A. REFLECTION MEASUREMENTS ON POTASSIUM HALIDES
IN THE FAR INFRARED REGION

1. Introduction

Most ionic crystals have strong reflection bands, known as Reststrahlen bands, in the far infrared region. These are due to lattice vibrations. The lattice resonances have been observed at temperatures down to 5°K for several potassium halides, by measuring the reflection from single crystals at an incident angle of 10°.

The following crystals have been investigated: KCl, KBr, and KI.

2. Experimental Procedure

The interferometer and detector used for this measurement have been described elsewhere. The reflectivity values indicated below are relative to the reflectivity of a front-aluminized reference mirror.

3. Experimental Results

The measured reflectivity spectral profiles are shown in Fig. VII-1 for T = 5°, 80°, 195°, and 300°K, except for KCl which was not investigated at 195°K. The main absorption peak can be identified as the transverse optical fundamental of frequency, \(\omega_T\), at the zone center. Also, all of the alkali halides show a sideband on the high-frequency side of the main peak.

The Reststrahlen bands of KCl, KBr, KI have been fitted to a classical dispersion formula by machine programming. We found that this could not be done without assuming the existence of a second sideband between the main peak and observed sideband. The dispersion constants obtained in this way are tabulated in Table VII-1.

Here, \(S_i\) denotes the oscillator strength, and \(\gamma_i\) the damping constant of oscillator \(i\). All frequencies are in cm\(^{-1}\); \(\omega_L\) is the frequency of the longitudinal optical fundamental.

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*This work was supported in part by the Joint Services Electronics Programs (U.S. Army, U.S. Navy, and U.S. Air Force) under Contract DA 28-043-AMC-02536(E), the U.S. Air Force (ESD Contract AF19(628)-6066), and the Sloan Found for Basic Research (M.I.T. Grant).
Fig. VII-1. Reflectivity of potassium halides at various temperatures.

- Measured.
- ••••• Calculated by using the classical dispersion analysis.
Table VII-1. Dispersion constants obtained from the classical oscillator model.

<table>
<thead>
<tr>
<th></th>
<th>$S_T$</th>
<th>$\omega_T$</th>
<th>$\gamma_T$</th>
<th>$S_1$</th>
<th>$\omega_1$</th>
<th>$\gamma_1$</th>
<th>$S_2$</th>
<th>$\omega_2$</th>
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<th>$\varepsilon_0$</th>
<th>$\omega_L$</th>
<th>$\omega_{LST}$</th>
<th>$\varepsilon^*/\varepsilon$</th>
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<tr>
<td>KCl (300°)</td>
<td>215</td>
<td>143</td>
<td>5</td>
<td>55</td>
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<td>31</td>
<td>41</td>
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</table>
(VII. OPTICAL AND INFRARED SPECTROSCOPY)

at the zone center, and \( \omega_L^\text{(LST)} \) is that same quantity calculated from the Lyddane-Sacks-Teller relation:

\[
\omega_L^\text{(LST)} = \sqrt{\varepsilon_0 \varepsilon_\infty} \omega_T
\]  

(1)

The effective charge on an ion, \( e^* \), is obtained from the Szegetti relation

\[
\omega_T^2 = \frac{4\pi N}{9m} \varepsilon_0 \varepsilon_\infty^2 \left( \varepsilon_\infty^2 + 2 \right)^2 \varepsilon_0 \varepsilon_\infty
\]  

(2)

where \( N \) is the number of ion pairs per unit volume, and \( m \) is the reduced mass of an ion pair.

We have tentatively identified the frequency \( \omega_1 \) with the multiphonon compensation \( \text{TO} + \text{TA} \) at the zone boundary, and \( \omega_2 \) with \( \text{TO} + \text{LA} \).

All of the values of \( \varepsilon_\infty \) that we used were obtained from the CRC tables. The values of \( \varepsilon_0 \) were obtained from the reflectivity spectra extrapolated to \( \omega = 0 \).

We would like to thank Professor Alexander Smakula and Mr. J. Kalnajs, of the Center for Materials Science and Engineering, M.I.T., for the samples.

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References


B. LATTICE VIBRATIONS IN CdS/Se MIXED CRYSTALS

1. Introduction

The infrared transmittance and reflectance of pure crystals of CdS and CdSe have been studied and reported several years ago. More recently, the infrared transmittance and reflectance of the hexagonal mixed crystals of CdS/Se have been studied, and several preliminary reports have been published or informally exchanged between researchers at the Massachusetts Institute of Technology and elsewhere. At M.I.T., several mixed crystals of \( \text{CdS}_x \text{Se}_{(1-x)} \) (0.29<\( x < 0.93 \)) were studied in transmission at temperatures down to that of liquid Helium, and in reflection at temperatures down to that of liquid nitrogen, with the use of the FS520 Fourier spectrophotometer. A preliminary analysis of these results is presented here.

2. Discussion of Results

The CdS/Se systems appear to form good mixed crystals with hexagonal unit cells like pure CdS and CdSe. Such a unit cell for CdS with the lattice constants "a" and "c"
labeled is shown in Fig. VII-2. A quantitative analysis of 7 samples of CdS/Se determined the relative weights of Cd and Se in each sample. These two weights for each sample were then used to calculate independent values of $x$ in the empirical formula $\text{CdS}_x\text{Se}_{1-x}$. For all but one sample (sample H), these two values of $x$ agreed within 1% of each other, thereby showing that the crystals were indeed stoichiometric mixtures of CdS and CdSe. X-ray measurements on 5 of these samples were performed to obtain the lattice constants "a" and "c". All of the diffraction peaks were sharp, indicating unique lattice constants and no evidence of clustering, thereby confirming that the CdS/CdSe systems formed good mixed crystals for the range of concentrations studied. Plots of $a$, $c$, and $a^2c$ (volume of unit cell) against $x$ are shown in Figs. VII-3, VII-4, and VII-5, established for the pure samples; thus it is shown that the lattice parameters vary uniformly and nearly linearly with concentration. Moreover, the conclusion that CdS/Se does form good mixed crystals has also been confirmed by other researchers who measured these and other properties such as fluorescence of the CdS/Se system.\textsuperscript{1-6, 8-10}

The reflection spectra of the mixed crystals of CdS/Se show at least two optically active lattice vibrations. Figure VII-6 shows the reflectivity of one of the samples.
Fig. VII-3. Plot of $a$ against $x$.

Fig. VII-4. Plot of $c$ against $x$.

Fig. VII-5. Plot of $a^2c$ (volume of unit cell) against $x$. 
Fig. VII-6. Reflectivity vs frequency at room temperature.

compared with pure CdSe at room temperature. Whereas the reflectivity of mixed crystals of the alkali halides and NiO/CoO show only a single peak whose frequency varies with the atomic concentration of the crystal's constituents\(^5\)\(^-\)\(^7\); the reflectivity of CdS/Se shows two distinct peaks whose frequencies remain nearly constant but whose intensities vary with the atomic concentration parameter \(x\). Thus, the mixed II-VI compound shows some of the properties of the covalent-type bonding characteristic of the mixed III-V compounds like GaAs/P, but without the clustering found in GaAs/P\(^3\),\(^9\). Also, Verleur and Barker\(^10\) have shown that some of the theoretical tools used to analyze the GaAs/P system may also be applied to the CdS/Se system.

Table VII-2 shows the principal room-temperature multiphonon absorption bands of

| Table VII-2. Principal absorption bands, \(\nu > 300 \text{ cm}^{-1}\). |
|------------------|------------------|
| CdS              | CdSe             |
| 334 cm\(^{-1}\)  | 310 cm\(^{-1}\)  |
| 345-355          | 360              |
| 388              | 405              |
| 404              | 470              |
| 415              |                  |
| 498              |                  |
| 518              |                  |

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pure CdS and CdSe above 300 cm\(^{-1}\). Figure VII-7 shows the room-temperature absorption spectrum of one of the typical mixed crystals of CdS/Se. As can be seen by comparing this graph with Table VII-2, the absorption of the mixed crystal looks much like the product of the two pure absorption curves.

Although the experimental evidence shows that CdS and CdSe do form good, uniform mixed crystals, the infrared optical properties appear to behave as if determined by two nearly independent crystal lattices, one being due to the CdS, and the other to the CdSe. At present, a theoretical analysis of the experimental measurements of the transmission and reflection of the mixed crystals of CdS/Se, based upon the observations presented in this report and the classical oscillator model, is being completed.

We would like to thank Dr. S. S. Mitra, of the University of Rhode Island, and Dr. D. Reynolds, of Wright-Patterson Air Force Base, Ohio, for the samples, and to thank J. A. Kalnajs of the Center for Materials Science and Engineering, M.I.T., for the x-ray analysis.

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References


