

Letters to the Editor

THE Letters to the Editor section is subdivided into three parts entitled Communications, Comments and Errata, and Notes. These three sections are all subject to the same limitations on length. The textual material of each Letter is limited to a number of words equal to 950 minus the following: (a) 200 words for each average-sized figure; (b) 50 words for each displayed equation; (c) 7 words for each line of table including headings and horizontal rulings. No proof will be sent to the authors of Communications. Proof will be sent to authors of Comments, Errata, and Notes. The publication charge for Letters is \$40 per page, with a minimum of \$40 per Letter. The publication charge, if honored, entitles the author's Institution to 100 reprints without covers at no extra charge. See the issue of December 1961 for a fuller description of Letters to the Editor.

Communications

Temperature Coefficient of Resistance of Iodine and Selenium at High Pressure*

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IN a recent paper¹ the resistance of selenium and iodine was presented as a function of pressure to several hundred kilobars. For selenium, a discontinuity

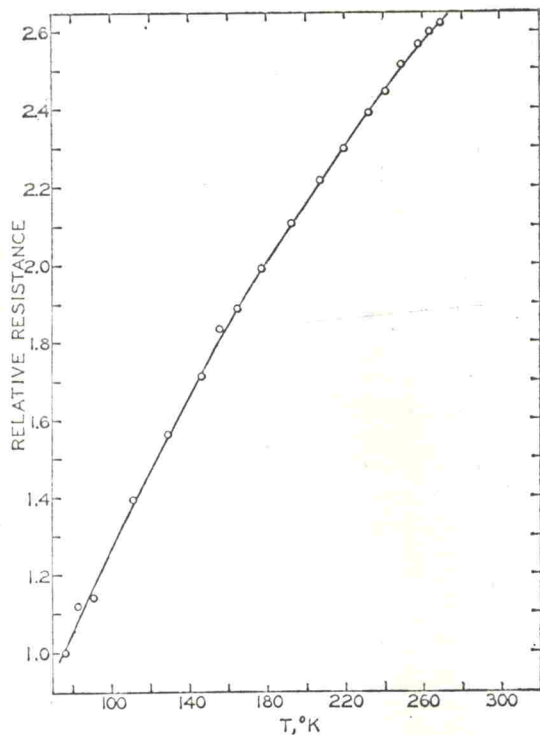


FIG. 1. Resistance vs temperature, selenium-170 kbar.

in the pressure-resistance curve was observed at 128 kbar. Since this coincided with the pressure where the optical absorption edge extrapolated to zero,² it was

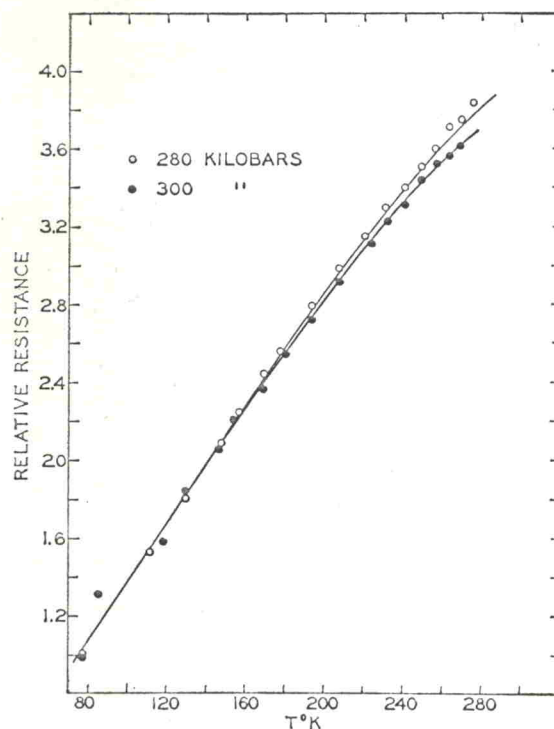


FIG. 2. Resistance vs temperature, iodine-280, 300 kbars.

proposed that this corresponded to the disappearance of the energy gap between conduction and valence band and the beginning of metallic conduction. For iodine, there was a discontinuity in the slope of the resistance-pressure curve at 235 kbar which again coincided with the point where the absorption edge extrapolated to zero. It was proposed that this again represented the beginning of metallic conduction.

Recently, it has been possible to extend our high-pressure electrical measurements to liquid-nitrogen temperature.³ The resistance cell is just as previously described,^{4,5} but the press has been modified. An accurate pressure calibration at low temperature has not yet been established. The technique used largely to date has been to apply pressure to the desired level measuring resistance, then to cool quickly to nitrogen temperature maintaining constant applied force, and to warm slowly measuring resistance. At room temperature and at nitrogen temperature there is negligible Seebeck effect on the leads. At intermediate temperatures, while warming, the effect must be measured and the resistance corrected. In Fig. 1 is a typical run for selenium at 170 kbar. The resistance is indeed metallic and increases as $T^{0.77}$. (Since no correction for contact resistance has been made, the exponent may actually be larger.) Figure 2 presents two runs on iodine at 280

and 300 kbar. Again the resistance is metallic with a temperature dependence of $T^{1.06}$. X-ray experiments are being planned to determine the structure and interatomic distances in both materials at high pressure.

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¹ A. S. Balchan and H. G. Drickamer, J. Chem. Phys. **34**, 1948 (1961).

² H. L. Suchan and H. G. Drickamer, J. Chem. Phys. **31**, 355 (1959).

³ B. M. Riggelman, R. A. Stager, and H. G. Drickamer (unpublished).

⁴ A. S. Balchan and H. G. Drickamer, Rev. Sci. Instr. **32**, 308 (1961).

⁵ H. G. Drickamer and A. S. Balchan, in *Modern Very High Pressure Techniques*, edited by R. H. Wentorf, Jr. (Butterworths Scientific Publications, Ltd., London, 1962).

Electron Magnetic Resonance of Triplet States and the Detection of Energy Transfer in Crystals*

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THE transfer of excitation energy from molecules of one chemical species in triplet states to molecules of a second species with production of triplet states in the second species has been previously observed in liquid solutions¹ by optical methods and in glasses by both optical methods² and electron magnetic resonance methods.³ We here report the observation, by means of

electron resonance, of transfer of energy in single crystals from optically excited phenanthrene molecules to naphthalene molecules with creation of triplet states in the latter. This transfer has been observed in single crystals of the two species in biphenyl.

The magnetic spectra show that both species occurred as oriented molecules having gone into the biphenyl structure substitutionally for biphenyl molecules and having their principal magnetic axes parallel to those of the biphenyl molecules.

Observations of magnetic resonance of triplet states of phenanthrene and of naphthalene occurring together and separately as solutes in biphenyl crystals have been made at the boiling point of liquid nitrogen both (a) at high fields using $2.3 \times 10^{10} \text{ sec}^{-1}$ radiation and (b) at fields of 75 to 4 G using radiation of appropriate frequencies. The mole fractions of phenanthrene and naphthalene in biphenyl were approximately 9×10^{-3} and 5×10^{-4} , respectively, as determined by ultraviolet absorption. We have observed the ratios of (a) the intensities of the resonance signals of the crystalline solutions in the presence of a high-frequency cutoff filter between the light source and the crystalline solution to (b) the intensities in the absence of such a filter. The filter consisted of a 12.8 g liter⁻¹ solution of naphthalene in iso-octane as described by Kasha.⁴ The light source was an A-H6 lamp. In Table I we list the values of these ratios.

The change in temperature of a single crystal of phenanthrene in biphenyl upon insertion of the filter was measured at the temperature of the experiments and found to be -3°K . The change in $(D-E)/hc$ for naphthalene with temperature was found to be $-1.3 \times 10^{-5} \text{ cm}^{-1} \text{ deg}^{-1}$ at the temperature of the experiments. The changes in transition frequencies

TABLE I.

Solvent	Solute	Magnetic resonance	Intensity with filter		$D+E/hc \text{ cm}^{-1}$	$D-E/hc \text{ cm}^{-1}$	$-2E/hc \text{ cm}^{-1}$
			Value at low field	Value at high field			
Biphenyl	Naphthalene	Naphthalene	0.290	0.35	0.08373	0.11469	
	Phenanthrene		± 0.015	± 0.04	± 0.00003	± 0.00003	(0.03096) ^a
Biphenyl	Naphthalene	Naphthalene	<0.011	<0.076	...	0.11476 ± 0.00002	...
	Naphthalene						
Biphenyl	Phenanthrene	Phenanthrene	0.530	0.44	0.05385	0.14700	
	Phenanthrene		± 0.008	± 0.07	± 0.00002	± 0.00001	(0.09315) ^a
Biphenyl	Phenanthrene	Phenanthrene	0.491	0.46	0.05387	0.14701	0.09315
	Phenanthrene		± 0.006	± 0.04	± 0.00002	± 0.00002	± 0.00003
Durene	Naphthalene	Naphthalene	...	...	0.08708	0.11529	(0.02821) ^a
Fluorene	Phenanthrene	Phenanthrene	...	...	...	...	0.09045 ± 0.00003

* Calculated from other entries in the row.