCl but the ODMR lines are broadened. This proves that AgCl crystals are formed inside KCl matrix.

The spectrum 2 in Fig. 1 was measured in a part with lower Ag concentration. It corresponds partly to the ODMR ascribed to STE in the AgCl nanocrystals as reported in [3]. The parameters of this spectrum are considerably different from those of STE in bulk AgCl. In our measurements additional lines which probably belong to hole and electron centers in nanocrystals were also observed with different spectral dependencies.

In bulk AgCl crystals multiquantum transitions with the absorption of up to seven microwave quanta (total energy $7 \times 35 = 245 \text{ GHz}$) were found which allowed to measure

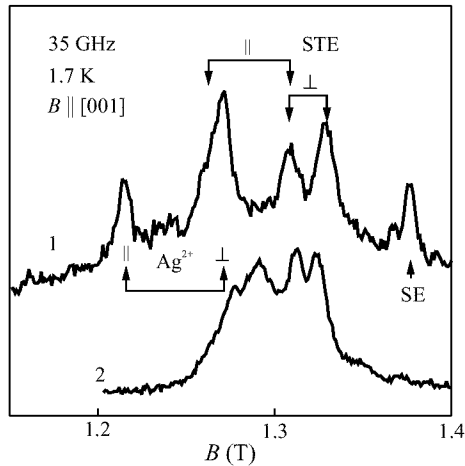


Fig. 1. ODMR of two samples cut from different parts of a KCl:AgCl single crystal. The spectra were recorded by monitoring the luminescence intensity at 500 nm (1) and 550 nm (2).

the singlet-to-triplet splitting of STE for with a very high accuracy: $J = -161.0 \pm 0.1$ GHz [7].

In the sample 1 we have observed multiquantum transitions in ODMR of AgCl in KCl only within the triplet state of STE, which may imply a different (larger) value of the singlet-triplet splitting. A rather strong non-resonant background signal which had a weak dependence on magnetic fields and corresponded to an increase of the emission intensity by microwaves was also observed. In the sample 2 the background signal was much smaller.

SE centers are believed to play an important role in the latent image formation process, which occurs in the silver halides, when they are irradiated with light. Since STE in AgCl consist of a very diffuse electron attracted by a strongly localized STH, the exchange splitting between the singlet and triplet states is small. It should be noted that a value of the singlet-to-triplet splitting can be a measure of the space distribution of the electron wave function and therefore can give information about the effect of confinement of SE centers and shallow electron in STE due to the nanocrystals size. The confinement of the wave function distribution will affect the g -factor shift of SE centers.

Thus ODMR investigations have shown that there exist AgCl microcrystals of different size embedded in KCl crystalline matrix and that the AgCl lattice symmetry axes are oriented parallel to the axes of the surrounding KCl lattice. This conclusion was unambiguously proved by the observation of angular dependencies of ODMR spectra of the STH and STE in AgCl and EPR of Ag^{2+} centers in KCl. The Ag^{2+} centers in KCl were produced by UV irradiation at absorption bands of Ag^+ ions in KCl:Ag as reported in [2].

ODMR in such complicated KCl:AgCl and KBr:AgBr systems was also investigated by monitoring the tunneling afterglow, which is observed after irradiation of the crystals by ionizing radiation. In our previous papers we investigated the tunneling recombination afterglow in crystals with small concentration of Ag (less then 0.5%) [9, 10].

In conclusion, self-trapped excitons, self-trapped holes and shallow electron centers in AgCl microcrystals embedded in KCl monocrystals and maintaining the orientation of the host lattice were studied by ODMR and EPR. This new system seems to be very promising for the investigation of spatial confinement effects in nanocrystals since it provides a possibility to study oriented nanocrystals in a transparent matrix and to apply such a pow-

erful techniques as ODMR to study variations of the parameters of STE, STH and shallow electron centers which are well known for bulk silver halides.

Acknowledgements

This work was partly supported by the Russian program PhSSN (grant 99-3012).

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