

Letters to the Editor

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Ionization Energies of Groups III and V Elements in Germanium

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THE interesting differences in the ionization energies of Group III acceptors and Group V donors in silicon recently found from Hall effect measurements¹ led us to look for similar effects in germanium. Differences very similar to those found in silicon, though less pronounced, are found in germanium.

The ionization energies were determined by analyzing curves of carrier concentration *vs* reciprocal temperature. The carrier concentration (*n* or *p*) was computed from the Hall coefficient R_H by means of the relation

$$n(\text{or } p) = \mu_H / \mu R_H e,$$

where μ_H/μ is the ratio of Hall mobility to conductivity mobility and *e* the electronic charge. At all temperatures conditions were chosen such that the Hall voltage was linear with the applied electric and magnetic fields. Samples having a very low total impurity content were used to minimize interactions other than those between the added atoms and the germanium lattice. Anomalous effects which have been reported² were not found. In most cases, two samples from different crystals were measured for each added impurity. The experimental error in determining the slope of the carrier concentration is one percent. The major source of error in determining an absolute value for ionization energy probably is the uncertainty in the temperature dependence of μ_H/μ below 20°K. This ratio has been determined³ above 50°K for samples having the range of impurity concentration considered in this letter. It was assumed that $\mu_H/\mu = 1.00$ for electrons and remained constant with temperature. Above 50°K, μ_H/μ for holes was taken from reference 2. Below 50° it was assumed to become constant at 1.10.

Typical carrier concentration results are shown in Fig. 1. These results were fitted with computed curves⁴ which are shown in Fig. 1. In fitting the curves for all samples, a mass parameter m^*/m (effective mass/electronic rest mass) in the range 0.25 to 0.30 was used. This uncertainty in m^*/m is probably due to the

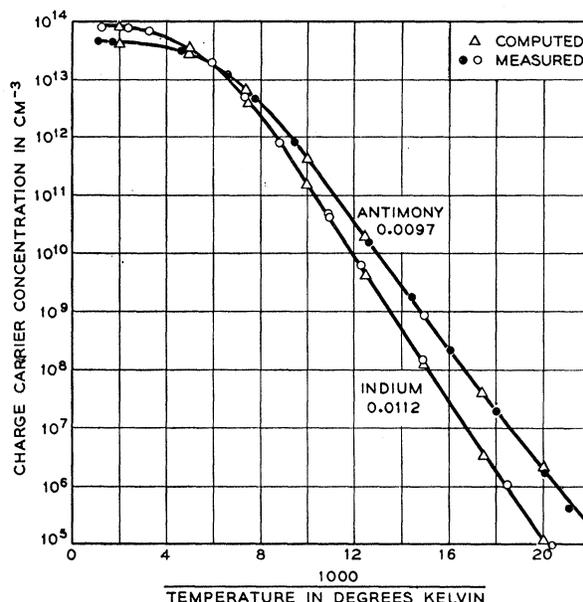


Fig. 1. Charge carrier concentration as a function of reciprocal absolute temperature in germanium samples containing indium (No. 1006) and antimony (No. 1010).

uncertainty in μ_H/μ over the temperature range 10° to 25°K. The other parameters computed for all samples are shown in Table I. The ionization energies of Group III acceptors show a tendency to increase with atomic weight as in silicon. The ionization energies of the Group V donors also vary as in silicon, the value for Sb being the lowest and that for As the highest. These results are independent of m^*/m . A qualitative idea of the dependence of the ionization energy upon the temperature dependence of μ_H/μ may be obtained from the results of the B and As samples. It is expected that the temperature dependence of μ_H/μ will be unaffected by neutral impurity scattering and strongly affected by ionized impurity scattering. In the case of the samples containing B, neutral impurity concentration was changed by a factor of six while keeping the ionized impurity concentration within a factor of two. This did not change the ionization energy. In the

TABLE I. Composition of samples and parameters obtained in analyzing carrier concentration data.

Sample No.	Added element	Concentration of		ionization energy in ev
		majority impurity	minority impurity	
1003	B	5.1×10^{13}	2.9×10^{13}	0.0104
1004	B	3.2×10^{14}	1.4×10^{13}	0.0104
1001	Al	1.0×10^{14}	2.6×10^{13}	0.0102
1002	Al	3.2×10^{14}	4.2×10^{13}	0.0102
1005	Ga	8.7×10^{13}	2.1×10^{13}	0.0108
1006	In	9.5×10^{13}	1.2×10^{13}	0.0112
1011	P	1.02×10^{14}	1.1×10^{12}	0.0120
1007	As+Ga	1.2×10^{14} (As)	2.8×10^{13} (Ga)	0.0133
1008	As	9.6×10^{13}	2.9×10^{12}	0.0127
1010	Sb	6.2×10^{13}	1.4×10^{13}	0.0097

samples containing As, ionized impurity concentration was changed by a factor of ten by adding Ga. This resulted in an increase in the apparent ionization energy as determined from the slope of the carrier concentration curve. This effect is in the right direction but somewhat too large to be entirely accounted for by predictions of theory (based on spherical energy surfaces)⁵ regarding the dependence of μ_H/μ upon ionized impurity scattering. The experimental results thus suggest that the ionization energies determined are somewhat too high, particularly for those samples having 10^{18} or more ionized impurities at low temperatures. However, since most of the samples have about the same ionized impurity concentration at low temperatures the calculated ionization energies are comparable on a relative basis and the variations found should be significant.

We are indebted to J. P. Maita for preparation of samples, to G. W. Hull for aid in construction of the apparatus, and to C. Herring for discussion of the results.

¹ Morin, Maita, Shulman, and Hannay, *Bull. Am. Phys. Soc.* **29**, No. 5, 22 (1954).

² C. S. Hung and J. R. Gliessman, *Phys. Rev.* **79**, 726 (1950); H. Fritzsche, *Phys. Rev.* **94**, 1415 (1954).

³ F. J. Morin, *Phys. Rev.* **93**, 62 (1954).

⁴ For the method used, see Sec. 16.4, W. Shockley, *Electrons and Holes in Semi-conductors* (D. Van Nostrand and Company Inc., New York, 1950).

⁵ H. Jones, *Phys. Rev.* **81**, 149 (1951).

Low-Temperature Luminescence of Cadmium Sulfide

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THIS is to report the existence of six emission bands in the wavelength range 5100–5400Å at 4°K for single crystal hexagonal cadmium sulfide grown by M. E. Bishop.¹

These bands were obtained by exciting the cadmium sulfide with 3650Å radiation produced by a high-pressure Cenco mercury arc filtered with a 7–37 Corning filter. The luminescence was photographed with a Hilger medium glass spectrograph. The microphotometer trace of the spectrogram is shown in Fig. 1.

TABLE I. Observed and calculated values of ν .

Observed λ (Å)	Observed ν (cm ⁻¹)	(v' , v'')	Calculated ν (cm ⁻¹)
5133	19482	(1,0)	19488
5182	19298	(0,0)	19288
5212	19186	(1,1)	19192
5267	18986	(0,1)	18992
5290	18904	(1,2)	18896
5350	18692	(0,2)	18696

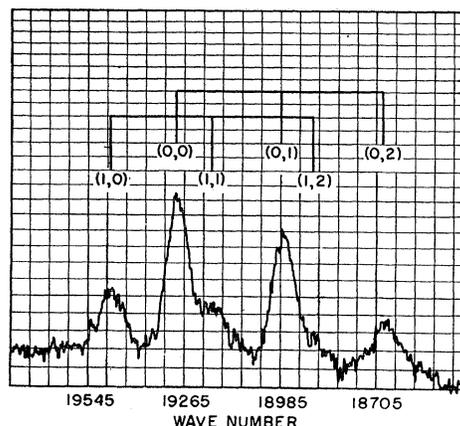


FIG. 1. Microphotometer trace of the emission of cadmium sulfide at 4°K from 5100 to 5400Å.

The spacing and relative intensities of these six bands together with the absence of photoconductivity² at this temperature suggested that the concept of localized complexes, or centers, might be applicable in this case. The center might consist, for example, of a group of ions surrounding a sulfur vacancy or surrounding a foreign ion which has replaced the sulfur. It was found that a molecular-type wave number equation for these bands,

$$\nu = \nu_e + \omega'(v' + \frac{1}{2}) - \omega''(v'' + \frac{1}{2}),$$

gave a reasonable fit where ν_e is the electronic jump; ω' and ω'' are the vibrational wave numbers for the first excited and ground states, respectively; and v' and v'' are the corresponding vibrational quantum numbers. By using the observed values of ν shown in the table below and quantum numbers selected according to the relative positions and intensities of the bands, the appropriate wave-number equation was calculated to be

$$\nu = 19336 + 199(v' + \frac{1}{2}) - 296(v'' + \frac{1}{2});$$

and from this the calculated values of ν corresponding to the observed values were obtained as shown in Table I, where the transition associated with 19298 cm⁻¹ has been assigned the quantum numbers (0,0). It should be pointed out, however, that although a molecular-type calculation has been made, the intensity distribution, as shown in Fig. 1, differs from typical molecular spectra intensity distributions. These centers are characterized by an electronic jump of 19336 cm⁻¹ (5172Å), a vibrational wave number of 199 cm⁻¹ (50 μ) in the first excited state and a vibrational wave number of 296 cm⁻¹ (34 μ) in the ground state. It is noteworthy that Plyler found a weak absorption band in the vicinity of 34 μ at room temperature as reported by Klick.

¹ M. E. Bishop and S. H. Liebson, *J. Appl. Phys.* **24**, 660 (1953).

² C. C. Klick, *Phys. Rev.* **89**, 274 (1953).

³ C. C. Klick, *J. Opt. Soc. Am.* **41**, 816 (1951).