

FAR INFRARED ABSORPTION OF CsBr AND CsI CRYSTALS DOPED WITH OH⁻ AND OD⁻

W. PRETTL and E. SIEP

Physikalisches Institut der Universität Freiburg, Germany

Received 9 December 1969

In CsBr:OH⁻ both librational transitions and the "non Devonshire" line have been found. CsBr:OD⁻ displays the expected isotope shift of a libration. Narrow lines in CsBr and CsI, observed directly above the two phonon lattice absorption, are tentatively explained as due to OH⁻ aggregates.

Alkali halide crystals doped with OH⁻ and OD⁻ ions exhibit in the spectral range above the two phonon absorption of the fundamental lattice vibrations (200 - 500 cm⁻¹) several absorption lines, which are explained as transitions between librational levels of the OH⁻ and OD⁻ ion respectively [1,2]. The fundamental librational frequency occurs at about 300 cm⁻¹ for OH⁻ and 220 cm⁻¹ for OD⁻. This isotope shift corresponds approximately to the square root of the moments of inertia. In addition, the so called "non Devonshire" line at about 30 cm⁻¹ has been observed in several alkali halide crystals [3,4].

We have studied the far infrared absorption of CsBr:OH⁻, OD⁻ and CsI:OH⁻, OD⁻ up to 400 cm⁻¹. In the absorption curves of CsBr:OH⁻ the librational line, labelled A in fig. 1a, appears at 289 cm⁻¹. This line and weaker librational sidebands at 320, 441, 444, and 545 cm⁻¹ were reported by Harrison and Lüty [5]. Among these sidebands the line at 320 cm⁻¹ was in the frequency range covered by our measurements, and we really found a rather weak sideband, B in fig. 1a at 314 cm⁻¹, which might be equivalent to that reported in ref. [5]. The CsBr crystal doped with OD⁻ shows three lines: A', B' and C' at 212, 228 and 328 cm⁻¹ respectively (fig. 1b). It also contains OH⁻ ions, which is indicated by the presence of the OH⁻ line A. The line A' is the main librational line of the OD⁻ molecule corresponding to the line A of OH⁻. This is concluded from the frequency shift $\omega_A/\omega_{A'} = 1.36$, which is in very good agreement with the expected isotope effect $\omega_{OH^-}/\omega_{OD^-} = \sqrt{\theta_{OD^-}/\theta_{OH^-}} = 1.37$ [2]. In the same way the line B' at 228 cm⁻¹ can be related to the sideband B at 314 cm⁻¹ in CsBr:OH⁻. The line C' and the OH⁻ librational doublet at 441 and 444 cm⁻¹ [5] exhibit rather well

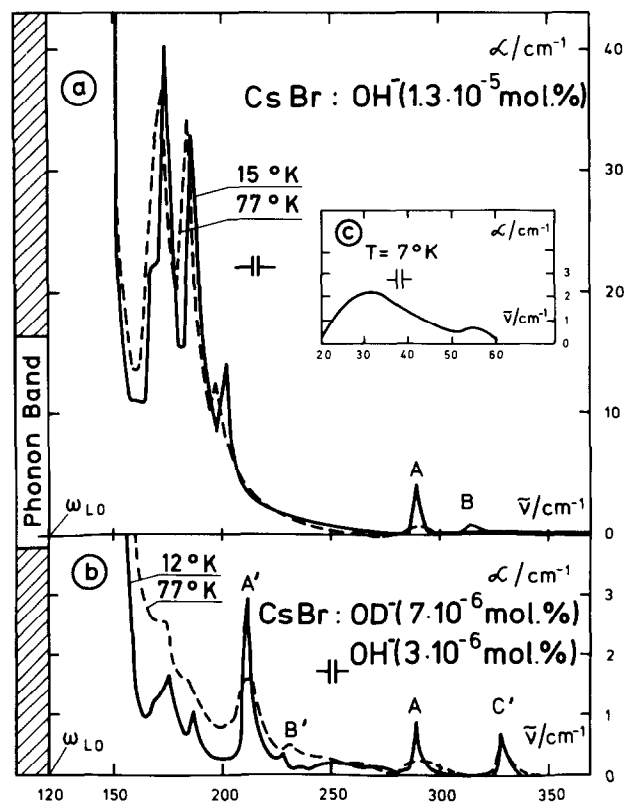


Fig. 1. Impurity induced absorption: a) CsBr:OH⁻. b) CsBr:OD⁻, the crystal contains also OH⁻; this can be seen by the OH⁻-librational line A. c) the "non Devonshire" line in CsBr:OH⁻. ω_{LO} is the longitudinal optic phonon frequency and indicates the upper limit of the phonon band.

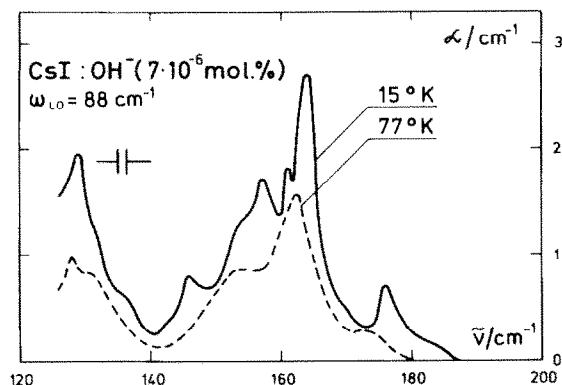


Fig. 2. Impurity induced absorption in CsI:OH⁻.

the isotope shift relation, but C' is a single line within our instrumental resolution of 2.5 cm⁻¹. In CsI doped with OH⁻ or OD⁻ ions no corresponding absorption occurs, which can be attributed to the librational mode of the impurities. Measurements of OH⁻ doped samples in the frequency range of the phonon bands of the crystals yielded the "non Devonshire" line in CsBr (see fig. 1c); again CsI:OH⁻ shows no additional absorption.

In addition to the librational transitions of the hydroxyl ion three strong and narrow absorption lines appear in CsBr:OH⁻ directly above the two phonon absorption of the host crystal. They are also shown in fig. 1a. In CsI:OH⁻ a similar spectrum is found (fig. 2). In CsBr the shape of these lines remains nearly unchanged up to liquid nitrogen temperature, whereas in CsI the lines show a stronger temperature broadening. Measurements on several CsBr:OH⁻ samples showed that the integral absorption of these additional lines is proportional to the square of the hydroxyl concentration. The absorption strength of the OH⁻ main librational band A has been taken as a measure of the OH⁻ concentration. From this result we suppose that these transitions are caused by OH⁻ aggregates. The CsCl structure favours the interaction of two OH⁻ impurities on neighbouring anion sites, because there is no host lattice ion between them, as in NaCl structure crystals. Isotopic substitution of OD⁻ for OH⁻ yield no new "aggregate" modes for both host crystals. The "aggregate" lines appearing in the absorption curve of CsBr:OD⁻ (fig. 1b) must be attributed to the OH⁻ impurities, also present in this crystal. This is deduced by comparing the integral absorption of these lines with the OH⁻ concentration. Possibly, OH⁻ - OD⁻ and OD⁻ - OD⁻ "aggregate" frequencies are lower

than the two phonon absorption of the host crystals. These considerations should be taken as a tentative trial to explain these transitions, not fitting into a simple librational model.

An interesting feature of the spectrum of the doped CsBr crystals is the increasing impurity absorption by approaching the one phonon cut off (120 cm⁻¹) from above. Other measurements of Tl⁺ and Na⁺ doped CsBr in the phonon band region * yielded a strong temperature dependent impurity absorption. This together with the above mentioned increasing absorption near ω_{LO} can be understood by assuming impurity induced multiphonon absorption.

The measurements were performed by a RIIC-Michelson interferometer, FS 720, and a Fourier transform computer, FTC 100. The single crystals were grown from u.p. material by the Czochralski technique in air or in an argon atmosphere, which made no difference in the spectra. The hydroxyl concentrations were determined by p.H. titration. Samples of few millimeter thickness were used, and cooled by conventional cryogenic techniques.

We wish to thank Professor L. Genzel for his interest in this work and helpful discussions, and Professors F. Kneubühl and P. Keller (both ETH Zürich) for stimulating conversations. Furthermore we are greatly indebted to M. Schumacher (Freiburg), and U. Gross (TH Stuttgart) for growing the crystals, and to the Deutsche Forschungsgemeinschaft for support of the spectroscopic devices.

* will be published elsewhere.

REFERENCES

- [1] D. Harrison and F. Lüty, Bull. Am. Phys. Soc. 12 (1967) 82.
- [2] M. V. Klein, B. Wedding and M. A. Levine, Phys. Rev. 180 (1969) 902.
- [3] D. R. Bosomworth, Solid State Commun. 5 (1967) 681.
- [4] B. Wedding and M. V. Klein, Phys. Rev. 177 (1969) 1274.
- [5] D. Harrison and F. Lüty, Intern. Symp. on Color Centers, Rome (1968).