reached adiabatically from A. Let the co-ordinates be the internal energy U, and deformation co-ordinates (volumes, magnetic fields, etc.) $v_1, v_2, \ldots$. Keeping $v_1, v_2,$ . . . fixed, take the system from a point $B(U_B < U_A)$ in N to the point A. With the v_i constant, no work is done. The increase in internal energy is due to heat $Q > 0$ having been supplied. Because B is in N, the system can be returned from A to B by an adiabatic process, using appropriate changes of the deformation co-ordinates. The drop in internal energy is now entirely due to mechanical work W which has been done by the system. Conservation of energy during the cycle $B A B$ demands that $W = Q$, so that heat Q has been completely converted into work, contrary to Kelvin's principle. It follows that points such as A cannot exist. Hence, in every neighbourhood of every point C in thermodynamic phase space there are points adiabatically inaccessible from C. The same argument can be used if, instead of Kelvin's principle, one assumes the impossibility of a perpetuum mobile of the second kind.

The foregoing argument shows that the conventional and the geometrical methods of developing thermodynamics, which have been regarded as very different[2], are in fact intimately related. It seems desirable to use the best of each in an exposition of thermodynamics, namely, to start with the motivation of the conventional approach and then to switch by the foregoing argument to the more precise concepts of the geometrical method.

It is a pleasure to acknowledge that the stimulus for this communication was provided by questions raised by Prof. D. E. Littlewood at a lecture given by me at the University College of North Wales, Bangor.

P. T. LANDSBERG
University College of South Wales and Monmouthshire, Cardiff.

[1] Born, M., *Natural Philosophy of Cause and Chance*, 39 (Oxf. Univ. Press, 1949). Landsberg, P. T., *Thermodynamics with Quantum Statistical Illustrations*, 53, 61 (Interscience, 1961).

[2] Planck, M., *S.B. preuss. Akad. Wiss.*, 453 (1926).

CRYSTALLOGRAPHY

Orthorhombic Form of Diperoxotriamine-chromium(IV)

WORK on the crystal structure of diperoxotriaminechromium(IV) $[Cr(O_2)_2(NH_3)_3]$ was begun in 1958 but was abandoned when McLaren and Helmholz[1] reported their X-ray investigation of the monoclinic form of this compound by means of two-dimensional Fourier methods. They suggested that it might be considered a superoxo compound containing chromium in the oxidation state $+2$ with all its electrons paired in order to explain the magnetic susceptibility of the compound. This view has been questioned[2] and the present three-dimensional crystal structure analysis was therefore taken up again.

The orthorhombic form of diperoxotriaminechromium (IV) belongs to space group $Pnma$ (No. 62). The dimen-

Fig. 1

sions of the elementary cell are: $a = 9.79_1$ Å, $b = 22.66_2$ Å and $c = 7.65_3$ Å. The cell contains twelve formula units, and the atoms occupy 8- and 4-fold positions. Parameter values for all the atoms have been determined by three-dimensional Fourier methods and a couple of least-squares refinement cycles (Table 1). The value of the reliability index obtained is $R_{hkl} = 0.112$.

The chromium is 7-co-ordinated (Fig. 1), the geometrical configuration being a distorted pentagonal bipyramid. The mean value of the oxygen–oxygen bond distance in the peroxo groups is 1.434 ± 0.023 Å. Therefore, it seems natural to consider the compound a peroxo compound with tetravalent chromium.

The least-squares refinement will be continued to convergence and a complete report of the structure will soon be published elsewhere.

ROLF STOMBERG

Division of Inorganic Chemistry,
Chalmers University of Technology,
Gothenburg, Sweden.

[1] McLaren, E. H., and Helmholz, L., *J. Chem. Phys.*, 63, 1279 (1959).

[2] Cotton, F. A., and Wilkinson, G., *Advanced Inorganic Chemistry*, 692 (Intersci. Pub., John Wiley and Sons, Inc., 1962).

Table 1. PARAMETER VALUES FOR $[Cr(O_2)_2(NH_3)_3]$. SPACE GROUP $Pnma$

Atom	No. of positions	x	y	z
Cr_1	8d	0·2014	0·0859	0·1332
Cr_2	4c	0·1091	1/4	0·6400
O_1	8d	0·2087	0·0028	0·1140
O_2	8d	0·3291	0·0267	0·1887
O_3	8d	0·1827	0·1670	0·1582
O_4	8d	0·3125	0·1463	0·2193
O_5	8d	0·1140	0·1659	0·6403
O_6	8d	0·9972	0·1911	0·7301
N_1	8d	0·0038	0·0870	0·0114
N_2	8d	0·1166	0·0747	0·3795
N_3	8d	0·2914	0·0971	0·8853
N_4	4c	0·2951	1/4	0·4881
N_5	4c	0·2242	1/4	0·8679
N_6	4c	0·0006	1/4	0·3963

Recrystallization of Evaporated Films of ZnSe

Gilles and Van Cakenberghe[1] recrystallized evaporated layers of CdS by a two-stage process. This process consists of evaporating copper on CdS films and baking the double layer at about 600° C. More recently we have recrystallized CdS by simply heating the evaporated layers between 250° C and 450° C in an inert liquid medium to which an organometallic compound has been added[2].

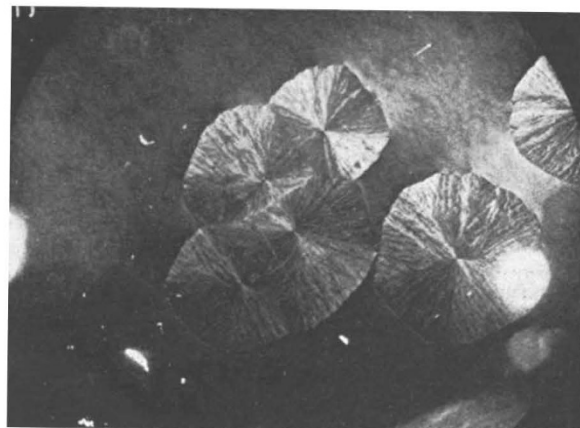Fig. 1. Spherulites ZnSe (× 100)