This technique becomes difficult with meshes finer than about 100 British Standard. However, having sealed the edges, even though the working surface may not be rectangular, and consequently estimating the number of apertures becomes laborious; once the number is counted the operation need never be repeated. A photographic enlargement of the mesh is useful here.

For counting the finer particles, electrolytically deposited grids have been used. These have excellent mechanical strength and can be cut easily to produce a standard rectangular working surface. Sealing the edges is not necessary as it is with meshes and this is a decided advantage. However, preliminary results indicate that they are slightly inferior to woven mesh, for often two particles occupied one aperture. The grid is thinner than the correspondingly sized mesh, and its wires are rough and rectangular in section as against smooth and circular ; observation indicates that these factors may have some influence on the adverse effects noted. Nevertheless, a technique for using these grids could probably be developed.
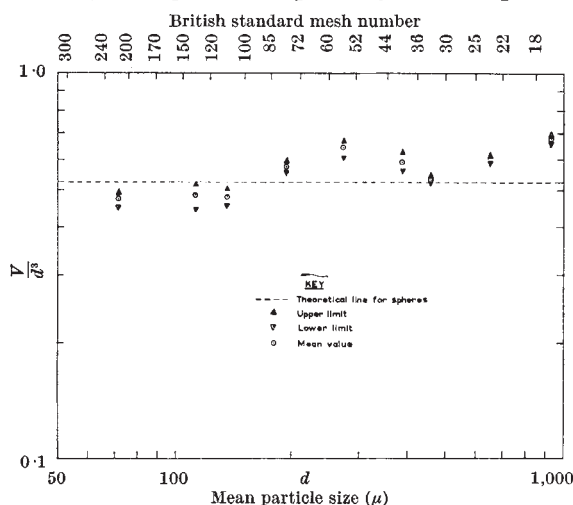

Fig. 3. Relationship between shape factor and mean particle size : coal sample

It is suggested that suitable fine meshes could be specially woven for this purpose. These would contain a standard number of apertures to British Standard or any other specification surrounded by a closely woven edging which would serve both to suitably terminate the working surface and to strengthen the mesh. A large number of these standard aperture count meshes could be woven simultaneously as one piece of cloth, the 'pattern' being (say) 5-cm. squares of working surface separated by 1-cm. wide stripes of close weave. These could be cut and suitably mounted. It should be noted that for 100 British Standard mesh material a 5-cm. square of working surface would contain about 40,000 apertures.

Preliminary results were reported earlier[7,8] where with a particular coal sample an average of $k = 0.54$ was obtained. Interesting confirmation of this value based on Heywood's work has since been communicated (Bramley, J., private communication, reproduced in ref. 8).

Some recent measurements on coal samples are illustrated in Fig. 3, which demonstrates a variation in k with particle size. The method of plotting is clearly more revealing to changes in k than the usual logarith-

mic plot of V against d. Also, if a differently defined measure of particle size is introduced as a ratio with d then a plot by dimensionless groups follows ; this could be useful in correlating shape factor data.

This work is part of a project concerned with the moisture retention properties of fine coal.

I wish to thank Prof. J. T. Whetton and my colleagues in this Department for interest, and especially Mr. D. Howitt, who carried out the experimental work.

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[1] Herdan, G., "Small Particle Statistics" (Elsevier, Amsterdam, 1953).
[2] Dallavalle, J. M., "Micromeritics", second ed. (Pitmans, New York, 1948).
[3] Orr, C., and Dallavalle, J. M., "Fine Particle Measurement" (Macmillan, New York, 1959).
[4] British Standards Institution, "Test Sieves", 410 (1943).
[5] Heywood, H., "Symposium on Particle Size Analysis", 14 (Inst. Chem. Eng., 1947).
[6] Needham, L. W., and Hill, N., *Fuel*, 14, 222 (1935).
[7] Harris, C. C., and Smith, H. G., "Second Symposium on Coal Preparation", paper 9 (University of Leeds, 1957).
[8] Harris, C. C., Ph.D. thesis, University of Leeds (1959).

Appendix. A Method for making Standard Aperture Count Meshes

(1) Commence with a suitably sized mesh rectangle which has been cleaned in a grease solvent. A 7·5-cm. square was used here.

(2) Stick a strip of opaque 'Cellotape' on to the mesh so that the outer edge of the tape lies along and covers a wire situated about 1 cm. from the edge of the mesh. Repeat on the reverse side of the mesh for the same wire.

(3) Repeat the operation for the opposite edge of the mesh.

(4) Apply a layer of plastic material to both sides of one uncovered edge and quickly spread evenly on both sides with a spatula. Treat the opposite edge in the same way. An epoxy resin and a proprietary brand of plastic solder have both been used successfully.

(5) When the plastic is dry, but still soft, peel the 'Cellotape' away and a straight clean edge should result. To assist this it is sometimes advantageous to score the plastic gently with a sharp knife.

(6) When the plastic has hardened treat the remaining edges in the same way.

D. HOWITT

Gallium Arsenide as a Semi-insulator

SOME semiconductors have comparatively low resistivity, and this is due to their containing electrically active impurities with energy-levels near a band edge. Others have very high resistivity and this is due to their containing a predominance of impurities with levels far from the band edges, that is, far compared with the thermal energy kT. These latter materials are often referred to as insulators, but since they can carry electronic currents we prefer to introduce the term 'semi-insulator' to describe them. A material such as cadmium sulphide, which by suitable choice of impurity content can be made a semiconductor or a semi-insulator, is of particular interest and much work has been done on cadmium sulphide in the past few years. Gallium arsenide is another substance with the same property, but has the advantage that both n- and p-type material may be readily prepared.
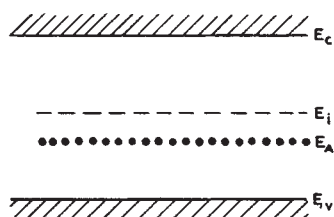
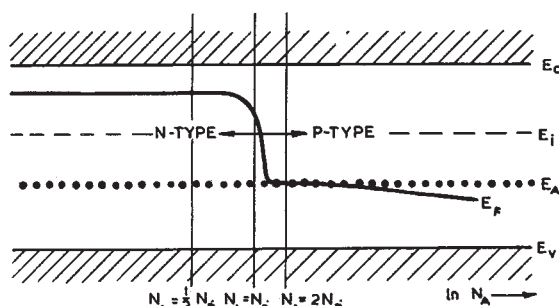Fig. 1.   Energy-levels of the model to be considered

Fig. 2.   Fermi-level as a function of acceptor concentration for fixed donor concentration (schematic)

As normally prepared in this laboratory undoped gallium arsenide is n-type with about 10^{16} electrons/cm.^{3}, which come from a residual impurity acting as a shallow donor. Under conditions in which oxygen is present during the preparation high-resistivity material is obtained. The most reasonable hypothesis is that oxygen gives rise to a deep acceptor-level which compensates the donors. It is therefore of interest to consider the behaviour of a system with a given concentration of donors N_D and a variable number of deep acceptors with concentration N_A. My experiments suggest that the acceptor-level at E_A lies below the intrinsic Fermi-level E_i, as shown in Fig. 1. The Fermi-level varies with N_A in the manner shown schematically in Fig. 2. It will be of advantage to introduce a quantity:

$$\chi \equiv \frac{N_A}{N_D}$$

which I shall call the 'degree of compensation'. Four regions of interest may be distinguished:

(1) $N_A \ll N_D$, $\chi \ll 1$. The concentration of electrons in the conduction band n is, to a good approximation, equal to N_D and the material is low resistivity n-type.

(2) $N_A \simeq N_D$, $\chi \simeq 1$. The Fermi-level drops from a position near the conduction band to one near the acceptor-levels, this change occurring over a very small change of N_A. For example, if N_A is $0 \cdot 9\ N_D$ then n is $0 \cdot 1\ N_D$ and the material is still of fairly low resistivity, the Fermi-level having dropped from its position in region 1 by only kT ln10 (about $0 \cdot 06$ eV. at room temperature), while if N_A is $1 \cdot 1\ N_D$ then the Fermi-level has dropped to a position only kT ln10 above the acceptor-level, and n will decrease by many orders of magnitude. In the present model which has E_A below E_i the material will change from high resistivity n-type to high resistivity p-type in this region. When N_A is greater than but not much greater than N_D the electron concentration is given by:

$$n \simeq \frac{1}{\chi - 1} \cdot N_c \cdot \exp \frac{E_A - E_c}{kT} \qquad (1)$$

that is, it is determined by the degree of compensation and the acceptor energy-level only. From the absolute

magnitude of n and its variation with temperature both χ and $E_c - E_A$ may be determined.

(3) $N_A > N_D$, $\chi > 1$. As soon as N_A becomes appreciably greater than N_D the Fermi-level becomes locked near the acceptor-level and the material is high resistivity p-type. In this region the hole concentration is given by:

$$\rho \simeq (\chi - 1) \cdot N_v \cdot \exp \frac{E_v - E_A}{kT} \qquad (2)$$

It should be noted that the range of validity of equation 2 is the same as that of equation 1, for both hold when the position of the Fermi-level is determined by N_A and N_D alone, p and n both being negligible.

(4) $N_A \gg N_D$, $\chi \gg 1$. The position of the Fermi-level is now determined by the distribution of electrons between the valence band and the impurity-level. As N_A increases the hole concentration increases, but since E_A is far from E_v then p cannot be large and the material is still high resistivity p-type. In this region:

$$p \simeq (N_v N_A)^{\frac{1}{2}} \exp \frac{E_v - E_A}{2kT} \qquad (3)$$

By considering Fig. 2 it is easy to see what modifications to this behaviour are introduced if E_A lies above E_i. The general shape of the curve of E_F against N_A is unchanged but now the point of intersection of E_F with E_i is moved to the right, that is, the change from high resistivity n-type to high resistivity p-type occurs at a much higher acceptor concentration, and in practice this may not be attainable.
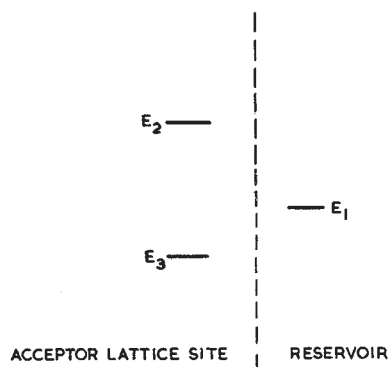

Fig. 3.   The energy scheme for the formation of an acceptor during auto-compensation

Experimentally it is found that in semi-insulating gallium arsenide E_A does lie below E_i. The existence of n-type high resistivity material requires that $\chi \sim 1$ and we find from the experiments, using equation 1, that $\chi - 1$ is as little as 10^{-5}. Clearly it is unlikely to happen in a large number of specimens that N_A should approach N_D so closely just by chance, and some mechanism of automatic compensation must be operative. A rather general model for this is illustrated in Fig. 3. Again we regard N_D as a fixed given quantity. There is a reservoir of lattice defects (in which term I shall include impurities) which are in an electrically inactive state at energy E_1. These can go over to lattice sites at which they behave as acceptors, with energy E_2. If in this site they accept an electron the energy of the crystal decreases by an amount $E_c - E_A$, and this state has energy E_3. One then has a problem in statistical thermodynamics in which defects are distributed over levels E_1, E_2, E_3 and electrons over levels

E_v, E_A, E_c, the two systems being coupled by the fact that the level E_3 has an electron associated with it. To investigate this model in detail requires a more exact specification of the states ; but it is immediately obvious that if the energy differences $E_2 - E_1$ and $E_1 - E_3$ are both large compared with kT and the entropy difference between the states is not too great then almost exact compensation will occur as long as the reservoir contains sufficient defects. In other words, it is energetically advantageous for defects to become acceptors so long as there is an electron for them to accept, but not otherwise.

An alternative possibility is that acceptors and donors form associated pairs[1], but this mechanism should lead to an increase in electron mobility, contrary to observation. Also the calculated degree of pairing is insufficient to account for the exactness of compensation found.

In the case of semi-insulating gallium arsenide it seems probable that oxygen is dissolved in the lattice in two different sites, being electrically active in one site (as an acceptor) and inactive in the other (as the reservoir). In the case of cadmium sulphide and similar compounds, the work of Kröger and Vink[2] shows clearly that the deep levels are associated with crystal defects arising from non-stoichiometry, and the reservoir of such defects is obviously the ambient atmosphere. In cadmium sulphide one can vary χ by annealing crystals at various temperatures and in various atmospheres, and similarly in gallium arsenide one should be able to vary χ by suitable heat treatment.

My model suggests that semi-insulators of the type I have described, that is, those in which a shallow donor is auto-compensated by a deep acceptor, should exhibit pronounced hole trapping effects but little electron trapping. This has a number of practical implications. For example, the high photoconductivity of these materials is readily explained. Also the existence of large space-change currents in certain crystals of cadmium sulphide[3] but not in others may be explained by variations in χ between the crystals. One might predict that semi-insulating gallium arsenide suitably heat-treated might also show such currents.

The ideas expressed here were developed while attempting to account for the experimental results of Dr. G. T. Wright on cadmium sulphide and of Dr. C. Hilsum and his colleagues on gallium arsenide. I wish to thank them both for extensive discussion of the problems involved.

Acknowledgment is made to the Admiralty for permission to publish this communication.

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[1] Prener, J. S., J. Chem. Phys., 25, 1294 (1956).
[2] Kröger, F. A., and Vink, H. J., Physica, 20, 950 (1954).
[3] Wright, G. T., Nature, 182, 1296 (1958).

Gallium Arsenide for γ-Ray Spectroscopy

CRYSTAL conduction counters offer an improvement in energy resolution over ionization chambers or scintillation counters for spectroscopy of nuclear particles. Semiconductor counters which employ a p-n junction are useful only for heavy charged particles of moderate energy. For energetic charged particles or γ-rays with ranges exceeding 1 mm. of silicon a crystal with efficient charge collection

throughout its bulk is required. Most crystals of sufficiently high resistivity contain so many electron traps that collection of the ionization current is inefficient, and only diamond has previously been found to count single γ-ray events. The usefulness of diamond as a crystal counter is restricted.

We have found that the semiconductor gallium arsenide with resistivity at room temperature exceeding 10^6 ohm-cm. is an efficient particle counter. When a bar of this material is bombarded with γ-radiation from cobalt-60, pulses of charge are readily observed. The time for the pulse-rise is about 5 μsec., and pulses of 0·5 mV. across a megohm load are seen with an applied field of 200 V./cm. This effect occurs in both n-type and p-type gallium arsenide of high resistivity. The samples used in these experiments were of dimensions 1 cm. × 0·2 cm. × 0·1 cm., but there appears to be no reason why larger crystals should not be made. We are examining the spectrum of the pulse-height and resolution of energy, and our results will be reported elsewhere.

Acknowledgment is made to the Admiralty for permission to publish this communication.

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ENGINEERING

Pump Fluids for Higher Vacuums

IN the decade after Burch introduced petroleum oils[1] as working fluids for the Langmuir condensation pump, the silicones, octyl alcohol esters and petroleum pump fluids converged to a low-pressure optimum at about 10^{-7} mm. mercury, which the succeeding 20 years has lowered, perhaps, to 5×10^{-8} in an untrapped three-stage glass pump when measured at an ambient temperature of 25° C.

Recently, particle accelerators and the conquest of space have made demands for pressures ten or a hundred times lower, to be induced in relatively enormous containers, and it has been necessary to augment the pumps with traps filled with liquid nitrogen or helium, together with means for periodic baking out. The proliferation of apparatus occasioned by these and other alternatives is becoming far too cumbersome and expensive.

In April 1959, learning of their use as high-temperature lubricants, I began examination of a class of phenoxy benzenes and polyphenyl ethers[2] of the general formulæ :

 (1)

 (2)
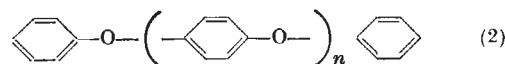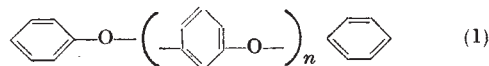
which may restore simplicity to the vapour pump. Not only can some of the compounds give pressures in the 10^{-8}–10^{-10} range untrapped, but also their tendency to wander through vacuum labyrinths is reduced many hundredfold over previously used fluids. Thus a Bayard–Alpert ionization gauge[3]