Quenching of Fluorescence by van der Waals Forces

In a recent communication under the above title, S. Sambursky and G. Wolfsohn[1] attribute solvent quenching of anthracene in solution to the formation of van der Waals compounds between solute and solvent molecules.

Experimental work in this Laboratory on the variation of the fluorescence of rubrene solutions with solvent and with temperature (− 60° to + 60° C.) has shown that two effects are distinguishable by the differences of their temperature coefficients and limiting values.

In hexane solution, rubrene has a fluorescence efficiency of near unity[2] and independent of temperature except for a slight falling off at the ends of the above range. In acetone, ethyl and *n*-butyl alcohols and dioxane solutions, the fluorescence efficiency is again unity at low temperatures, but falls off at higher temperatures. This cannot be ascribed to 'compound formation', as the latter should decrease with temperature rise and allow of increased fluorescence. The quenching seems 'internal' in character, explicable as the 'crossing' of excited and ground-state potential energy curves; and the height of the 'crossing' above the lowest part of the excited state curve is obtainable from a log plot of quenching constant against $1/T$. The values so obtained are 6·5–7·3 kcal./mole. In benzene and toluene solutions the fluorescence efficiencies also diminish with rise of temperature but less rapidly than with the above solvents, and the limiting values at low temperatures are less. This difference can reasonably be ascribed to a certain amount of 'dispersion force' compound formation between the flat aromatic molecules with heats of formation about 1 kcal./mole.

With stronger quenchers of hydrocarbon fluorescence in inert solvents (bimolecular or external quenching) the above two classes are even more marked, and positive and negative temperature coefficients of quenching constants are distinguishable[3]. This difference depends on the relation of the 'life-times' of the assumed complex and of the fluorescent state. It may be concluded that the apparently sharply divided concepts of 'compound quenching' and 'collisional quenching' really merge into one another in an imperceptible manner.

E. J. Bowen.
E. Coates.

Physical Chemistry Laboratory,
Oxford.
March 9.

[1] *Nature*, **157**, 228 (1946).
[2] Bowen, E. J., and Williams, A. H., *Trans. Farad. Soc.*, **35**, 765 (1939).
[3] Bowen, E. J., Barnes, A. W., and Holliday, P., *Trans. Farad. Soc.*, in the press.

Orientation of Ferromagnetic Domains near a Crystal Surface

Considerations of minimum energy have suggested that ferromagnetic domains are lamellar, with the lamellæ parallel to one of the directions of easy magnetization, and alternate lamellæ magnetized in opposite directions[1]. Becker and Döring[2] have shown that if the direction of magnetization tends to be parallel to the crystal surface, certain experiments of Williams[3] could be explained that would otherwise indicate that iron crystals are not magnetically isotropic in low fields[4].

In order to obtain more direct evidence of such orientation of domains by the proximity of a crystal surface, measurements were made of the torque acting on a single-crystal disk in a magnetic field. The plane of the disk was practically the (011) plane of the crystal. Thus the ± [100] directions lay in the plane of the disk, while ± [010] and ± [001] were inclined at 45°. If the proximity of the crystal surfaces has a tendency to orient the domains, there should be more domains magnetized in the ± [100] directions than in either the ± [010] or the ± [001]; and when placed in a small magnetic field the disk should tend to turn so as to bring the nearer of the ± [100] directions into the field direction. It is easy to show that if only the [100] directions in the plane of the sheet were effective as domain directions, the torque per c.c. would have the form

$$C(\theta) = -\alpha H^2 \sin 2\theta, \text{ with } \alpha = 1/2N,$$

where N is the demagnetizing factor of the disk, H is the applied field, and θ is the angle between [100] and H. If, however, there is no orienting effect, so that all three cube axes are equally favoured as domain directions, the torque would vanish in small fields.

A disk of 2·1 per cent silicon-iron was suspended in the magnetic field of a pair of Helmholtz coils, both the plane of the disk and the field of the coils being horizontal. The direction of the field relative to [100] was varied in steps of 10°, the torque being measured at each step. The effect of rotational hysteresis was eliminated by making two sets of measurements with opposite directions of rotation and averaging. For a given field-strength the torque was indeed found to be a sinusoidal function of 2θ, but the amplitude was considerably smaller than indicated by the above equation. For the disk used the coefficient $1/2N$ should have approximately the value 2·6 dyne cm./c.c./gauss², but the experimental values of α were 0·07 at 30 gauss, 0·13 at 10 gauss, 0·27 at 3 gauss, 0·43 at 1 gauss, and 0·61 at 0·3 gauss. Similar but slightly larger results were obtained in another series of measurements in which hysteresis was eliminated by heating the disk above its Curie point *in vacuo*. The rapid increase of the coefficient with decreasing field suggests that it might attain its theoretical value, or in other words that the directions of domain magnetization would be confined to the disk, in vanishingly small fields.

As a matter of interest, measurements were also made in higher fields, to follow the transition of the torque-angle curve from sinusoidal to its well-known saturation shape[3], having a zero at [111] as well as [100] and [011]. At values of I about 0·57 of saturation, the $C(\theta)$ curve shows a tendency to flatten out beyond $\theta = 60°$, and for I about 0·62 of saturation the positive loop between [111] and [011] appears. It is tempting to identify this rather sudden change in the character of the curve with the change in the mechanism of magnetization. At low fields the chief process is that the domains take up the [100] directions nearest to the field direction; at high fields the direction of magnetization of the domains is pulled more nearly into the field direction. For the [111] direction this change takes place for I about $1/\sqrt{3}$, or 0·58, of saturation.

This work forms part of a programme sponsored by the British Electrical and Allied Industries Research Association, to whom we are indebted for permission to publish.

D. Shoenberg.
A. J. C. Wilson.

Cavendish Laboratory,
Cambridge.
Feb. 28.

[1] Landau and Lifschitz, *Phys. Z. Sow.*, **8**, 153 (1935). Becker and Döring, "Ferromagnetismus" (1939), 187. Elmore, *Phys. Rev.*, **62**, 486 (1942). Lifschitz, *J. Phys. U.S.S.R.*, **8**, 337 (1944).
[2] Becker and Döring, "Ferromagnetismus" (1939), 153.
[3] Williams, *Phys. Rev.*, **52**, 747 (1937).
[4] Bozorth, *J. App. Phys.*, **8**, 575 (1937).

Pseudo-cubic Compounds of Alkaline Earth Oxides with Tungsten and Molybdenum Oxides

There are well-recognized anhydrous tungstates of the alkaline earths calcium, strontium and barium typified by the composition RWO_4. The mineral scheelite, $CaWO_4$, is an example, and its crystal structure conforms to the tetragonal system with an axial ratio approximately 2·17[1]. These tungstates are readily prepared synthetically by precipitation methods or by heat treatment of the appropriate mixtures of the alkaline earth carbonate with tungsten oxide. Calcium tungstate in particular is an important inorganic luminescent compound, and is utilized for a variety of purposes, for example, as an ingredient of X-ray intensifying screens.

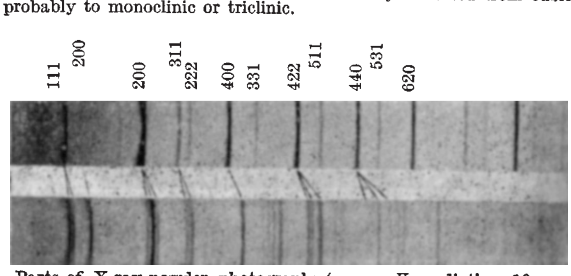
We have found, however, that when an excess of an alkaline earth oxide is caused to combine with tungsten oxide, new compounds are formed characterized by a distinctive crystal structure. For example, the interfacial reaction product detected on the core metal of the well-known 'oxide' cathode of a thermionic device, if the cathode consists of tungsten coated with barium/strontium oxide, gives a distinctive X-ray powder photograph not identifiable with a substance of scheelite-like structure. Similar materials are formed when the oxide cathode is of the type often employed in hot cathode discharge lamps, with a rod of the active constituent enclosed in a spiral of tungsten wire.

Synthesis of the new tungstates, identifiable by their X-ray powder photographs, is accomplished by firing, in air, mixtures of the alkaline earth carbonate with tungstic oxide in the molecular proportions 3 : 1 at temperatures of the order of 1,000° C. or greater. It is thought, therefore, that the molecular composition is represented by the formula R_3WO_6, where R is the alkaline earth metal. A wide variety of tungstates of this composition has been prepared, including some containing two or more alkaline earths. Magnesia can partially replace the oxide of calcium, barium or strontium, but a pure magnesium compound of the same structural type has not been prepared. The tungsten may be replaced by molybdenum.

The crystal structures of these complex tungstates and molybdates are of particular interest. The structures, as revealed by X-ray powder photographs, approach cubic symmetry closely, but compounds of different composition display varying degrees of distortion of the ideal cubic lattice.

One of us has directed attention in a previous letter to the distortions of the ideal cubic structure exhibited by a large number of compounds of the structural type of calcium titanate[2]. Although a few, like strontium titanate, give X-ray powder lines as expected for a cubic lattice, many others, such as calcium stannate, give multiple and extra reflexions, revealing departures from true cubic symmetry. Powder photographs of members of the series of new alkaline earth tungstates and molybdates indicate that these compounds have similar structural relationships and could be described as pseudo-isomorphous. Ideally, the symmetry of the structure is face-centred cubic, and, for some compounds that have been prepared, the lines of their X-ray powder photographs fall in the sequence demanded by the face-centred cubic arrangement. An example is given in the upper part of the accompanying reproduction, for a tungstate in which the alkaline earth comprises both barium and calcium in the atomic ratio 2 : 1. The value of the lattice parameter for this compound is approximately 8·38 kX.

With other members of the group, for example, tri-calcium tungstate, the X-ray diffraction pattern (lower part of reproduction) is of considerable complexity, the principal lines being split and a number of extra reflexions appearing. The pseudo face-centred cubic cell has $a_0 \sim 8{\cdot}0$ kX., but the true structure is clearly distorted from cubic, probably to monoclinic or triclinic.



Parts of X-ray powder photographs (copper $K\alpha$ radiation, 19 cm. camera): above, $(Ba,Ca)_3WO_6$; below, Ca_3WO_6.