LOCAL OSCILLATIONS IN KCl CRYSTALS WITH HYDROGEN CENTERS

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Ultraviolet irradiation at low temperatures of potassium chloride crystals with U centers (substitution hydrogen ions in the anion sublattice) causes photodisintegration of the U centers into anion vacancies and U_1 centers, which are interstitial hydrogen ions H_i^- [1]:

$$[H^-] \xrightarrow{h\nu} H_i^- + \square. \qquad (1)$$

The quantum energy of the ultraviolet light that destroys the U centers and by the same token produces the U_1 centers is insufficient to move the hydrogen ion knocked out of the site a considerable distance from the anion vacancy. Therefore the produced U_1 centers are stable when the probability of annihilation of the interstitial hydrogen ion and of the anion vacancy is sufficiently low, or in other words at low temperatures. On the basis of these results it was generally concluded in [1 - 5] that U_1 centers are stable only at sufficiently low temperatures.

To assess the possibility of producing in alkali-halide crystals U_1 centers that are stable at room temperature, we generated U_1 centers by methods that differ from those used in [1 - 5]. We investigated KCl crystals grown by the Kiropoulos method using hydroxyl OH^- ions, and also samples not containing OH^-.

From the intensity of the infrared spectra we estimated the amount of OH^- in the KCl crystals (at T = 300°K), using the formula [6]:

$$C\ [\text{mol.}\%] = K\kappa[\text{cm}^{-1}]/a^3[\text{Å}], \qquad (2)$$

where K = 10 (±10%) for OH^-, a is the lattice constant, and κ is the absorption coefficient at the maximum of the band. The maximum OH^- concentration turned out to be 0.02 mol.%.

Samples in the form of single-crystal plates measuring (2 - 10) × 10 × 25 mm were bombarded with γ rays from a Co^{60} source or in the indium-gallium radiation loop of a nuclear reactor [7]. The radiation doses ranged from 4×10^5 to 5×10^7 r.

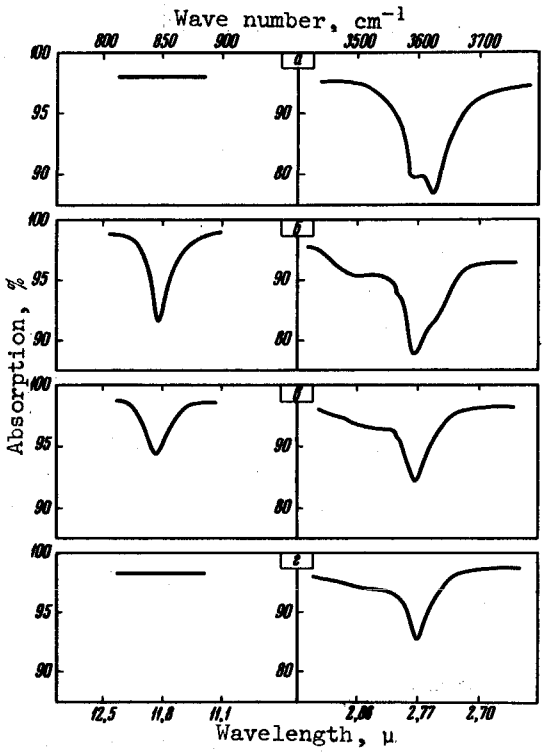
The figure shows the infrared absorption spectra of a KCl crystal with OH^- impurity before and after irradiation with the Co^{60} γ source. It is seen from the figure that after the irradiation there is observed an absorption band with a maximum in the region of 850 cm^{-1} (this absorption band does not appear in the samples without impurities).

This band first increases with increasing irradiation dose, then decreases starting with a dose of 2.4×10^7 r, after which it disappears completely. This fact must be explained by starting from the fact that the centers responsible for the 850 cm^{-1} band, which are the products of OH^- decay, are accumulated during the initial stage of the irradiation, while during the later stage of the irradiation, as the decay of OH^- proceeds (see the figure, the 3624 cm^{-1} absorption band drops), the ionization of the 850 cm^{-1} centers prevails. The appearance of the 850 cm^{-1} band in the vibrational spectrum correlates with the appearance of a broad band in the region of 260 - 300 nm in the electronic absorption spectrum of the irradiated KCl cyrstals; the latter band is connected with electronic transitions inside the U_1 center [1].

This fact, and also the coincidence of the spectral position of the observed 850 cm^{-1} band with the frequency of the local oscillation of the U_1 center in KCl [3], as well as the fact that this band is observed only in crystals containing OH^- ions, all lead to the conclusion that this band is due to U_1 centers. These centers result from the decay of the hydroxyl ions under the influence of the γ radiation [8]:

$$[OH^-] \xrightarrow{h\nu} [O^-] + H_i^0,$$
$$2[O^-] \xrightarrow{kT} [O_2^-] + \square + e, \qquad (3)$$
$$H_i^0 + \square + e \xrightarrow{kT} H_i^- + \square.$$

A comparison of (1) and (3) shows that regardless of whether the irradiated crystals contain U centers [1 - 5] or hydroxyl ions in the lattice, the final products of the radiolysis are the same in our case, namely U_1 centers and anion vacancies.



Vibrational spectra of KCl:KOH crystal irradiated with a Co^{60} γ source: a) prior to the irradiation, b - d) after irradiation with doses of 1.2×10^7, 2.4×10^7, and 3.6×10^7.

The stability of the U_1 centers in KCl at room temperature in our case is explained by the fact that, unlike the energy of the ultraviolet quanta [1 - 5], the energy of the γ quantum is sufficient to move the interstitial ion H_i away from the anion vacancy to a distance exceeding 10 lattice constants [3], when the probability of annihilation of the U_1 center with the anion vacancy becomes negligible.

Thus, the conclusion of [1 - 5] that the U_1 centers are stable only at low temperatures turns out to be in error. We have demonstrated the possibility of producing interstitial hydrogen ions that are stable at room temperature, by eliminating the interactions that lead to the annihilation of the U_1 centers.

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