Fig. 1). The results revealed that tungsten atoms, like those of other metals[1,2], also behave as electron donors in the surface of the semiconductor. We may note that, after the adsorption of tungsten atoms on the semiconductor films has ceased, the change in conductivity remains constant for an indefinite period, but after heating the ZnO and TiO₂ films at 330–350°C for 2 h, the conductivity returns to the initial value.
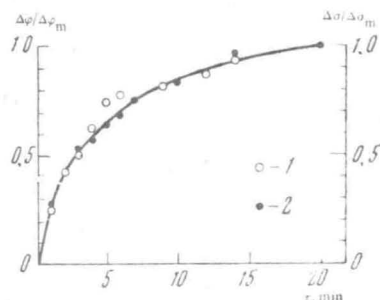

Figure 3. Variation of the conductivity and electron work function in relative units during the adsorption of tungsten atoms on ZnO: 1) $\Delta\varphi/\Delta\varphi_m$; 2) $\Delta\sigma/\Delta\sigma_m$.

Fig. 2 shows that, with increase of conductivity (curve 1) following the adsorption of tungsten atoms on ZnO, the electron work function diminishes (curve 2). The change in electron work function in our experiments amounted to 0.1 eV. These results confirm that tungsten atoms behave as electron donors on the surface of the semiconductor.

If the changes in electron work function $\Delta\varphi$ and in conductivity $\Delta\sigma$ are expressed in relative units $\Delta\varphi/\Delta\varphi_m$ and $\Delta\sigma/\Delta\sigma_m$ ($\Delta\varphi_m$ and $\Delta\sigma_m$ are the maximum changes in electron work function and conductivity), then, as can be seen from Fig. 3, they are equal. This implies that in our experiments $\Delta\varphi$ and $\Delta\sigma$ are proportional to one another.

We may note that a similar relation was observed also in the adsorption of alkyl radicals on the surface of semiconductor oxides[6].

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The Phase Diagram for Indium

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The phase diagram for indium has been plotted up to 7500 atm with the aid of a very accurate method, developed by the author. A singularity has been observed on the fusion curve and has been attributed to a polymorphic transition in solid indium from a face-centred hexagonal structure to a face-centred cubic structure.

In the measurement of the fusion curve for indium to within 0.02 degC, thermostatted high-pressure vessels were employed[1]. The phase transition was determined from the change in the resistivity of indium. For this purpose, a nickel wire was lowered into a small Teflon tube and the latter was filled with indium. Nickel is almost insoluble in indium. The phase transition was achieved by a smooth variation of pressure. The following equation was fitted to the experimental results in the Table:

$$P = 32\,057\,[(T/429.42)^{2.71} - 1].\qquad(1)$$

The Table shows that at pressures close to 3000 kgf cm^{-2} there is a slight discrepancy between the curve represented by Eqn. (1) and experimental points.

Data for the indium phase diagram.

T, °K	P_{exp}, kgf cm^{-2}	$P_{exp} - P_{calc}$, kgf cm^{-2}	T, °K	P_{exp}, kgf cm^{-2}	$P_{exp} - P_{calc}$, kgf cm^{-2}
430.24	161	−5.2	439.10	2000	3.7
430.74	265	−2.7	440.09	2216	1.1
431.23	365	−2.5	441.06	2410	0.2
431.70	459	−4.4	442.10	2643	12.5
432.17	547	−1.2	442.96	2827	13.3
432.21	556	−1.2	443.17	2878	19.5
432.72	664	−8.0	443.92	3043	24.2
433.16	758	−4.3	444.23	3115	29.7
433.76	885	−0.6	444.51	3181	35.7
434.15	957	−8.9	444.95	3248	8.1
434.20	968	−8.3	445.27	3287	21.7
434.71	1062	−2.0	446.16	3463	−37.6
435.21	1172	−1.3	447.59	3787	−23.2
435.37	1207	−1.1	448.98	4082	−30.9
435.85	1305	−1.2	450.93	4538	−2.2
436.02	1340	−1.3	453.28	5045	−14.3
436.16	1373	−1.0	453.90	5201	3.9
436.34	1410	0.2	455.79	5592	−2.7
436.65	1484	−5.3	457.54	5969	−4.3
437.07	1566	−1.7	458.81	6489	1.9
437.46	1651	1.6	461.65	6897	−49.1
437.76	1717	1.3	463.86	7416	−38.2
438.18	1816	—	—	—	—

This suggests that the phase transition in solid indium affects the fusion curve. We may note that earlier studies on the fusion curve for indium[2-4] failed to reveal a phase transition. However, the accuracy of these experiments was much lower than that of the present investigation, which is important (as will be shown below) in the determination of a weak phase transition.

We shall now verify whether a phase transition in indium is possible. Indium belongs to Group IIIB (together with aluminium, gallium, and thallium). These elements crystallise in various modifications: aluminium has a face-centred cubic lattice of type A-I, gallium an orthorhombic lattice, indium a face-centred tetragonal

lattice of type A-III, and thallium a close-packed hexagonal lattice of type A6. With increase of pressure, all these elements undergo phase transformations. It is interesting that, with increase of pressure to 12 kbar, gallium assumes a face-centred tetragonal lattice of type A-III, i.e. the same as that of indium. The axial ratio is $c/a = 1.104$ for gallium and $c/a = 1.075$ for indium, i.e. the indium lattice is distorted less. On further increase of pressure to 70 kbar, the gallium A-III lattice is converted into a face-centred cubic lattice[5]. It would be logical to postulate the occurrence of the same transition in indium at lower pressures, since its lattice is distorted less.

The following indirect facts may be adduced as proof. It has been shown[6] by X-ray diffraction analysis that, with increase of pressure, indium becomes less tetragonal. Indium exhibits equivalent behaviour also on addition of impurity atoms. Thus, following the addition of 19.6% of thallium, the face-centred tetragonal indium is converted into a face-centred cubic form[7]. Using these data, we shall perform certain thermodynamic calculations.

The Gibbs free energy difference between two phases is given by the expression

$$\Delta G_{(T,P)}^{\alpha \to \beta} = \Delta H^{\alpha \to \beta} - \Delta S^{\alpha \to \beta} T + 24 \int_{P_0}^{P} \Delta V^{\alpha \to \beta} \, dP, \qquad (2)$$

where ΔG, ΔH, ΔS, and ΔV are respectively the Gibbs free energy, enthalpy, and entropy of transition and the corresponding volume change, T and P are the temperature and pressure, and α and β denote various modifications of the substance; the superscripts can also be replaced by $\alpha \to L$ and $\beta \to L$, i.e. denoting the transition to the liquid phase. From tabulated data for indium[8] we find $\Delta H^{\alpha \to L} = 782.2$ cal mole^{-1}, $\Delta S^{\alpha \to L} = 0.324$ cal mole^{-1} deg^{-1}, $\Delta V^{\alpha \to L} = 0.324$ cm^3 mole^{-1}, and

$$\Delta G^{\alpha \to L} = 782.2 - 1.82\,T + 24\,(0.324)P. \qquad (3)$$

In order to estimate $\Delta G^{\alpha \to L}$, we shall employ an empirical rule for close-packed metals[9]: $V\Delta S/\Delta V \simeq 60$ cal mole^{-1} deg^{-1}. For indium, we have $\Delta V/V = 0.020$ and therefore one can postulate that $\Delta S^{\beta \to L} = 1.213$, whence it follows that $\Delta S^{\alpha \to \beta} = \Delta S^{\alpha \to L} + \Delta S^{L \to \beta} = 0.607$ cal mole^{-1} deg^{-1}. $\Delta S^{\alpha \to \beta}$ can also be determined using data for the transition of indium to the face-centred cubic structure following the addition of impurities:

$$\Delta S = -Nk[N\ln N - (1 - N)\ln(1 - N)]. \qquad (4)$$

We substitute $N = 19.6\%$ and obtain $\Delta S^{\alpha \to \beta} = 0.968$ cal mole^{-1} deg^{-1}. Thus one can assume that $\Delta S^{\alpha \to \beta} \simeq 0.8$ cal mole^{-1} deg^{-1}. $\Delta H^{\alpha \to \beta}$ may be estimated from the data of Graham et al.[6] Extrapolation shows that this transition might occur at 686°K. Then $\Delta H^{\alpha \to \beta} = 548.8$ cal mole^{-1}. According to Moore et al.[7], the change in the lattice parameters of indium in the transition from the face-centred tetragonal to the face-centred cubic lattice is from $c = 4.800$ Å and $a = 4.737$ Å to $a = 4.758$ Å, i.e. $\Delta V^{\alpha \to \beta} = 0.003$ cm^3 mole^{-1}. We obtain

$$\Delta G^{\alpha \to \beta} = 548.8 - 0.8\,T - 24\,(0.003)P. \qquad (5)$$

For the estimation of $\Delta G^{\beta \to L}$, it is easy to find $\Delta S^{\beta \to L} = 1.02$ cal mole^{-1} deg^{-1} and $\Delta V^{\beta \to L} = 0.327$ cm^3 mole^{-1}. Using the above equations, we found that the

transition pressure and temperature (triple point) are $P \simeq 2950$ kgs cm^{-2}, and $T \simeq 441°$K. The experimental coordinates of the triple point are $P = 3240$ kgf cm^{-2} and $T = 444.9°$K. If these coordinates are assigned to the triple point, the fusion lines for α-indium and β-indium can be described by Simon's equations:

$$P = 20578[(T/429.42)^{4.155} - 1] \quad \text{and} \quad P = 28004[(T/444.90)^{3.673} - 1]$$

with a discrepancy of $+4.86$ kfg cm^{-2} with experimental points.

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Variation of the Equivalent Conductance of Electrolyte Solutions with Ion Hydration Energy†

A. A. Reikhardt

An empirical relation has been found between the equivalent conductance of an aqueous electrolyte solution and the sum of the reciprocals of the ion hydration energies divided by the electrovalences of the ions. The accuracy of the calculation of the equivalent conductances of solutions of electrolytes of different valence types in their concentration range $0.5-1$ N is $\pm\,10-20\%$ at $18-20°$C.

Analysis of the experimental conductivity data for binary aqueous strong electrolyte solutions reveals an approximate relation between the equivalent conductance Λ and the sum of the reciprocals of the hydration energies of the ions divided by their electrovalences:

$$\Lambda \propto [1/(\Delta\Phi_c/z_c) + 1/(\Delta\Phi_a/z_a)]^n, \qquad (1)$$

where $\Delta\Phi_c$ and $\Delta\Phi_a$ are the hydration energies of the cation and anion at infinite dilution and 25°C[1,2] in

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