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## Effect of the isotopic mass of gallium on the indirect gap of GaP

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**A**

We have obtained pair recombination luminescence spectra of four GaP crystals with different gallium isotopic compositions. The frequency shifts measured vs. average isotopic mass allow us to determine  $dE_0/dM = 0.19(1)$  meV/amu, where  $E_0$  is the indirect gap and  $M$  the average gallium isotopic mass. From this mass derivative, a contribution of the gallium vibrations to the zero-point mass renormalization of the gap of 27 meV is estimated. Subtracting this contribution from the total zero point renormalization, as determined from the temperature dependence of the indirect gap, yields a contribution of 59 meV of the phosphorus vibrations to the gap renormalization. These results are discussed in comparison with similar data for group IV, III–V, and II–VI semiconductors. A comparison with theoretical calculations is also presented.

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**I**

The availability of semiconductor crystals with a wide range of isotopic compositions has triggered considerable interest in the dependence of their physical properties on isotopic mass. Foremost among these properties are the phonon frequencies [1,2] and the electronic energy gaps [3,4]. The dependence of gap energies on isotopic mass is a consequence of the zero-point ( $T = 0$ ) renormalization of those energies by the electron–phonon interaction, which depends on the phonon frequencies, i.e. on the isotopic mass [5,6]. For monatomic crystals (e.g. diamond [3], silicon [7], or germanium [8]) the zero-point renormalization  $\Delta E_0$  of a given gap  $E_0$  is proportional to  $\langle M \rangle^{-1/2}$ , where  $\langle M \rangle$  is the average isotopic mass. Hence, the isotope effect on the gap can be written as:

$$\frac{dE_0}{d\langle M \rangle} = -\frac{1}{2} \frac{\Delta E_0}{\langle M \rangle} \quad (1)$$

Although two distinct contributions to  $\Delta E_0$  are present, that due to the effect of the vibrations on the lattice constant [9] and the direct effect of the electron–phonon interaction [10], for the present purpose they can be treated together [5,6] and Eq. (1) can be assumed to apply to the joint effect of both contributions. For binary (e.g. GaP) or multinary (e.g. CuGaS<sub>2</sub>) compounds the situation is more complicated, albeit more interesting. The derivatives of  $E_0$  with respect to the different masses are expected to be different having, under special circumstances, even opposite signs [4]. The contributions of the vibrations of the various atoms to the zero-point renormalization are also expected to be different [4]. Whereas no experimental investigation of these effects for semiconductors with more than two different atoms are known to the authors, a number of binary compounds have been measured, including GaAs [11], ZnSe [12], CdS [13] and the cuprous halides [4]. Here we discuss the dependence of the indirect ( $\Gamma \rightarrow \Delta$ ) energy gap of GaP on the average isotopic mass of Ga as extracted from the pair luminescence spectra of four GaP samples with different gallium isotopic compositions corresponding

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to  $\langle M \rangle = 69, 69.5$  (near natural),  $70.1$  (so-called ‘antinatural’), and  $71$ . The effect of varying the mass of phosphorus (consisting of a single stable isotope  $^{31}\text{P}$ ) is estimated from the total zero-point renormalization derived from the temperature dependence of the indirect gap [5,6,14]. It is concluded that lighter atoms contribute more to  $\Delta E_0$  than their heavier counterparts.

### Results

The pair luminescence spectra [15] were measured for four GaP samples that had already been used for the investigation of the dependence of the TO-phonon Raman spectra on isotopic mass [16].

The samples were immersed in liquid He at  $1.8\text{ K}$  and excited with the  $457.9\text{ nm}$  line of an argon-ion laser. The luminescence was analyzed by a Bomem DA8 interferometer, using a Si avalanche photodiode detector, and a  $546\text{ nm}$  interference filter ( $10\text{ nm}$  bandwidth) to pass only the luminescence energies of interest. All four samples had spectra dominated by the discrete and continuous donor–acceptor pair (DAP) transitions of the  $C_P$  acceptor together with the  $S_P$  donor [15]. The spectra were collected at an instrumental resolution of  $0.5\text{ cm}^{-1}$ , which was sufficient to completely resolve the discrete DAP lines, which had typical FWHM of  $2.4\text{ cm}^{-1}$ . After zero-filling, the interferograms were transformed at a resolution of  $0.1\text{ cm}^{-1}$ , and the eight components of the discrete pair lines corresponding to shells 10–15 [15], as shown in Fig. 1, were fitted using a curve fitting program to determine the line center energies. Relative to the

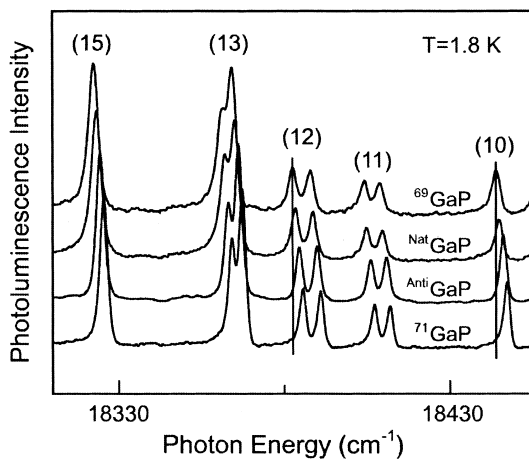


Fig. 1. Photoluminescence spectra of the four GaP samples are shown in the spectral region covering the (10) through (15) shells of the carbon and sulphur discrete donor–acceptor–pair transitions, as detailed in Ref. [15]. Vertical lines are drawn through the centers for the (10) and one of the (12) components of the  $^{69}\text{GaP}$  spectrum to aid the eye.

energies of the  $^{69}\text{GaP}$  sample, the energy shifts of the other spectra were  $(+0.8 \pm 0.1)\text{ cm}^{-1}$  for the natural GaP,  $(+2.0 \pm 0.1)\text{ cm}^{-1}$  for the ‘antinatural’ GaP and  $(+3.05 \pm 0.1)\text{ cm}^{-1}$  for the  $^{71}\text{GaP}$ .

In each case, the precision of the measurements is such that the stated error includes the shifts measured for all eight components. It should be noted that these energy shifts are strictly speaking equal to the energy shift of the band gap minus the S and C donor and acceptor binding energies, but as the donor and acceptor binding energies are expected to be almost independent of isotopic composition [17,18], the observed energy shifts can, with good accuracy, be taken to equal the band gap shifts between the samples.

The quality of our data can be better appreciated in Fig. 2 where the vibrationally-induced gap shifts are plotted vs. average gallium mass and fitted with a straight line. The slope of this line is  $dE_0/dM_c = 1.55(7)\text{ cm}^{-1}/\text{amu}$ , which corresponds to  $0.19(1)\text{ meV}/\text{amu}$ . This slope is compared in the first column of Table 1 with those measured for other diamond, zincblende, and wurtzite-like semiconductors, whose lowest gaps are either indirect (i) or direct (d). Calculated values are given in brackets. The gap shift induced by a change in the mass of phosphorus cannot be measured since P has only one stable isotope (as does As):  $^{31}\text{P}$ ,  $^{32}\text{P}$  and  $^{33}\text{P}$  have half-lives of about 20 days; the growth of GaP containing these isotopes remains a formidable challenge for an enterprising crystal grower. The effect of the anion mass variation  $dE_0/dM_a$  has been measured for ZnO, ZnSe and CdS and is also listed in Table 1.  $\Delta E_0^c$  ( $\Delta E_0^a$ ) in Table 1 represents the cation (anion) contribution to the zero-point gap renormalization as estimated from  $dE_0/dM_c$  ( $dE_0/dM_a$ ) with Eq. (1). Their sum  $\Delta E_0^c + \Delta E_0^a$  is also listed in Table 1 followed by  $-\Delta_{\text{exp}}E_0$ , the renormalization obtained by extrapolation of the temperature dependence of  $E_0$  to  $T = 0$  [5,6,14]. Subtracting  $\Delta E_0 = -27\text{ meV}$  from the total experimental

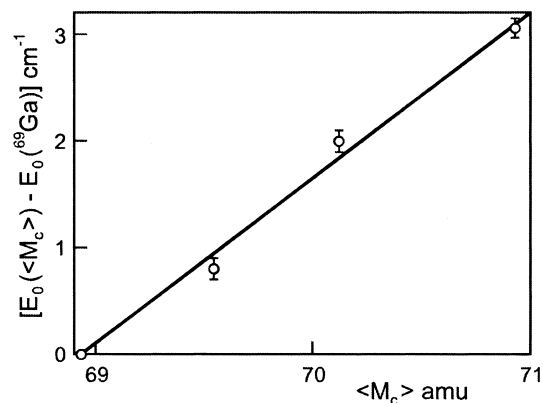


Fig. 2. Shift of the indirect ( $\Gamma \rightarrow \Delta$ ) gap of GaP vs. average isotopic mass yielding the slope  $1.55(7)\text{ cm}^{-1}/\text{amu} = 0.19(1)\text{ meV}/\text{amu}$ .

Table 1

Measured derivatives of the lowest gap energies of several tetrahedral semiconductors with respect to their isotopic masses [ $M_c$  ( $M_a$ ) = cation (anion) mass] in meV/amu.  $\Delta E_0^c$  ( $\Delta E_0^a$ ) represent the contribution of the cation (anion) vibrations to the zero-point gap renormalization (in meV).  $\Delta_{\text{exp}} E_0$  is the total zero-point mass renormalization estimated from the temperature dependence of  $E_0$ . Under  $\Delta_{\text{theory}} E_0$  calculated values of this renormalization are listed. (d) denotes a direct gap and (i) an indirect one. For group IV materials the combined effect of the two atoms per unit cell is listed

	$dE_0/dM_c$		$dE_0/dM_a$		$-\Delta E_0^c$		$-\Delta E_0^a$		$-(\Delta E_0^c + \Delta E_0^a)$		$-\Delta_{\text{exp}} E_0$	$-\Delta_{\text{theory}} E_0$
GaAs(d)	0.39(6) <sup>a</sup>	[0.28 <sup>b</sup> , 0.43 <sup>a</sup> ]		[0.34 <sup>b</sup> , 0.42 <sup>a</sup> ]	54 <sup>a</sup>	[60 <sup>b</sup> ]		[61 <sup>b</sup> ]		[121 <sup>b</sup> ]	54 <sup>c</sup>	[45 <sup>b</sup> ]
GaP(i)	0.19(1) <sup>d</sup>		0.95 <sup>d</sup>		27 <sup>d</sup>		59 <sup>d</sup>				86 <sup>c</sup>	
ZnS(d)		[0.44 <sup>b</sup> ]		[1.3 <sup>b</sup> ]		[58 <sup>b</sup> ]		[83 <sup>b</sup> ]			64 <sup>c</sup>	[63 <sup>b</sup> ]
ZnSe(d)	0.21(3) <sup>c</sup>	[0.35 <sup>b</sup> , 0.31 <sup>a</sup> ]	0.22(3) <sup>c</sup>	319 [0.28 <sup>b</sup> , 0.30 <sup>a</sup> ]	28 <sup>c</sup>	[41 <sup>a</sup> ]	29 <sup>c</sup>	[46 <sup>a</sup> ]	57 <sup>c</sup>	[87 <sup>a</sup> ]	47 <sup>c</sup>	[56 <sup>b</sup> ]
ZnTe(d)		[0.44 <sup>b</sup> ]		[0.10 <sup>b</sup> ]		[58 <sup>b</sup> ]		[26 <sup>b</sup> ]			33 <sup>c</sup>	[60 <sup>b</sup> ]
CdS(d)	0.068(13) <sup>f</sup>		0.74(0.10) <sup>f</sup>		15.3 <sup>f</sup>		47 <sup>f</sup>		62 <sup>f</sup>		68 <sup>f</sup>	
ZnO(d)	0.375 <sup>g</sup>		3.4 <sup>g</sup>		49 <sup>g</sup>		109 <sup>g</sup>		158 <sup>g</sup>			
Si(i)		1.0(3) <sup>h</sup>	–						56 <sup>h</sup>		65 <sup>c</sup>	[86 <sup>i</sup> ]
Ge(i)		0.36(1) <sup>j</sup>	[0.44 <sup>m</sup> ]						51 <sup>j</sup>		47 <sup>c</sup>	[64 <sup>m</sup> ]
Ge(d)		0.44(1) <sup>j</sup>	[0.49 <sup>b</sup> , 0.65 <sup>a</sup> ]						71 <sup>j</sup>		60 <sup>k</sup>	[64 <sup>m</sup> ]
Diamond(i)		13.6(1) <sup>l</sup>	[17 <sup>m</sup> ]						326 <sup>l</sup>		267 <sup>c</sup>	[628 <sup>m</sup> ]

<sup>a</sup> Ref. [11].<sup>b</sup> Ref. [19].<sup>c</sup> Ref. [14].<sup>d</sup> Present work.<sup>e</sup> Ref. [12].<sup>f</sup> Ref. [13].<sup>g</sup> Ref. [21].<sup>h</sup> Ref. [7].<sup>i</sup> Ref. [20].<sup>j</sup> Ref. [8].<sup>k</sup> Ref. [5].<sup>l</sup> Ref. [3].<sup>m</sup> Ref. [22].

renormalization listed in Table 1 for GaP ( $\Delta E_0 = -86$  meV), we estimate  $\Delta E_0^c = -59$  meV and, using Eq. (1),  $dE_0/dM_a = 0.95$  meV/amu.

### 3

Table 1 also displays, in brackets, theoretical values for the isotopic mass effects and the zero-point renormalization of gaps. Most of the calculations are based on lattice dynamical models of the phonon frequency dispersion and eigenvectors plus the electron–phonon interaction as obtained by differentiating the potentials that generate semi-empirical band structures. The band structure models use either empirical pseudopotentials [10,11] or a tight-binding scheme [19]. The only fully *ab initio* calculation available corresponds to the indirect gap of Si [20] and uses a method rather different from the perturbation theory employed in the semiempirical treatments. Basically, the total temperature dependent phonon energy is calculated for the electronic ground state and in the presence of an electron-hole excitation across the gap. The difference yields the temperature dependence of  $E_0$  and, for  $T = 0$ , its zero-point renormalization. All data in Table 1 include the zero-point effect of the vibrations on the lattice constant, except for the calculated ZnS and ZnTe data. However, because of the small volume dependence of  $E_0$  in these materials, this ‘zero-point thermal expansion’ effect should not be very important. Note that a large value of  $dE_0/dM_a$  is not only found for GaP but also for CdS [13] and ZnO [12] and, last but not least, for diamond [3]. The values of  $(\Delta E_0^c + \Delta E_0^a)$  shown in Table 1 agree rather well with the directly measured  $\Delta E_0$  and the calculated ones, with the exception of GaAs where the calculated  $-(\Delta E_0^c + \Delta E_0^a)$  are considerably larger (a factor of two) than  $-\Delta E_0$  (either measured or calculated). The reason for this discrepancy is not known. In all other cases shown in Table 1, consistency between the various values of these parameters exists. The large value of  $-\Delta E_0^a$  estimated for GaP ( $-E_0^a = 59$  meV), and the corresponding value of  $dE_0/dM_a = 0.95$  meV/amu, follow the trend exhibited by the corresponding values calculated for ZnS and ZnTe. Note that for ZnS, a material isoelectronic with GaP, the calculated  $dE_0/dM_a$  is much larger than  $dE_0/dM_c$  (whereas the opposite is true for ZnTe). Experimental values of these derivatives are needed to confirm this trend, which seems to be characteristic of atoms with small masses (see also the data for diamond in Table 1).

### 4

We have measured the dependence of the indirect gap of

GaP on the isotopic mass of the Ga and compared it with similar effects in other semiconductors with zincblende and wurtzite structures. The corresponding effect of the phosphorus mass cannot be measured because this element has only one stable isotope ( $^{31}\text{P}$ ). However, it has been estimated by combining the value for  $dE_0/dM_c$  with the zero point renormalization of  $E_0$ , which includes the effect of the gallium as well as that of the phosphorus vibrations. The large value of  $dE_0/dM_a$  estimated for GaP reproduces the trend calculated for the series ZnS–ZnSe–ZnTe. Large values of  $-\Delta E_0$  and  $dE_0/dM_a$  seem to be characteristic of small atomic masses and the concomitant large vibrational amplitudes. In diamond, however, there may be an additional enhancement of  $-\Delta E_0$  and  $d\Delta_0/dM$  related to the absence of *p*-electrons in the atomic cores.

### 5

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### 6

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