

and would be of great interest since the density difference between the two phases should be considerably reduced. Recombination radiation studies have been reported by Bageev, Galkina, and Gogolin,<sup>1</sup> which indicate a large reduction in metallic state binding. Benoit à la Guillaume, Salvan, and Voos<sup>15</sup> have measured a density of  $2 \times 10^{16} \text{ cm}^{-3}$  in the metallic phase which is somewhat larger than the value of  $1.2 \times 10^{16} \text{ cm}^{-3}$  that we find.

In conclusion we find that the large binding energy of the metallic state of the electron-hole liquid in Ge is due mainly to its special band structure. For simple band structure, such as in strained Ge, the binding is much weaker if indeed the metallic phase is bound. A detailed account of the calculations reported here will be published elsewhere.

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## Normal Modes of Vibrations in CuI

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Phonon dispersion curves for CuI have been measured at room temperature for the [100], [110], and [111] symmetry directions by using inelastic neutron scattering. The results are interpreted in terms of a rigid-ion model. Estimations are given for elastic constants.

Continuing the study of the lattice dynamics of cuprous-halide crystals with zinc-blende structure, we report in this paper the results of coherent inelastic neutron scattering from CuI.

Our interest in these compounds dates from some years ago, since the unfruitful attempt to fit zero-wave-vector phonons of CuCl with an oversimplified rigid-ion-lattice dynamical model.<sup>1</sup> Mar-

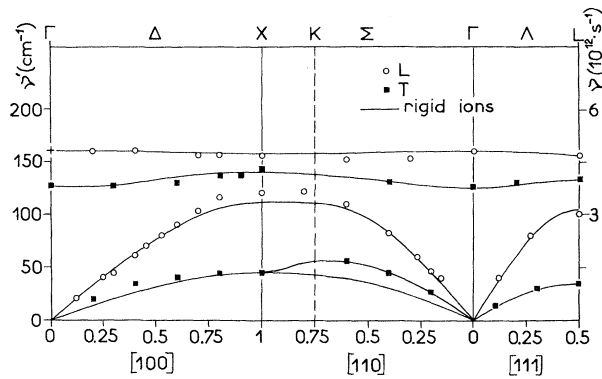


FIG. 1. Experimental and theoretical dispersion curves for CuI.

tin<sup>2</sup> pointed out the peculiar behavior of CuCl relative to other crystals with the same symmetry. In a previous paper, Carabatos *et al.*<sup>3</sup> emphasized both the curious shapes of experimental dispersion curves of CuCl (namely, in the [110] direction) and serious difficulties in the attempts to fit usual theoretical models to the measured curves. Supposing a possible interaction between 3d electrons of neighboring copper ions in CuCl, we decided to study the phonon dispersion curves in CuI where, the iodine ionic radius being greater than that of chlorine, this interaction should decrease.

All the measurements were done on the triple-axis spectrometer of the EL3 reactor at Centre d'Etudes Nucléaires de Saclay. The monochromator and the analyzer were, respectively, germanium and copper single crystals. According to the shape of the dispersion curves, we used either the  $Q$ -constant (for flat branches) or the  $\nu$ -constant technique for waves propagating along the high-symmetry directions [100], [110], and [111]. The first measured phonons and a rigid-ion model were used to calculate approximate inelastic structure factors in order to optimize the search of new phonons, particularly for optical branches.

The sample was prepared by one of us (C.S.) using the flux-growth technique. It had a volume of about 2.5 cm<sup>3</sup> and was a part of a cylinder 1.6 cm in diameter and 2.5 cm long. The cylinder axis was approximately parallel to a  $\langle 110 \rangle$  crystallographic axis. The crystal purity was determined by spectrochemical analysis with the following results: Ca  $\approx 3 \times 10^{-5}$ , Fe and K  $\approx 10^{-5}$ , Mg  $\approx 5 \times 10^{-6}$ , and Ag  $\approx 10^{-6}$  per weight; its mosaicity was estimated to be better than 0.1°.

Most of the determinations were made at room

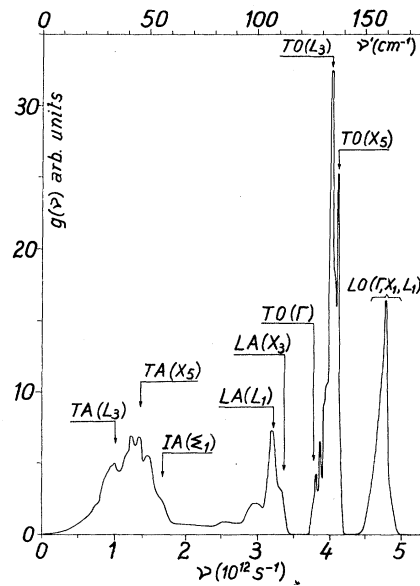


FIG. 2. Phonon density of states for CuI according to the rigid-ion model.

temperature with the (110) planes horizontal and parallel to the momentum of the neutrons. Some phonons were also measured at 90°K at the X, L, and  $\Gamma$  points of the first Brillouin zone.

Experimental results at room temperature are shown in Fig. 1 together with a rigid-ion-model fit using six short-range parameters. The agreement is surprisingly good, considering the simplicity of the model and compared with the results for CuCl.<sup>3</sup> The transverse-optical frequency at the  $\Gamma$  point previously found by infrared absorption and reflectivity measurements<sup>4</sup> agrees well with our neutron results within 2%. The main differences with the observations in CuCl are the disappearance of the singular shape of the pseudo-LA branch in the [110] direction, and the non-crossing of optical branches. In Fig. 2 is given the phonon density of states obtained with the help of an extrapolation method<sup>5</sup> using 527 crude mesh cubes uniformly distributed in  $\frac{1}{24}$  of the first Brillouin zone. From the initial slopes of the acoustical branches, we have estimated the elastic constants of CuI; the results as well as the rigid-ion-model parameters are summarized in Tables I and II.

At 90°K, we have observed an increase in the frequencies of about 8 cm<sup>-1</sup> for TA and LA phonons at the X point and of 10 cm<sup>-1</sup> for the LA at the L point; for the  $\Gamma$  point, only the  $\omega_{TO}$  frequency was accurately measured, giving a shift of 8 cm<sup>-1</sup> toward increasing energies. It must

TABLE I. Experimental values of the Reststrahlen frequencies and elastic constants of CuI; values in parentheses are relative to 90°K measurements. The uncertainty in the elastic constants is  $\pm 10\%$

$C_{44}$	$C_{12}$ ( $10^{12}$ dyn/cm <sup>2</sup> )	$C_{11}$	$\nu_{LO}'$ (cm <sup>-1</sup> )	$\nu_{TO}'$ (cm <sup>-1</sup> )	Source	
...	...	...	(224) <sup>a</sup>	211 <sup>a</sup>	(132) 124.2	Ref. (4)
0.158	0.305	0.405	(168)	160	(134) 126	This work

<sup>a</sup>Deduced by the Lyddane-Sachs-Teller relation and dielectric constants given in Ref. (4).

be noted that these displacements are just indicative, because they are only slightly greater than the uncertainty of the measurements at these points.

In conclusion, and before any fitting with a more complete model, we may consider our hypothesis concerning the influence of the overlap and hybridization of the 3d electron wave functions in cuprous halides as likely to be true; considering the ionic radii of chlorine, bromine and iodine, CuBr should present an intermediate behavior.

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TABLE II. Rigid-ion-model parameters for CuI; force constants are in  $e^2/v$  ( $v$  is the volume of a unit cell).  $Z_{Cu}^* = 0.69$ .

1	s	s'	$\alpha$	$\beta$	$\Phi_{\alpha\beta}(0_s; 1_{s'})$
(0, 0, 0)	1	2	1	1	2.812
	2	1	1	2	3.734
			1	1	0.562
	1	1	1	2	0.393
$\frac{1}{4}a(2, 2, 0)$	2	2	1	3	-0.253
			3	3	-0.6

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## Direct Optical Observation of the Subsidiary $X_{1c}$ Conduction Band and Its Donor Levels in InP

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Zero-phonon and phonon-assisted optical transitions from the  $\Gamma_{1c}$  conduction band to the subsidiary  $X_{1c}$  conduction band and its donor levels have been observed in InP at 8°K. The  $X_{1c}$ - $\Gamma_{1c}$  interband energy is measured at  $960 \pm 5$  meV, and the binding energies of donors associated with the subsidiary  $X_{1c}$  band are found to be 106 and 175 meV ( $\pm 5$  meV) for Te and Si, respectively.

We report here on a measurement of the  $\Gamma_{1c}$   $\rightarrow$   $X_{1c}$  inter-conduction-band energy in InP by means of optical absorption, utilizing the wavelength-derivative technique. The interband free-carrier absorption in InP has been measured by Dumke, Lorenz, and Pettit.<sup>1</sup> With the present

measurement technique we have observed for the first time phonon structure associated with the  $\Gamma_{1c}$   $\rightarrow$   $X_{1c}$  indirect transition in degenerately doped InP, as well as transitions from the  $\Gamma_{1c}$  conduction band to donor levels associated with the subsidiary  $X_{1c}$  conduction-band minima.