VII. OPTICAL AND INFRARED SPECTROSCOPY[*]

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

1. Introduction

Most ionic crystals have strong refelction 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.[1] 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, ω_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 γ_i the damping constant of oscillator i. All frequencies are in cm^{-1}; ω_L is the frequency of the longitudinal optical fundamental
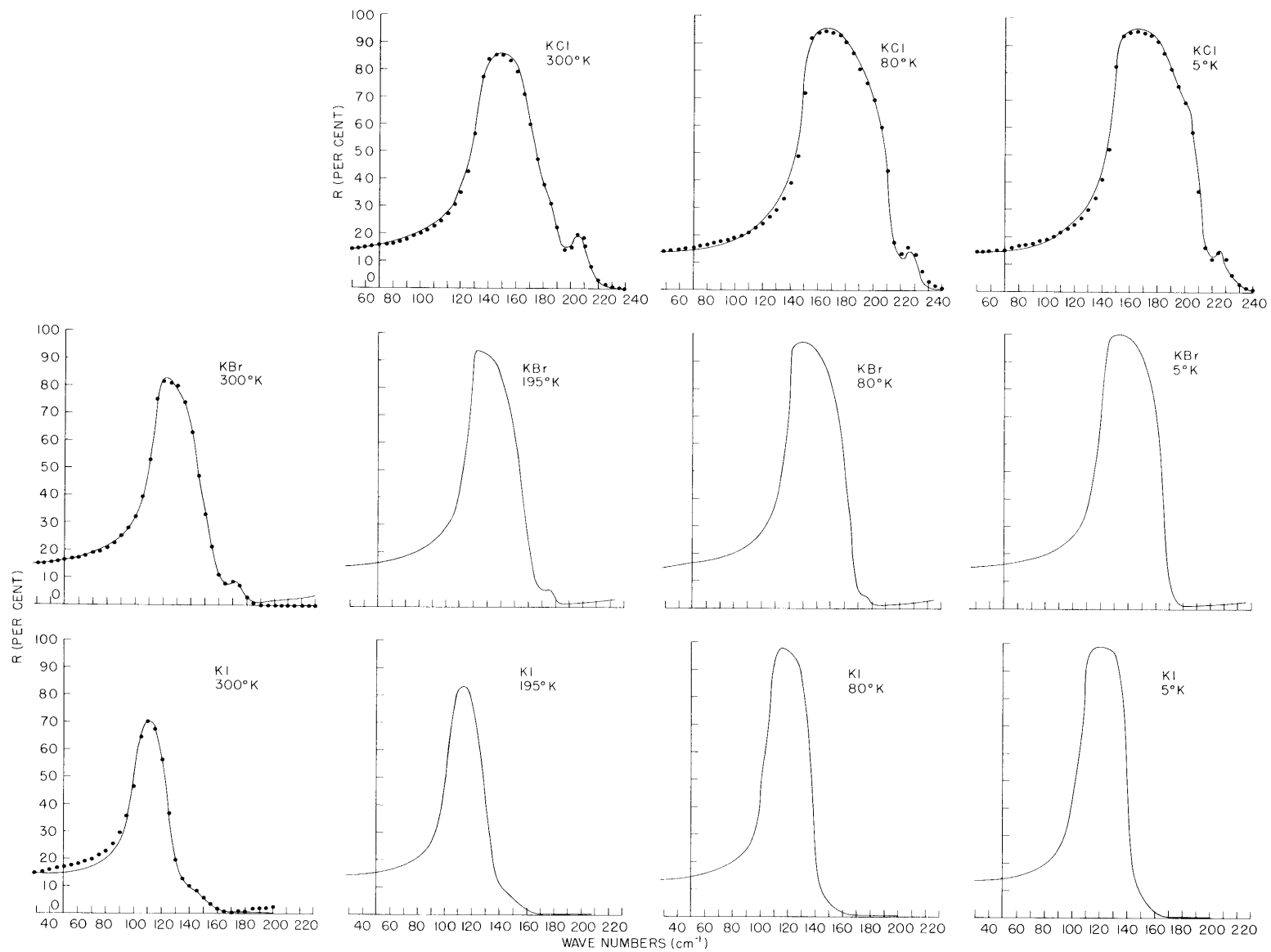
Fig. VII-1.   Reflectivity of potassium halides at various temperatures.
——————   Measured.
• • • • •   Calculated by using the classical dispersion analysis.

Table VII-1. Dispersion constants obtained from the classical oscillator model.

	S_T	ω_T	γ_T	S_1	ω_1	γ_1	S_2	ω_2	γ_2	ϵ_∞	ϵ_0	ω_L	ω_{LST}	e^*/e
KCl (300°)	215	143	5	55	189.5	31	41	210.5	14.5	2.22	4.6	203	206	.77
KCl (90)	230	151	2	35	193	30	40	222	17	2.22	4.61	216	216	
KCl (10)	230	150	1.0	35	193	30	40	222	17	2.22	4.64	215	216	
KBr (300°)	172	113	5	42	150	28	36.5	169	15	2.43	4.9	158	161	.74
KBr (195)	170	117	1.5	39	147	30	30	172	15	2.43				
KBr (90)	173	120	0.8	30	152	28	25	174	15	2.43				
KBr (10)	178	122	0.1	24	157	28	28	178	23	2.43				
KI (300°)	147	103.5	6.6	50	136	28	48	148	36	2.82	5.08	135	138	.71
KI (195)	151	106	3.5	44	138	27	38	149	25	2.82				
KI (90)	155	108	0.5	24	141	28	38	151	25	2.82				
KI (10)	161	110	0.2	15	144	28	41	153	25	2.82				

at the zone center, and ω_L(LST) is that same quantity calculated from the Lyddane-Sacks-Teller relation:

$$\omega_L(\text{LST}) = \sqrt{\epsilon_o/\epsilon_\infty}\ \omega_T \tag{1}$$

The effective charge on an ion, e^*, is obtained from the Szigetti relation

$$\omega_T^2 = \frac{4\pi N}{9m} e^{*2} \frac{(\epsilon_\infty + 2)^2}{\epsilon_o - \epsilon_\infty}, \tag{2}$$

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 ω_1 with the multiphonon compensation TO + TA at the zone boundary, and ω_2 with TO + LA.

All of the values of ϵ_∞ that we used were obtained from the CRC tables. The values of ϵ_o were obtained from the refelctivity 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.

<div align="right">Jeanne H. Fertel, C. H. Perry</div>

<div align="center">References</div>

1. C. H. Perry, R. Geick, and E. F. Young, J. Appl. Opt. 5, 1171 (1966).

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 $CdS_x Se_{(1-x)}$ ($.29 < x < .93$) 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
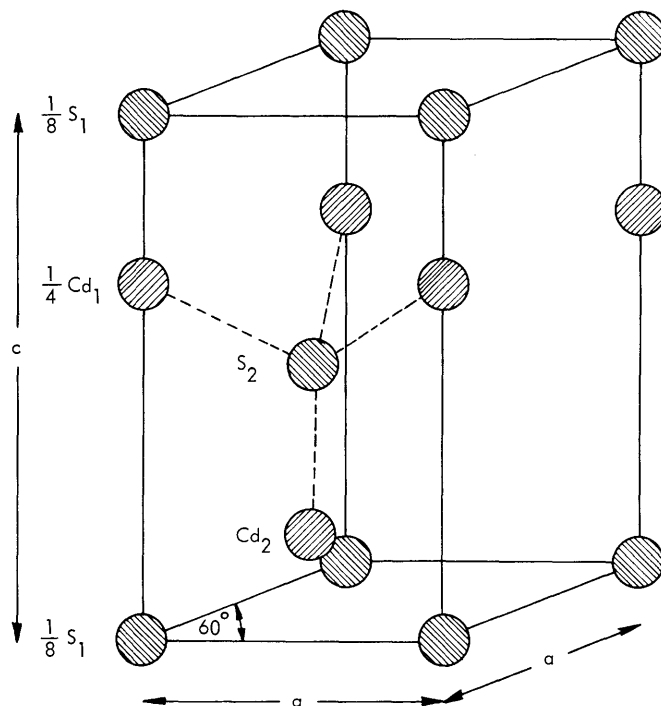

Fig. VII-2. Hexagonal CdS.

were then used to calculate independent values of "x" in the empirical formula $CdS_xSe_{(1-x)}$. 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.[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
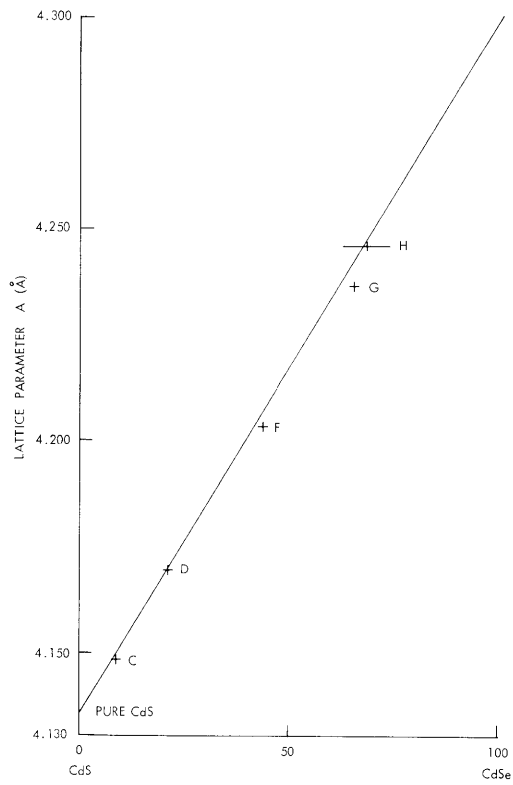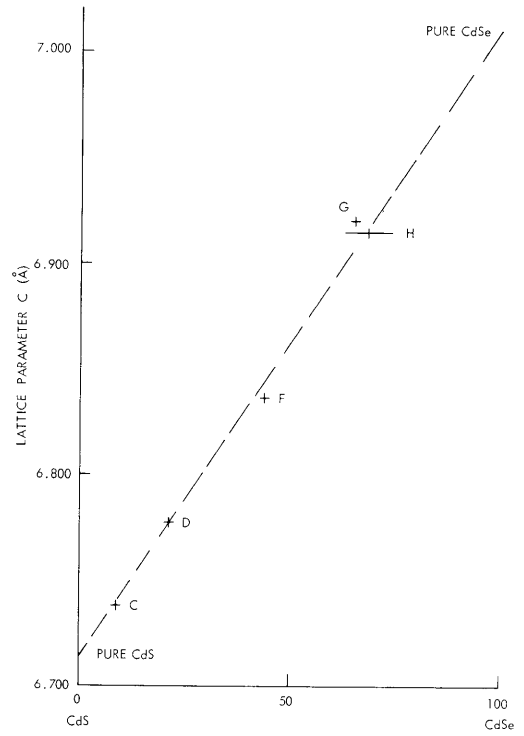
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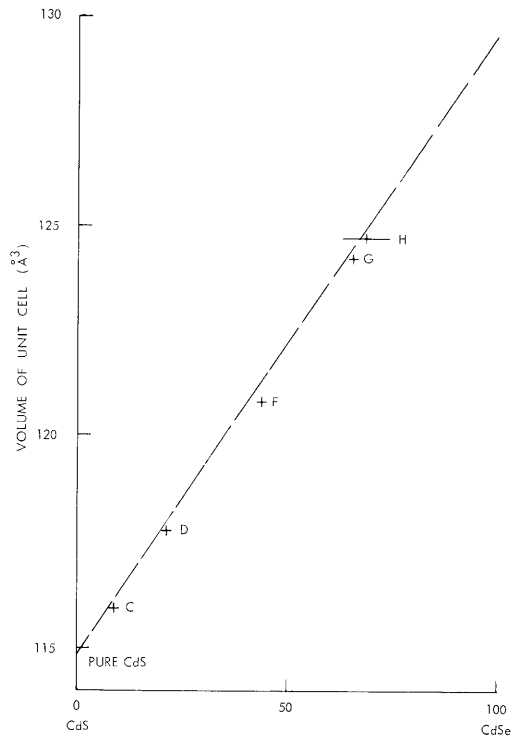Fig. VII-3. Plot of a against **x**.

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

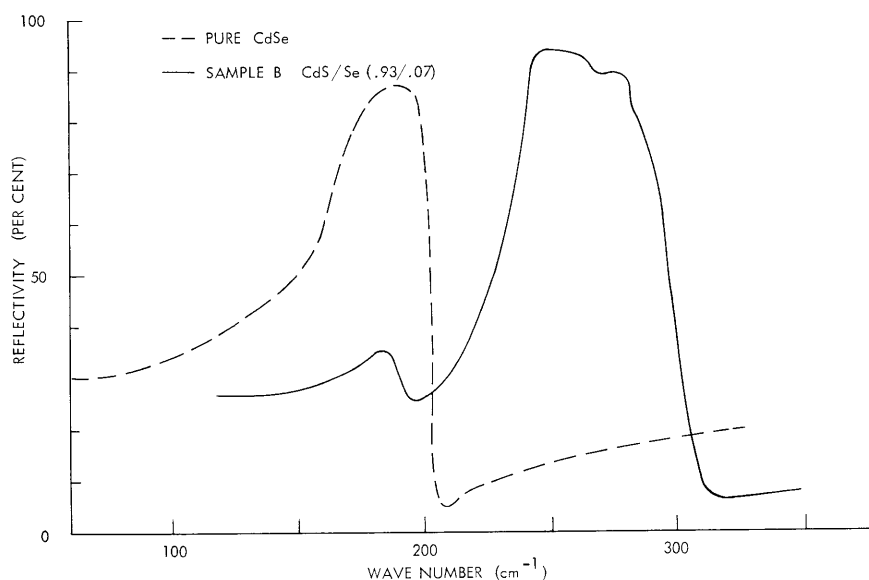Fig. VII-5. Plot of a^2c (volume of unit cell) against **x**.

Fig. VII-6. Reflectivity vs frequency at room temperature.

compared with pure CdSe at room temperature. Whereas the reflectivity of mixed crys-
tals 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, $v > 300$ cm^{-1}.

CdS	CdSe
334 cm^{-1}	310 cm^{-1}
345-355	360
388	405
404	470
415	
498	
518	

45

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
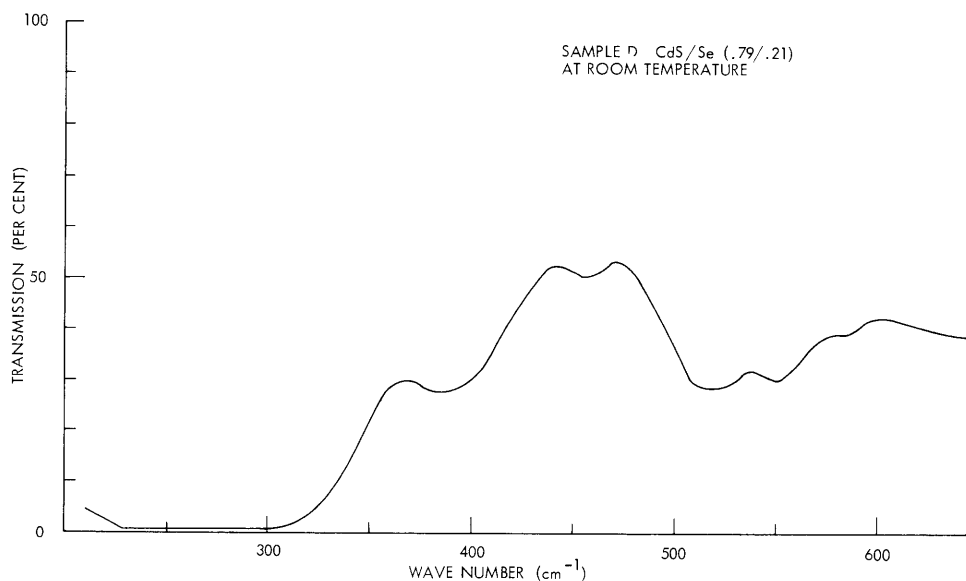

Fig. VII-7. Sample D CdS/Se (.79/.21) at room temperature.

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.

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