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Infrared Absorption Due to U-Centres in Highly Doped LiF:H⁻ Crystals

By

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Introduction   Substitutional hydride ions in alkali halides, known as U-centres, show a characteristic infrared absorption due to local vibrations of the H_a^- ions which was first observed by Schaefer /1/. In addition to the main U-centre absorption band, Schaefer also observed sidebands. They were caused by anharmonic coupling between the local mode and perturbed lattice modes /2/.

As the H_a^- ion is at a site of cubic (O_h) symmetry, the ground state (n = 0) wave function transforms as the A_{1g} irreducible representation of the O_h point group, and the first excited state (n = 1) as T_{1u}. The sixth degenerate second excited state (n = 2) is split by anharmonic perturbation into levels of A_{1g}, E_g, and T_{2g} symmetry. The third excited state (n = 3) splits into three triply degenerate levels (T_{2u} and two T_{1u}) and the non-degenerate level A_{1u} /3/ (Fig. 1).

Transitions between states of different parity can be observed in infrared absorption, while transitions between states of the same parity should by Raman active. Hence, the second harmonic of the local mode should be only observed by Raman scattering. The Raman results on the second harmonic U local mode have been obtained by Montgomery et al. /4/ for KI:H⁻, KBr:H⁻ and Kondo et al. /5/ for KCl:H⁻ and KCl:D⁻.

For O_h symmetry electric dipole transitions are allowed from the singlet A_{1g} ground state to the T_{1u} triply degenerate excited state. Thus transitions to n = 1 and n = 3 should be occur at frequencies ω and 3ω. However, up to now only the lowest transition to the first T_{1u} state has been observed by infrared absorption.

In highly doped LiF:H⁻ crystals we observed infrared absorption bands that are not present in more lowly doped samples. The absorption bands at 948 and 1044 cm^{-1} were studied in our previous work /6/. The intensity of these bands varies as the square of the U-centre doping concentration, suggesting that the bands are due to pairs of nearby H_a^- ions ($H_a^- H_a^-$ centres). This note reports new results of optical infrared absorption measurements of highly doped LiF:H⁻ crystals.

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harmonics   sidebands
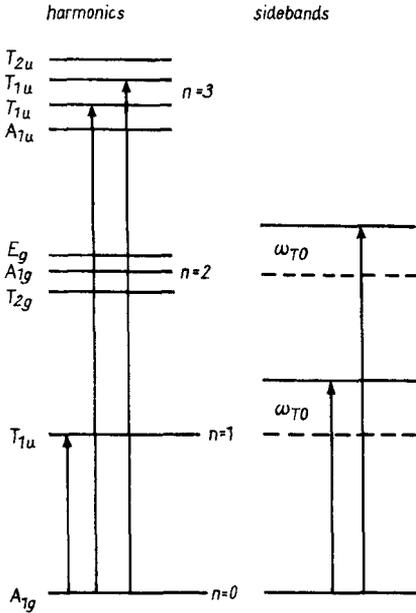
Fig. 1. Schematic representation of the vibrational energy levels of the U-centre in LiF. Observed transitions are indicated by vertical lines

Experimental technique   The preparation of the doped LiF:H$^-$ crystals used in this investigation has been described previously /7, 8/. The crystals contained 10^{18} to 10^{21} cm^{-3} U-centres. The concentration of the U-centres in the crystals was determined by infrared spectroscopy. In the low concentration range of the U-centres (10^{18} to 5×10^{19} cm^{-3}) the main band at 1012 cm^{-1} and in the higher concentration range the sideband at 1320 cm^{-1} were used. In contrast to /9/, in our crystals the intensity of the sideband at 1320 cm^{-1} is proportional to that of the main band (Fig. 2, curve 5). The ratio of the intensities between the main band and the sideband is 118 ∓ 7 at room temperature. The optical measurements are done by a Specord M-80 infrared spectrophotometer.

We have measured relative intensities of the bands in the following way. A thick crystal (10 to 50 mm) was used to measure the spectrum with the weaker band, then a thin slice (0.1 to 1 mm) was cleaved from the crystal and the stronger band was measured. The inaccuracy due to non-uniformity of the impurity distribution through the crystal was reduced by measuring slices from different parts of the thick sample.

Experimental result Fig. 2 shows a survey of the infrared absorption of LiF:H$^-$ crystals with three different concentrations of U-centres. At low U-centre concentration (10^{18} to 5×10^{19} cm^{-3}) the main local band at 1012 cm^{-1} (curve 1) and the sideband at 1320 cm^{-1} (curve 2) were observed at room temperature /9/. Two additional broad and relatively structureless bands at 2360 and 3020 cm^{-1} appear in the samples with higher concentration of the U-centres (curve 3).

The intensity of the bands increases linearly with the concentration of the U-centres in the crystal (Fig. 2, curve 6, 7). Therefore, they must be attributed to unknown transitions of the U-centre.

As the main local mode of the H$_a^-$ ion in LiF is located at 1012 cm^{-1}, the band at 3020 cm^{-1} must be due to the third harmonic of the U-local mode, which should be infrared active. Since the third excited state has two T$_{1u}$ levels, one expects to
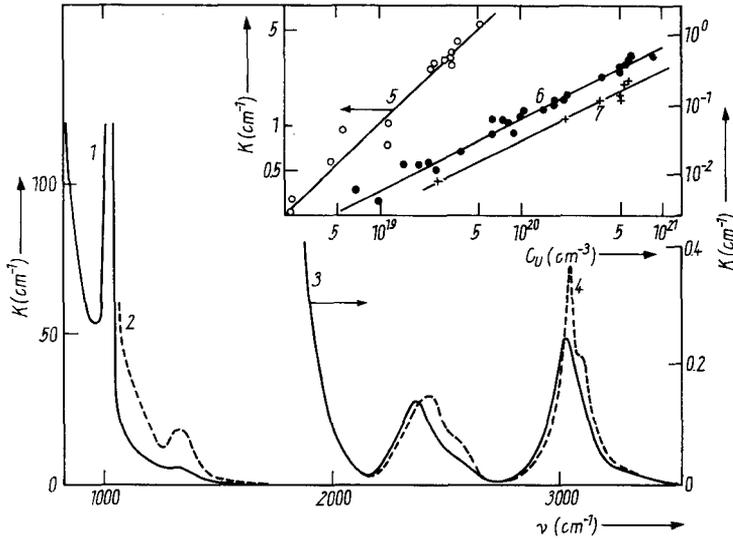
Fig. 2. Infrared absorption spectra of LiF:H⁻ crystals with different concentrations of U-centres; (1) 3×10^{19}, (2) 10^{20}, (3) 5×10^{20} cm^{-3} at 295 K, and (4) 5×10^{20} cm^{-3} at 80 K. The variation with the U-centre concentration of the absorption coefficient of the bands at (5) 1320, (6) 3020, and (7) 2360 cm^{-1} at 295 K is shown in the inset

observe two different transitions between the ground and T_{1u} third harmonic states by infrared absorption (Fig. 1) and at 80 K a two-line structure can be resolved at 3038 cm^{-1} and at about 3090 cm^{-1} (Fig. 2, curve 4).

The ratio of the integrated intensities at 300 K between the first local band and the band at 3020 cm^{-1} is $(26 \mp 0.5) \times 10^{2}$. Taking into account the oscillator strength of the first harmonic transition ($f_{\omega} = 0.4$ /7, 9/), the oscillator strength of the third harmonic transition, $f_{3\omega}$, is equal to $(1.5 \mp 0.3) \times 10^{-4}$.

The broad band at 2360 cm^{-1} increasing linearly with the H_a^- doping is a new and unexpected band which appears in the second harmonic region of the U local mode. Its large width (≈ 200 cm^{-1}) indicates that it originates from a broad phonon spectrum. The bandshape, together with its position, suggests strongly that it is caused by a combination effect of the second harmonic of the U local mode with lattice phonons.

Due to the large mass ratio between Li and F a preferred coupling of the local phonon to optical phonons was observed /9/. The transverse optic mode frequency ω_{TO} of LiF is 307 cm^{-1} /3/ and its value is close to the difference between the frequencies of the sideband at 1320 cm^{-1} and the main local mode at 1012 cm^{-1}. As the expected second harmonic of the local mode is at about 2025 cm^{-1}, the band at

2360 cm^{-1} may be attributed to the sideband of the second harmonic and the frequency difference between them close to a transverse optic mode frequency, ω_{TO}.

Apparently, the transition is allowed by coupling of the second excited state of the U-center to perturbed lattice phonons (Fig. 1).

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