

be taken as supporting evidence for the Kistiakowsky and Sternberg theory.

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¹ Jost, W., *Z. phys. Chem.*, **134**, 92 (1928); B3, 95 (1929).

² Schmitz, H., Schumacher, H. J., and Jäger, A., *Z. phys. Chem.*, B.1, 281 (1942).

³ Kistiakowsky, G. B., and Sternberg, J. C., *J. Chem. Phys.*, **21**, 2218 (1953).

⁴ Herzberg, G., "Spectra of Diatomic Molecules" (2nd edit., Van Nostrand and Co., New York).

A Relation between Hardness and Stoichiometry in Lead Sulphide Single Crystals

IN the course of an investigation concerning the semiconducting properties of lead sulphide, single crystals were prepared and reheated under various sulphur pressures at 1,200° K. in order to control the deviations from the exact stoichiometric composition. The concentration of impurities in these crystals was less than 10^{17} cm.⁻³ (5×10^{-6} atom per mole lead sulphide).

When equilibrium with the ambient gas atmosphere had been reached, the crystals were rapidly cooled to room temperature and the concentration of free-charge carriers was determined by measuring the Hall coefficient.

From these experiments the conclusion was drawn that introduction of excess lead into the crystal on a lattice site causes the formation of a sulphur ion vacancy (anion vacancy, V_A^-). Of the two electrons given off by the lead atom (when giving a Pb^{2+} ion), the first remains trapped at the positively charged sulphur vacancy and the second one is so weakly bound to the resulting V_A^- centre that at room temperature it behaves as a 'free' electron. Similarly, introduction of extra sulphur atoms gives rise to an equal concentration of lead vacancies that have trapped a hole (V_C^+) and free holes. In Fig. 1 the concentrations of free charge carriers (corresponding to the concentration of cation and anion vacancies) are plotted against the pressure of sulphur vapour in which the crystals had reached their equilibrium.

The hardness of these crystals was measured under a 100-gm. load and is given in the Vickers scale, Fig. 2.

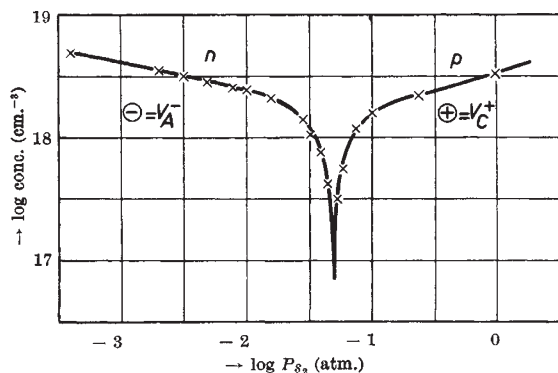


Fig. 1. Concentrations of free electrons and holes (being equal to the concentrations of sulphur vacancies, V_A^- , and lead vacancies, V_C^+ , respectively), measured at room temperature on lead sulphide single crystals after reheating under various partial pressures of sulphur (P_{S_2}) at 1,200° K.

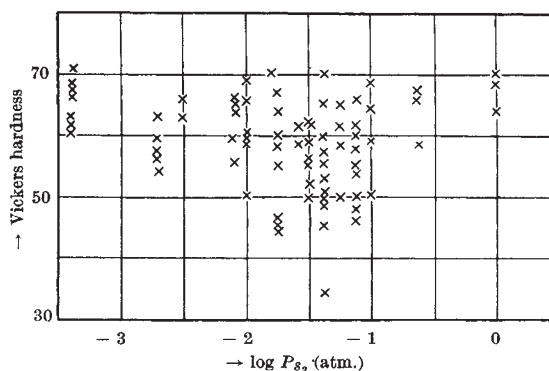


Fig. 2. Hardness, measured on cleavage planes of lead sulphide single crystals after reheating at 1,200° K. under various sulphur pressures

The results show considerable scatter, but it seems justified to conclude that among the stoichiometric crystals ($\log P_{S_2} = -1.4$ atm.) there are crystals showing a minimum hardness (about 40–50 Vickers); this is not the case for strong *n*- and *p*-type crystals, prepared by reheating at lower or higher sulphur pressures.

The results suggest that, although several other factors undoubtedly play a part in increasing the hardness, the concentration of vacancies is of importance, a low concentration being a necessary condition for the observation of a low hardness.

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Solution of Elastic Vibration Problems with the Resistance-Network Analogue

THE vibration of an elastic plate is described by the equation:

$$\nabla^4 w = a v^2 w \quad (1)$$

where the symbol ∇^4 stands for the operator $\frac{\partial^4}{\partial x^4} + 2 \frac{\partial^4}{\partial x^2 \partial y^2} + \frac{\partial^4}{\partial y^4}$, $w = w(x, y)$ is the displacement, a a constant describing the elastic properties of the plate, and v the frequency of vibration.

It was shown in a previous communication¹ that the equation:

$$\nabla^4 w = f \quad (2)$$

where $f = f(x, y)$ is a known function of the coordinates x and y , can be solved by a resistance-network analogue comprising two resistance-networks in cascade. The function f is represented in the analogue by the currents fed in at the 'upper' network of the network cascade, and the function w by the voltages appearing at the mesh nodes of the 'lower' network.

It has also been demonstrated^{2,3} that oscillation problems of the form:

$$\nabla^2 \phi = -\kappa^2 \phi \quad (3)$$

where κ^2 is a characteristic value parameter, can be solved by combining the resistance-network technique of solving Laplace- or Poisson-type problems with an iterative method in which the currents fed into the network junctions are cyclically readjusted until