

phys. stat. sol. (b) 169, K7 (1992)

Subject classification: 61.70; 61.80; 78.30; S9.11

Vinogradov Institute of Geochemistry,
Academy of Sciences of the USSR, Siberian Branch, Irkutsk¹⁾

H_x Centers in LiF and NaF

By

B.P. CHERNYAGO, A.V. EGRANOV, and V.V. OTROSHOK

Introduction The properties of local modes of hydrogen defects in alkali halides and alkaline-earth fluorides have been studied extensively by means of Raman scattering and infrared spectroscopy /1, 2/. The local modes of the charged defects are infrared active and H_{S,a}⁻, H_{S,a}⁻ pairs, and H_i⁻ centres give rise to well studied vibrational spectra /1, 3, 4/.

A vibrating interstitial hydrogen atom carries no ionic dipole moment and consequently the H_i⁰ local mode would be infrared inactive. However, there is some covalent bonding with the surrounding halogen ions implying some transfer of negative charge towards the H_i⁰ and infrared absorption of the H_i⁰ centres was actually observed with reasonable intensity in KCl and CaF₂ crystals /5/. More detailed investigation of the H_i⁰ local modes has been made in alkali halides by Raman scattering /6/.

Morato and Lüty /7/ have studied an interaction of mobile halogen interstitial atoms (H-centres) with H_{S,a}⁻ ions (U-centres) in KCl, KBr, KI, and RbBr, which leads to the formation of H_x⁻ defects with a highly localized vibration and a frequency 30 % higher than that of the H_i⁻ interstitial.

This note reports results of optical infrared absorption measurements of H_x⁻ centres in NaF and LiF crystals.

Experimental technique The LiF-H⁻ and NaF-H⁻ crystals were grown from the melt containing alkali hydride in hydrogen atmosphere ($\approx 4 \times 10^5$ Pa) by the Stockbarger method /8/. Specimens of LiF-OH⁻ and NaF-OH⁻ were obtained in a similar fashion from the melt containing hydroxyde in helium atmosphere. The concentrations of H⁻ and OH⁻ ions were determined by infrared spectroscopy using the characteristic absorption of these ions and were found in the range of 10^{-5} to 10^{-3} mole parts for U-centers and of 10^{-5} to 10^{-4} mole parts for OH⁻ ions. No trace of OH⁻ ions could be found by infrared spectroscopy in LiF-H⁻ crystals, but NaF-H⁻ crystals contain a small amount (about 3×10^{-5} mole parts) of OH⁻ centres.

The X-ray irradiation was performed at 40 kV and 50 mA. The optical experiments were carried out with a liquid-nitrogen cryostat with NaCl windows. To X-irradiate the samples at low temperatures, the cryostat was provided with a Be window at 45° to the optical path. Absorption measurements were carried out with the IR spectrophotometer Specord M-80.

¹⁾ Favorskii str. 1A, P.O. Box 4019, SU-664033 Irkutsk, USSR.

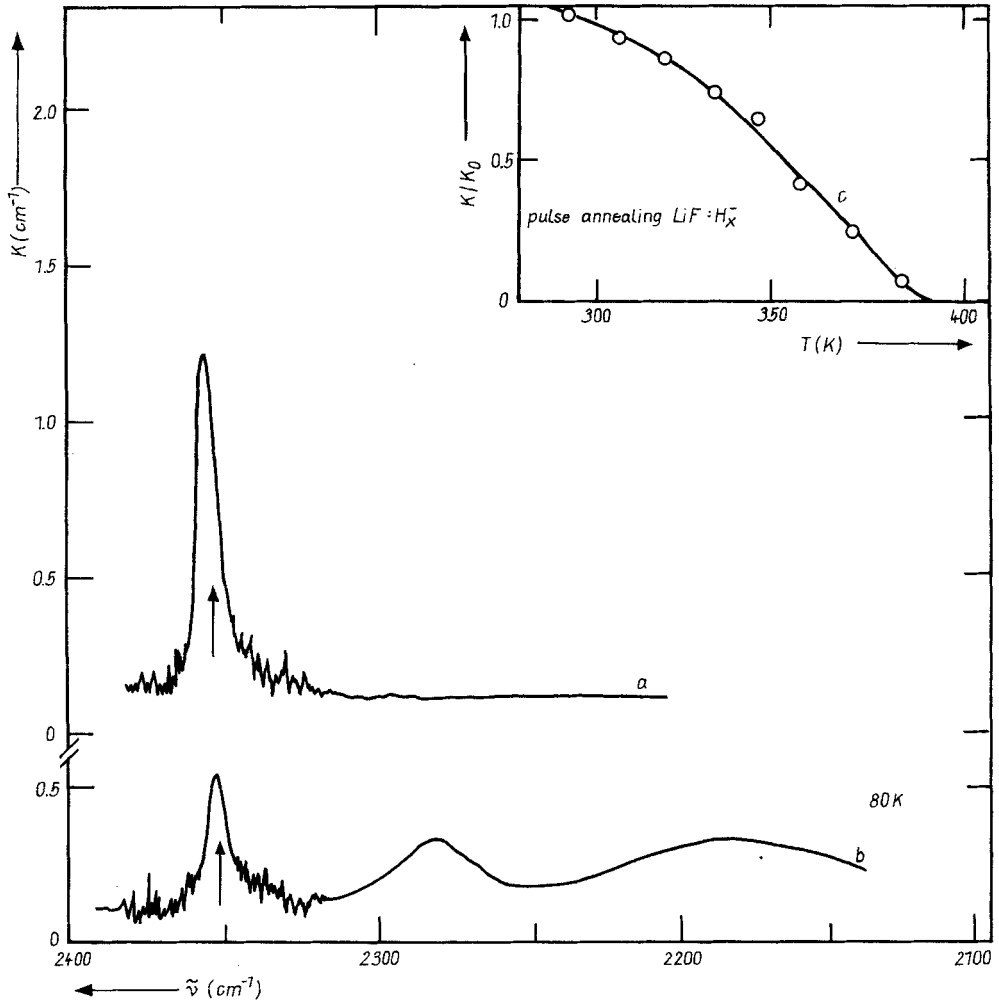


Fig. 1. IR absorption spectra of X-irradiated (a) $\text{LiF} \cdot 0.3 \times 10^{-3} \text{H}^-$ and (b) $\text{LiF} \cdot 1 \times 10^{-4} \text{OH}^-$ crystals measured at 80 K. The insert shows the annealing of the H_x^- band at 2350 cm^{-1} in LiF crystals as a function of temperature (c)

Experimental results The $\text{LiF} \cdot \text{H}^-$ crystals X-irradiated at room temperature exhibit an additional absorption line peaked at 2350 cm^{-1} with a halfwidth of 7 cm^{-1} at 80 K as shown in Fig. 1, curve a. Upon heating to room temperature the line shifts to 2303 cm^{-1} and its halfwidth is increased to 16 cm^{-1} . The centres responsible for this line are thermally unstable at room temperature and vanish during a few hours (Fig. 1, curve c). X-irradiation of the crystal at 80 K also

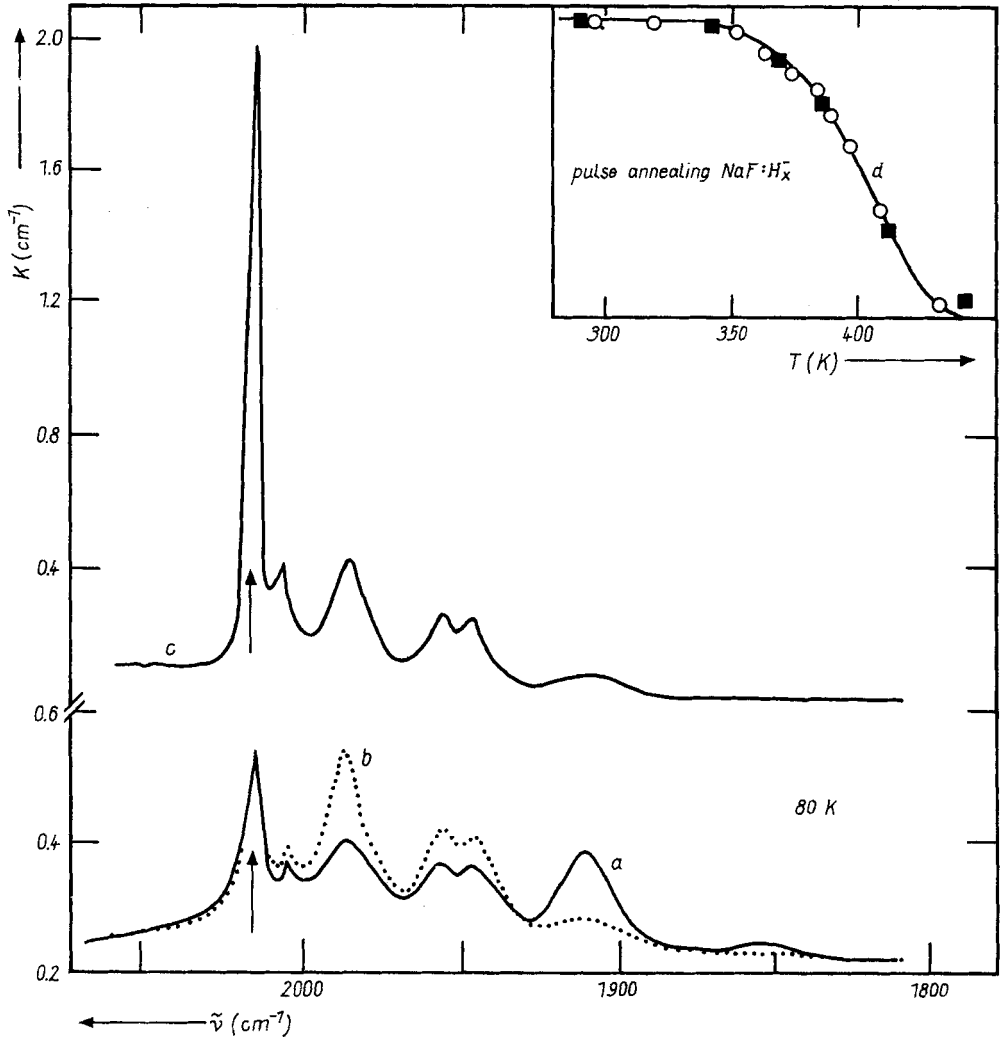


Fig. 2. IR absorption spectra of X-irradiated (a) $\text{NaF} \cdot 1 \times 10^{-4} \text{ OH}^-$, (b) $\text{NaF} \cdot 0.5 \times 10^{-3} \text{ OH}^-$, and (c) $\text{NaF} \cdot 0.5 \times 10^{-4} \text{ H}^-$ crystals measured at 80 K. The insert shows annealing of the H_x^- band at 2014 cm^{-1} as a function of temperature (d) in $\text{NaF} \cdot \text{H}^-$ (○) and $\text{NaF} \cdot \text{OH}^-$ (■) crystals

leads to the appearance of this line but with smaller efficiency. In addition to the line at 2350 cm^{-1} a weak absorption band at 1708 cm^{-1} , which thermally decays above 110 K, is observed. This band may be due to H_1^- centres.

Investigations of $\text{LiF} \cdot \text{OH}^-$ crystals were also carried out and in these samples after low X-ray exposure at room temperature we observed the same absorption

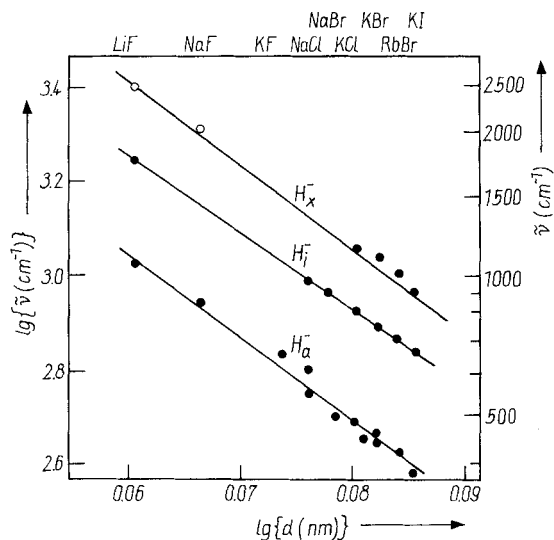


Fig. 3. Summary of the known wave number values of the $H_{s,a}^-$, H_i^- , and H_x^- centre local-mode absorptions in alkali halides, plotted in double logarithmic scale against lattice parameter

line as shown in Fig. 1, curve b but its intensity is much less than in the LiF-H^- crystals. Besides this line a broad band in the range 2000 to 2300 cm^{-1} appears. We should note that the absorption line at 2350 cm^{-1} is only created on the initial stage of X-irradiation, but prolonged irradiation leads to a decrease of the sharp line at 2350 cm^{-1} and to an increase of the broad band at about 2100 cm^{-1} . The sharp line is thermally bleached at the same temperature as in the case of LiF-H^- . The annealing temperature of the broad band is about 470 K.

X-irradiation of NaF-H^- crystals at room temperature produces a strong sharp line at 2014 cm^{-1} with halfwidth of about 2 cm^{-1} at 80 K (Fig. 2, curve c). Since the NaF-H^- crystals contain some amount of OH^- centers an additional number of lines is observed which are associated with OH^- ions. They are easily distinguished from the former line during annealing. Thus the line at 2014 cm^{-1} due to H^- doping decays at about 400 K (Fig. 2, curve d), on the other hand, the lines located in the range 1800 to 2000 cm^{-1} anneal at higher temperatures (about 480 K). The line at 2014 cm^{-1} is also observed in X-irradiated NaF-OH^- crystals at 295 K, but with smaller intensity (Fig. 2, curves a, b).

Discussion We suggest that the observed sharp lines at 2350 cm^{-1} in LiF-H^- and at 2014 cm^{-1} in NaF-H^- (at 80 K) are due to H_x^- centres, which were first discovered by Morato and Lüty /7/ in KCl , KBr , RbBr , and KI crystals, on the basis of the following results:

1. These absorption lines appeared in crystals in which hydrogen ions (U -centres) are present.
2. The variation of the local-mode frequencies among the investigated host crystals follows an Ivey law for the H_x^- centres, similar to the one for H_a^- and H_i^- local modes (Fig. 3).

The H_x^- centres have been shown /7/ to be a product of interaction of mobile halogen interstitials (X_i^0) with hydrogen ions ($H_{s,a}^-$ centres)- $H_{s,a}^- + X_i^0 \rightarrow H_x^-$ and

in terms of the building blocks involved, the H_x^- defects are equivalent to the H_i^0 centres.

The difference between the two configurations lies in the different behaviour of interstitial atoms of the halogen (H-centre) compared to that of the hydrogen (U_2^- centre). Thus the hydrogen atom occupies an interstitial site at the center of a cube consisting of the four halide ions and of the four alkali ions. On the other hand, the halogen atom X_i^0 is not stable at the interstitial site and is associated with halogen ions X^- in "pure" crystals to form X_2^- diatomic molecular ions. Thus, in hydrogen doped crystals, the X_i^0 may interact with a surrounding substitutional hydrogen ion, $H_{s,a}^-$, to form the H_x^- centre.

Finally, we have attempted to measure the ESR spectrum of the H_x^- centre in $LiF-H^-$, since the centre is expected to be paramagnetic. However, our search failed to yield an ESR signal because the strong ESR signal of the H_2^- centre /8/ in $LiF-H^-$ is present and the efficiency of the formation of the H_x^- centres is too low compared to that of the H_2^- centres.

References

- /1/ A.S. BARKER and A.J. SIEVERS, *Rev. mod. Phys.* **47**, 1 (1975).
- /2/ Y. KONDO, J.R. DUFFEY, and F. LÜTY, *Phys. Rev. B* **23**, 28 (1981).
- /3/ E. RADZHABOV, *Optika i Spektroskopiya* **68**, 467 (1990).
- /4/ A.V. EGRANOV, A.I. NEPOMNYASHCHIKH, V.V. OTROSHOK, and B.P. CHERNYAGO, *Optika i Spektroskopiya* **66**, 1319 (1989).
- /5/ R.E. SHAMU, W.M. HARTMANN, and E.L. YASAITIS, *Phys. Rev.* **170**, 822 (1968).
- /6/ J.F. ZHOU, E. GOOVAERTS, and D. SCHOEMAKER, *Phys. Rev. B* **29**, 5533 (1984).
- /7/ S.P. MORATO and F. LÜTY, *Phys. Rev. B* **22**, 4980 (1980).
- /8/ A.V. EGRANOV, A.I. NEPOMNYASHCHIKH, V.V. OTROSHOK, and B.P. CHERNYAGO, *phys. stat. sol. (b)* **155**, 365 (1989).

(Received October 1, 1991)