General and Inorganic Chemistry

Anomalies of the partition coefficient and properties of crystals in the region of low concentrations of an isomorphous admixture

1. Unusual decomposition of solid solutions of the NaCl—$CdCl_2$ system

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Solid solutions NaCl—$CdCl_2$ were studied in an interval of $CdCl_2$ concentrations of 0.05—3 mol.% by Raman spectroscopy. The molecular form Na_2CdCl_4 decomposes: $Na_2CdCl_4 \rightarrow 2Na^+ + Cd^{2+} + 2Cl_2^- + 2e^-$; $2Na + 2e^- \rightarrow 2Na^0$. Free sodium atoms form color centers of crystal (F centers) in the region of jumpwise changing the partition coefficient of $CdCl_2$ in NaCl (*K* jump).

Key words: NaCl—$CdCl_2$ system, Raman spectroscopy, isomorphous admixture, minor content, anomaly of properties, unusual decomposition of solid solutions.

The phenomenon of *K* jump represents a jumpwise change in the partition coefficient, which is observed for melt crystallization in the region of low concentrations of an isomorphous admixture (<2 at. (mol.)%).[1—3] It is believed[2] that this phenomenon can be best explained in the framework of the model of interaction of an admixture with crystal defects. The theory of the secondary crystal structure gives a resembling interpretation of the mechanism of *K* jump.[4—6]

Highly sensitive methods of investigations and measurements with high accuracy are needed to better understand the mechanisms of *K* jump.

The properties of solid solutions in the region of *K* jump are poorly studied, and data on the state of an admixture in the region of low concentrations are almost lacking. In particular, experimental data on the concentration plot of the properties of the solid solution are scanty. For example, the maximum of the quantum yield of X-ray luminescence was observed in the CsI—NaI system.[7]

The purpose of this work is to study the concentration plot of the properties of solid solutions and the state of an admixture in crystal in the region of *K* jump for model salt systems. The NaCl—$CdCl_2$ system, which was repeatedly studied by thermal analysis, was chosen as the model. It is known[8] that the compound Na_2CdCl_4 is present in the system. The region of solid solutions,[9] likely, NaCl—Na_2CdCl_4, was found at the concentration of $CdCl_2$ not exceeding 4.5 mol.%. The study of the concentration plot of the equilibrium partition coefficient

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 1, pp. 35—38, January, 2002.

(*K*) in this system by the method of directed crystallization[7] showed that the coefficient changes from 0.09 at a concentration of $CdCl_2$ of ~0.7 mol.% to 0.2 at ~0.4 mol.% $CdCl_2$ (*K* jump). The state of an admixture in this region was not studied.

In this work, solid solutions in the NaCl—$CdCl_2$ system were studied by light scattering Raman spectroscopy.

Experimental

Reagents NaCl (special-purity grade) and $CdCl_2$ (special-purity grade), of which the latter was additionally purified by multiple sublimation in a static vacuum and directed crystallization, were used for the preparation of the NaCl—$CdCl_2$ samples. Sodium chloride was dried *in vacuo* over P_2O_5 to a constant weight and re-fused in air. Solid solutions with concentrations <1% $CdCl_2$ were prepared by dilution of the NaCl—$CdCl_2$ (1 mol.%) sample. Samples were prepared in evacuated quartz ampules, they were thoroughly homogenized in melt and quenched in water from temperatures of 850—900 °C.

The Raman spectra were excited with Ar^+ and He—Ne lasers and recorded with a Triplemate SPEX Raman spectrometer and an LN-1340PB matrix detector. A sample was placed under a microscope, and the laser beam was focused into a spot with a diameter of 2 μm. Scattering geometry was 180°.

Results and Discussion

The Raman spectrum of crystalline NaCl contains no scattering line of the first order, whereas the spectrum of $CdCl_2$ crystals (Fig. 1) contains two intense lines: 132 cm^{-1} (doubly degenerate vibration) and 235 cm^{-1} (full-symmetry vibrations). The spectrum typical of the NaCl—$CdCl_2$ solid solution (Fig. 2) contains three intense lines at 120, 178, and 212 cm^{-1} (weak lines at ~130 and 235 cm^{-1} are assigned to residual isolations of the $CdCl_2$ phase).

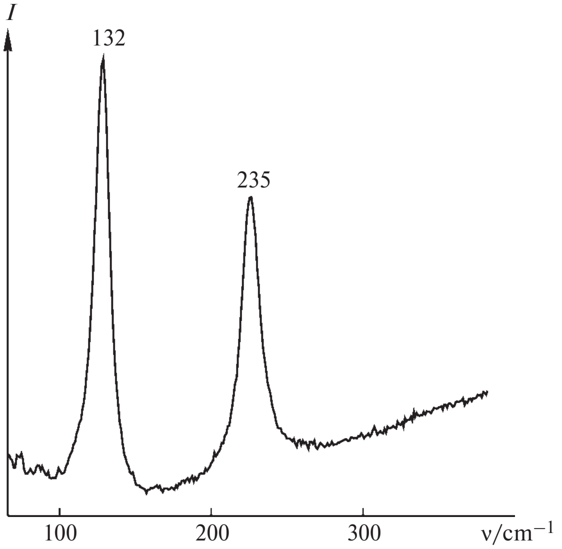

Fig. 1. The Raman spectrum of crystalline $CdCl_2$.

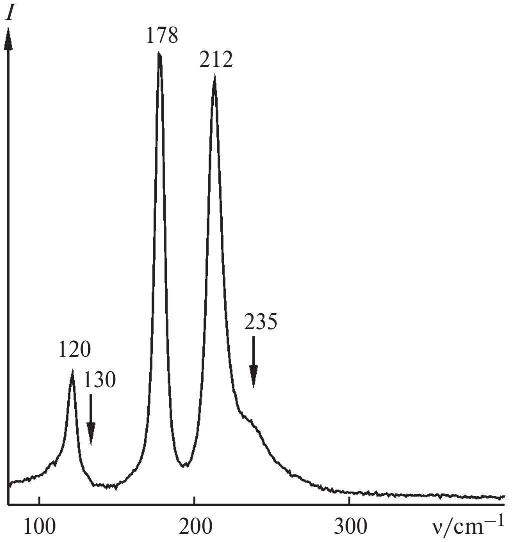

Fig. 2. The Raman spectrum of the NaCl—$CdCl_2$ (10 mol.%) sample.

Occurrence of $CdCl_2$ in the NaCl lattice can be explained by different processes.

1. Isomorphous replacement of sodium with cadmium following the mechanism of charge compensation. In this case, one can expect the appearance in the Raman spectrum of a broad scattering line at vibrations of NaCl with violation of the selection rules by the wave vector and a scattering line at local vibrations of cadmium.

2. Formation of the $CdCl_2$ phase (precipitates). Here the spectrum of the second phase should not differ from that of the individual $CdCl_2$ compound (see Fig. 1).

3. Appearance of molecular forms $CdCl_2$ or anions $CdCl_4^{2-}$ and $CdCl_6^{4-}$, and others. Evidently, the spectrum in Fig. 2 corresponds to the $CdCl_2$ molecular form. Since the presence of the Na_2CdCl_4 compound in this system was established by thermal analysis methods,[8] we may conclude that the observed Raman spectrum is a result of the $CdCl_4^{2-}$ form.

At a low concentration of $CdCl_2$, the spectra exhibit an intense line at 300 cm^{-1} (Fig. 3). This line is depolarized and has an obvious resonance character with overtone repetitions at $n{\cdot}\nu$ ($n = 1, 2, 3...$). The plot of the light intensity of the line at 300 cм$^{-1}$ *vs.* wavelength of exciting light, which is presented in Fig. 4, shows that the line is attributed to the molecular form of the compound in the NaCl lattice, having the resonance absorption band at ~480 nm.

The character of manifestation of the line at 300 cm^{-1} in the spectrum (see Fig. 3) is typical of resonance scattering on diatomic molecules of halogens. The frequency of vibration of the neutral $^{35}Cl_2$ molecule is 554 cm^{-1}.[10] Several states of the Cl_2^- ion are usually distinguished in

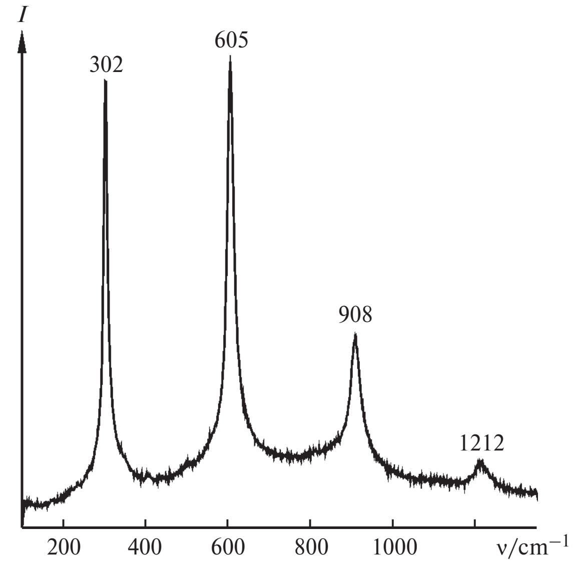

Fig. 3. The resonance Raman spectrum of the NaCl—$CdCl_2$ (0.1 mol.%) sample; 488-nm excitation.

the NaCl lattice.[11] One of them (V_K center) is a hole state, which captured an electron, formed by two adjacent chlorine ions displaced from their nodes toward each other. The vibration frequency of the V_K center in NaCl is 228 cm^{-1},[12] and the maximum of the absorption band lies at a frequency of 365 cm^{-1}. Another state of Cl_2^- in the lattice is the H center in which the center of the Cl_2^- molecular ion coincides with the anionic node. The vibration frequency of the H center in NaCl is 361 cm^{-1},[12] and the absorption band lies near 365 nm.[11]

An elevated concentration of V_K– or H centers in alkali-halogen crystals, which is necessary for the measurement of their content, is created by X-ray or electron irradiation. The centers obtained by the chemical method with a vibration frequency of 300 cm^{-1} and the absorption band at 480 nm have been observed, most likely, for the first time.

The plots of the intensities of the lines (*I*) of Na_2CdCl_4 (120, 178, and 212 cm^{-1}) and 300 cm^{-1} *vs.* composition of the solid solution are shown in Figs. 5 and 6. In region I (0.05—0.15 mol.% $CdCl_2$), the *I* value for lines of the first group lies below the detection limit (see Fig. 6). Then it increases non-monotonically with an increase in the concentration of $CdCl_2$ to 0.5% (II). In region III (0.6—2 mol.% $CdCl_2$), the intensity depends linearly on the concentration. Regions I—III correlate with the corresponding regions in the concentration plot of the of the partition coefficient (see Fig. 6).[7] Region II corresponds to the transition region of *K* jump (a sharp change in *K* from 0.09 to 0.2). The intensity values of the Raman lines are unsatisfactorily reproduced in the transition region.

In region III the intensity of the line at 300 cm^{-1} is close to zero, and in region II the intensity *I* has no constant value and increases sharply at low concentrations of $CdCl_2$ (region I). In this region the samples are light-yellow due to the absorption band (see Fig. 4). In region II the color of the compounds is not constant, and in region III the samples are colorless.

At a concentration of $CdCl_2$ of 0.2—0.4 mol.% and lower (see Fig. 6, region I) the molecular Na_2CdCl_4 form

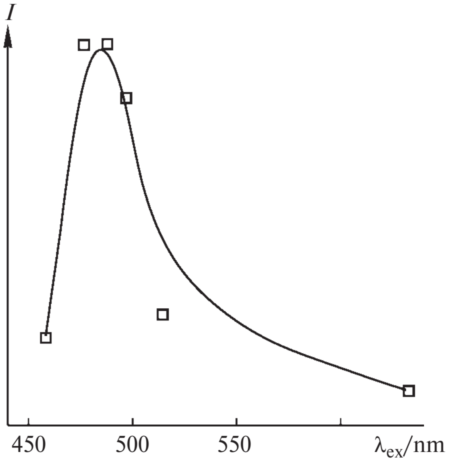

Fig. 4. Influence of the wavelength of exciting radiation on the intensity of the resonance line at 300 cm^{-1}.

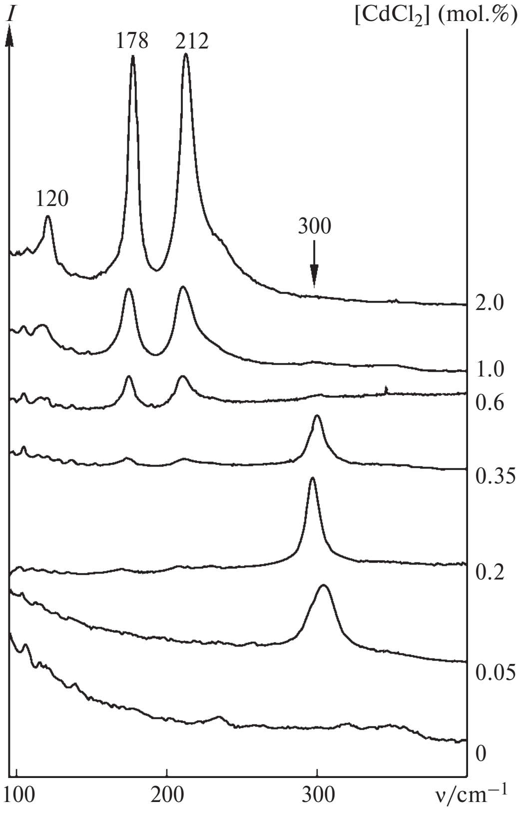

Fig. 5. Raman spectra of solid solutions NaCl—$CdCl_2$ with different concentrations.

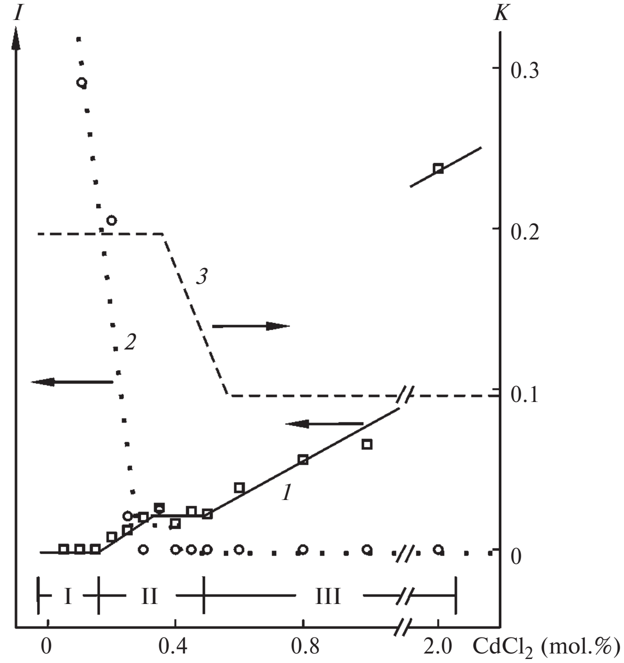

Fig. 6. Influence of the concentration of $CdCl_2$ on the intensities of the line of the $CdCl_4^{2-}$ form at 178 cm^{-1} (*1*) and resonance line at 300 cm^{-1} (*2*) and on the partition coefficient of $CdCl_2$ in NaCl (*3*).[7]

disappears and the Cl_2^- ion appears (see Figs. 3, 5, and 6). Thus, when the concentration of Na_2CdCl_4 decreases, the molecules decompose according to the equation

$$Na_2CdCl_4 \rightarrow 2\ Na^+ + Cd^{2+} + 2\ Cl_2^- + 2e^-.$$

Excessive electrons can reduce sodium ions

$$2\ Na^+ + 2\ e^- \rightarrow 2\ Na^0.$$

As known, excessive Na atoms introduced into the NaCl crystal by the diffusion way (heating in sodium vapor) form color centers (F centers) and impart the yellow color to the crystal. These F centers have an absorption band with a maximum at ~470 nm[13] (this agrees with the data in Fig. 4 where the center of the band is arranged at ~480 nm). It is most likely that the decomposition of the Na_2CdCl_4 molecular form results in the formation of free sodium atoms and F centers, whose absorption band lies near the resonance band of the Cl_2^- ion.

The region of solid solution NaCl—Na_2CdCl_4 exists in the NaCl—$CdCl_2$ system at the concentration of $CdCl_2$ lower than 4.5 mol.%.[9] The free energy of formation of a solid solution is $\Delta G_{mix} = \Delta H_{mix} - T \cdot \Delta S_{mix}$, and the enthalpy of mixing is positive due to the deformation energy of the lattice. When the concentration of Na_2CdCl_4 decreases, the free energy increases, and the decomposition of a molecule becomes energetically favorable (increase in entropy). Evidently, in this case, $T \cdot \Delta S_{mix} > \Delta H_{mix}$. This decomposition differs from that in the solvus curve when the driving force of the process is an increase in ΔH_{mix} due to an increase in the deformation energy. According to published concepts,[4,5] the fragments of a compound can be arranged in nodes of the lattice or in defects. The question about the existence of the Cd^{2+} ion after decomposition, which is substantial for the problem of *K* jump, needs to be additionally studied.

The author thanks B. A. Kolesov for spectroscopic measurements and discussion of the results.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 99-05-64598).

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Received June 6, 2001