gen vacancies plus trapped electrons; Mitchell and Paige[3] had proposed such centres, corresponding to two absorption bands in the ultra-violet region. The quenching of the luminescence of the aluminium centres is evidence for the interaction of these and the ultra-violet absorbing centres. The probability of the interaction would be expected to increase as the concentrations increased and therefore the luminescence showed a maximum at an intermediate dose.

Lithium can play a predominant part in the interaction of these centres while bleaching. The lithium in an interstitial position would be quite mobile, especially after being discharged by electron capture. Phosphorus ions, as well as lithium ions, can stabilize the aluminium in the substitutional position required in the precursor. However, the low mobility of the substitutional phosphorus in comparison with the high mobility of the discharged lithium should have a strong influence on the degree of interaction of the centre upon bleaching. It is planned to extend the investigation of thermoluminescence to silica (aluminium, phosphorus) to test this proposal, and to fused silica with controlled impurities so that the absorption bands can be studied and correlated with the luminescence.

J. R. Hensler

Bausch and Lomb Optical Co.,
Rochester 2,
New York.
Jan. 14.

[1] O'Brien, M. C. M., *Proc. Roy. Soc.*, A, **231**, 404 (1955).
[2] Cohen, A. J., *J. Chem. Phys.*, **25**, 904 (1956).
[3] Mitchell, E. J. W., and Paige, E. G. S., *Phil. Mag.*, Ser. 8, **1**, 1085 (1956).

Beta-Polymorphs of Uranium and Thorium Disilicides

Thorium disilicide was first described by Brauer and Mitius[1], who isolated single crystals and reported the crystal structure to be tetragonal with the space group *I*4/*amd*. Later, Zachariasen[2] described an isostructural uranium disilicide observed initially during metallurgical examinations by Kaufmann, Cullity and Bitsianes[3]. Another phase, thought by Kaufmann *et al.* to be U_2Si_3 and also studied by Zachariasen, was found to have a hexagonal crystal structure of the AlB_2-type, space group *C*6/*mmm*. The crystal structure results led Zachariasen to suggest that this compound was a second form of uranium disilicide and he designated it β-USi_2. The tetragonal uranium and thorium disilicides accordingly became the alpha forms. More recently, Jacobson, Freeman, Tharp and Searcy[4] obtained a thorium silicide isostructural with Zachariasen's β-USi_2, but observed that the silicon content was lower than that of α-$ThSi_2$. They used the description 'β-$ThSi_2$' but suggested that the true composition was $ThSi_{1\cdot5\pm0\cdot2}$.

We have prepared all the above phases by arc-melting and have examined them by metallographic and X-ray diffraction techniques. A noticeable feature of the preparations is the formation of 'β-USi_2' and 'β-$ThSi_2$' from mixtures containing 62–63 atomic per cent silicon, compared with the 66·7 atomic per cent required for the formation of the alpha disilicides. The compositions of these so-called beta phases accordingly appear to be U_3Si_5 and Th_3Si_5. Our values for the structure cell dimensions are:

U_3Si_5: $a_0 = 3\cdot843 \pm 0\cdot001$ A.; $c_0 = 4\cdot069 \pm 0\cdot001$ A.
Th_3Si_5: $a_0 = 3\cdot985 \pm 0\cdot001$ A.; $c_0 = 4\cdot228 \pm 0\cdot001$ A.

During an investigation into reactions between the silicides of uranium and thorium and liquid bismuth, two new silicide phases have been isolated. X-ray analysis shows that they are hexagonal with space group *C*6/*mmm*. These new phases, like the above M_3Si_5 compounds, have the AlB_2-type crystal structure, but the cell dimensions are different and, in particular, the axial ratio $c/a < 1$ compared with $c/a > 1$ for the M_3Si_5 compounds.

Heat treatment of the new thorium–silicon compound in the temperature-range 1,200–1,300° C. transforms it into α-$ThSi_2$, while heat treatment of α-$ThSi_2$ at 850° C. yields the new thorium–silicon phase. It is clear that this compound is in fact the true β-$ThSi_2$ and the analogous uranium compound the true β-USi_2. The structure cell dimensions obtained from X-ray diffraction results are:

β-USi_2: $a_0 = 4\cdot028 \pm 0\cdot001$ A.; $c_0 = 3\cdot852 \pm 0\cdot001$ A.
β-$ThSi_2$: $a_0 = 4\cdot136 \pm 0\cdot001$ A.; $c_0 = 4\cdot126 \pm 0\cdot001$ A.

Structural characteristics and structure-cell dimensions of the alpha and new beta polymorphs have been compared and a mechanism has been deduced to explain the structure transformation. Furthermore, it appears probable that the atomic arrangements of the M_3Si_5 structure can be derived from that of the β-structure by omission of one-sixth of the silicon atoms. As a consequence, the axial ratio changes from a value less than unity in the beta structure to a value greater than unity in the M_3Si_5 structure.

A more complete and detailed account of the work outlined above is in preparation.

A. Brown
J. J. Norreys

Research Laboratories,
The General Electric Co., Ltd.,
Wembley, Middlesex.
Jan. 26.

[1] Brauer, G., and Mitius, A., *Z. anorg. Chem.*, **249**, 325 (1942).
[2] Zachariasen, W. H., *Acta Cryst.*, **2**, 94 (1948).
[3] Kaufmann, A. R., Cullity, B., and Bitsianes, G., *Trans. Amer. Inst. Mech. Eng.*, **209**, 203 (1957).
[4] Jacobson, E. L., Freeman, R. D., Tharp, A. G., and Searcy, A. W., *J. Amer. Chem. Soc.*, **78**, 4850 (1956).

Effect of the Carrier Gas on the Sensitivity of a Thermal-conductivity Detector in Gas Chromatography

In a recent communication[1], the sensitivity, dt/dx, of a thermal-conductivity cell to small amounts of organic vapours was derived from:

$$t_1 - t_0 = a/K_1 \qquad (1)$$

where t_1 and t_0 are the temperatures of the hot wire and body of the cell respectively, a is constant, and K_1 is the thermal conductivity of the carrier gas. The sensitivity was then shown to be:

$$\frac{dt}{dx} = -\frac{a(K_1 - K_2)}{K_1^2}, \text{ approximately} \qquad (2)$$

where K_2 is the thermal conductivity of the organic vapour and x is its concentration in the carrier gas. From equation 2, carrier gases of low thermal conductivity would be expected to produce the highest sensitivities. However, in practice a is usually varied, and sensitivities should be compared at equal values of t_1. Carrier gases of high thermal conductivity would then give the highest sensitivities.