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THE INFRARED SPECTRUM OF Cd_3As_2

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We present new measurements of infrared reflectivity of Cd_3As_2 at 15 K. One plasmon and eleven phonon characteristics are determined by the fitting process that reveals weak dipolar moments in the structure.

CADMIUM ARSENIDE is a semiconductor which has attracted some attention over the years mainly because of its unusual transport properties and its inverted band structure. However little attention has been paid to its phonon properties which in principle might constitute quite a challenge in view of the peculiar crystal structure of cadmium arsenide. The unit cell of the α phase (which exists at room temperature and below) is composed of 160 atoms and is classified as body centered tetragonal (C_{4v}^{12}) [1].

The first infrared and Kramers–Kronig analysis of Cd_3As_2 did not however bring forth a rich phonon spectrum. Gelten and Van Es [2] only deduced three phonon modes from their data whereas Thielmann *et al.* [3] observed five modes. These data did however display plasmon–phonon coupling as expected since cadmium arsenide is always a degenerate (n-type) semiconductor. A study of the Raman spectrum [4] only revealed nine Raman-active phonons although 118 were predicted. One is led to conclude that the polarizability tensors are very weak in this material.

Among the numerous transport results available from the literature it has been possible to deduce the high frequency and static dielectric constants (ϵ_∞ and ϵ_0) of Cd_3As_2. From the fit of the electron mobility at 4.2 K using the inverted band structure model, a lower limit of $\epsilon_0 = 36$ was obtained [5]. An analogous treatment [6] for 77 and 300 K led to an approximate value of $\epsilon_\infty = 12$.

The 240 normal modes of Cd_3As_2 at the center Γ of the Brillouin zone can be described by the irreducible representations of the C_{4v} point group as [4]

$$\Gamma \equiv 64E + 28(A_1 + A_2 + B_1 + B_2).$$

According to the group analysis one expects $63E$ and $27A_1$, modes to be infrared active. These numbers are in sharp contrast with the three and five modes observed in the infrared reflectivity of references [2] and [3].

In this paper we will present new infrared reflectivity results along with the corresponding fitting of the phonons and plasmon characteristics.

We measured the concentration n and the mobility of electrons of the Cd_3As_2 sample used in the infrared reflectivity measurements and found respectively $0.6 \times 10^{18}\,e\,cm^{-3}$ and $4.6\,m^2\,V^{-1}\text{-sec}^{-1}$. The infrared reflectivity spectra were obtained with a Perkin–Elmer model 180 spectrophotometer operated in the double-beam mode. The calibration in reflectivity was obtained with a front surface aluminum mirror. The measurements were made with a globar and an Hg source with a thermopile and a pyroelectric detector in the frequency range $4000–50\,cm^{-1}$ at 15 K. The incident electric field was parallel to the (1 1 2) crystal plane.

No structure was found in reflectivity for frequencies higher than $500\,cm^{-1}$. In Fig. 1 we present the measured reflectivity analyzed by finding the parameters of the damped phonon oscillator factorized form plus a modified plasmon term that describes large plasmon bands [7]. The corresponding dielectric constant $\epsilon(\omega)$ becomes:

$$\epsilon(\omega) = \epsilon_\infty \prod_{j=1}^{M} \frac{\omega_{jLO}^2 - \omega^2 - i\gamma_{jLO}\omega}{\omega_{jTO}^2 - \omega^2 - i\gamma_{jTO}\omega} - \epsilon_\infty \frac{\tilde{\omega}_p^2 + i(\gamma_p - \gamma_0)\omega}{\omega(\omega - i\gamma_0)}.$$

$\epsilon(\omega)$ gives the theoretical reflectivity that best approximates the experimental spectrum by minimizing the chi-square function χ^2. ϵ_∞ is the high-frequency dielectric constant, ω_{jTO}, γ_{jTO} and ω_{jLO}, γ_{jLO} are the frequency and damping of the j-th oscillator for the transverse and longitudinal phonon, respectively. γ_0 and γ_p stand for the static and frequency dependent plasmon attenuation $\tilde{\omega}_p$ is the plasmon resonance frequency and $\omega_p = \sqrt{\epsilon_\infty}$ $\tilde{\omega}_p$ is the plasmon frequency given by $\omega_p^2 = 4\pi e^2 n/m^*$. The fitted parameters of the phonons and the plasmon are given in Table 1.

A relatively small number of phonons were sufficient

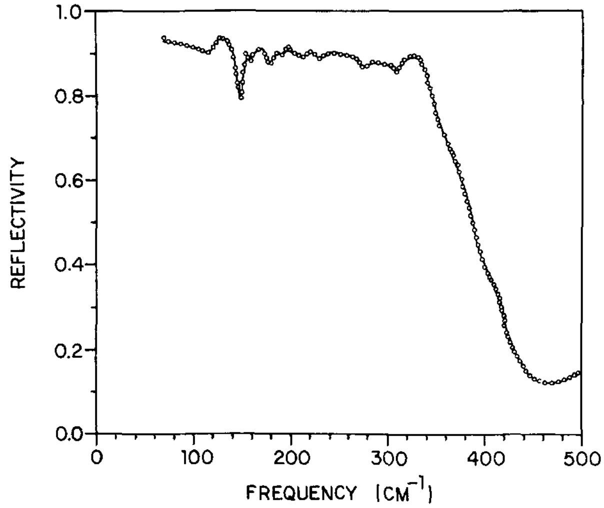

Fig. 1. Cd_3As_2 reflectance spectrum at 15 K (data points) and oscillator-plasmon fit (solid line).

to obtain an excellent fit. The electric field being parallel to the (1 1 2) plane both the $63E$ and $27A_1$ phonons should be detectable. This fact along with the small LO–TO splittings point to weak dipolar moments in the Cd_3As_2 structure.

The infrared plasmon characteristics are compatible with the d.c. measurements. With a mobility $\mu = 4.6$ $m^2\,V^{-1}\text{-sec}^{-1}$ and an established relative effective mass of 0.03 [5], the d.c. damping coefficient $e/m^*\mu c$ is 42 cm^{-1}. e, m^*, c are respectively the electronic charge, the effective mass and the speed of light. The corresponding infrared damping as mentioned in Table 1 is $\gamma_p = 62.7\,\text{cm}^{-1}$. The plasmon frequency, $\omega_p = 419\,\text{cm}^{-1}$ corresponds to a carrier concentration $n = 1.33 \times 10^{18}$ $e^-\,\text{cm}^{-3}$ which is of the same order as the electrically measured concentration.

In conclusion the fitting procedure of the infrared reflectivity of Cd_3As_2 is of high quality and characterizes satisfactorily the infrared phonons and the plasmon of the material. Also Cd_3As_2 develops weak dipolar moments along with the already observed weak polarizabilities [4].

Table 1. Oscillator and plasmon parameters to fit the infrared reflectivity spectrum of Cd_3As_2 at 15 K. Frequencies and damping constants are all in cm^{-1}

ω_{TO_i}	ω_{LO_i}	γ_{TO_i}	γ_{LO_i}
121.8	126.6	11.9	0.0
151.1	158.1	7.6	11.1
163.4	170.9	10.4	14.8
175.9	172.5	24.6	6.4
176.2	197.6	9.5	26.7
215.4	218.5	10.7	10.1
230.1	232.0	8.9	11.5
275.4	276.1	9.9	10.9
309.2	310.8	24.5	25.6
333.2	327.1	46.3	50.7
393.9	394.0	19.5	20.1

$\epsilon_\infty = 16.54$

$\omega_p = 419.3$ $\gamma_0 = 65.7$ $\gamma_p = 62.7$

$(\chi^2 = 0.27 \times 10^{-4})$

REFERENCES

1. G.A. Steigmann & J. Goodyear, *Acta Crystallogr. Sect.* **B24**, 1062 (1968).
2. M.J. Gelten & C.M. Van Es, *Proc. of the Int. Conf. on the Physics of Narrow Gap Semiconductors, Linz, 1981*, p. 167, Springer Verlag (1978).
3. J. Thielmann, M.V. Ortenberg, F.A.P. Blom & K. Strobel, *Proc. of the Int. Conf. on the Physics of Narrow Gap Semiconductors, Linz 1981*, p. 207, Springer Verlag (1978).
4. S. Jandl, S. Desgreniers, C. Carlone & M.J. Aubin. *J. Raman Spect.* **15**, 137 (1984).
5. J.P. Jay-Gérin, M.J. Aubin & L.G. Caron, *Solid State Commun.* **21**, 771 (1977).
6. J.P. Jay-Gérin, L.G. Caron & M.J. Aubin, *Can. J. Phys.* **55**, 956 (1977).
7. J.F. Banmard & F. Gervais, *Phys. Rev.* **B15**, 2316 (1977).