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Refinement of the Nd_2O_3 structure and determination of the neutron scattering length of neodymium.

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The scattering length of neodymium was redetermined from two independent measurements: one from a neutron powder pattern of Nd_2O_3 which was analysed by the profile analysis technique and the other from the data collected both with polarized and unpolarized neutrons on an $NdAl_2$ single crystal. The two experiments are in very good agreement and yield the value $b_{Nd}=0.769\pm0.005\ 10^{-12}$ cm. In the course of this study, Nd_2O_3 has been confirmed to belong to the space group $P\bar{3}m1$ according to the Pauling model.

In the course of a polarized neutron study of the intermetallic compound $NdAl_2$, the tabulated scattering length of neodymium $b_{Nd}=0.72\times10^{-12}$ cm (Bacon, 1972) appeared to be unsatisfactory. This value had been measured by Koehler & Wollan (1953) on Nd_2O_3. Subsequently (Nereson, Olsen & Arnold, 1966), it was found that 0.75×10^{-12} cm was more consistent with powder data of $NdAl_2$, and Schobinger-Papamantellos, Fisher, Vogt & Kaldis (1973) deduced a value of $0.75\pm0.01\times10^{-12}$ cm from NdSb powder data. This value is currently accepted (Bacon, 1974). We have employed two independent methods to determine an accurate scattering length for Nd; one was a profile refinement of the Nd_2O_3 powder diagram, the other a combined polarized and unpolarized neutron experiment on an $NdAl_2$ single crystal.

The crystal structure of the *A* form of the rare earth sesquioxides was first investigated by Zachariasen (1926, 1949) and then determined by Pauling (1928) who proposed a space group $P\bar{3}m1$ with atoms occupying the following positions

$$\begin{array}{lll} \mathrm{Nd} & \text{in } 2(d) & \pm(\frac{1}{3},\frac{2}{3},u) \\ \mathrm{O_I} & \text{in } 2(d) & \pm(\frac{1}{3},\frac{2}{3},v) \\ \mathrm{O_{II}} & \text{in } 1(a) & (0,0,0)\,. \end{array}$$

This structure was supported by the work of Koehler & Wollan (1953) who used neutron diffraction to determine the light-atom positions and found for La_2O_3 $u=0.245\pm0.005$ and $v=0.645\pm0.005$. More recently Müller-Buschbaum & Schnering (1965), studying a single crystal of La_2O_3 with X-rays, noted the systematic extinction $h-k=3n$ for l odd and proposed a model in space group $P6_3/mmc$ (D_{6h}^4) which assumes a statistical distribution for the La atoms on their site and also for one of the oxygen sites.

We have obtained the neutron-diffraction pattern of an Nd_2O_3 powder ignited first at 1300°C to remove any possible contamination with water and CO_2. The powder pattern was measured at the ILL reactor; the incident wavelength was 1·106 Å from the 533 reflexion of a Ge monochromator with a take-off angle of $2\theta_M=50°$ in order to yield a fairly flat resolution curve. 68 reflexions were recorded between $2\theta=8°$ and 80°. The diagram clearly shows the existence of the lines 003, 113, 005, 115, in contradiction to the statistical model and supporting the Pauling model. The structural parameters were determined by a profile refinement, minimizing the function

$$M=\sum_i W_i\left[Y_i(\mathrm{obs})-\frac{1}{k}\,Y_i(\mathrm{calc})\right]2$$

where k is the scale factor, Y_i(obs) and Y_i(calc) the observed and calculated intensity at any point and W_i the weighting factor for this point (Rietveld, 1967, 1969; Hewat, 1973). The scattering length used for oxygen was $b_O=0.580\times10^{-12}$ cm (Bacon, 1972) and the result of the refinement gives for neodymium $b_{Nd}=0.769\pm0.010\times10^{-12}$ cm.

The positional parameters and thermal coefficients are shown in Table 1.

Table 1. *Parameters for* Nd_2O_3

	x	y	z	B (Å^2)
Nd	$\frac{1}{3}$	$\frac{2}{3}$	0·2462 (3)	0·253 (40)
O_I	$\frac{1}{3}$	$\frac{2}{3}$	0·6466 (3)	0·593 (49)
O_{II}	0	0	0	0·847 (80)

The reliability index based on the profile is $R_{pr}=6.8\%$ and the one based on the individual Bragg intensities is $R_B=1.9\%$.

An attempt to refine anisotropic temperature factors (Hewat, 1973, UKAEA Harwell Report 73/897, unpublished) did not improve the fit and gave exactly the same value of b_{Nd}.

A second determination of b_{Nd} was obtained from polarized neutron measurements on an $NdAl_2$ single crystal (Boucherle & Schweizer, 1975). Usually polarized neutrons are used to determine the magnetic amplitudes knowing the nuclear ones; here they were used to measure the nuclear amplitude. At 4·2 K two different experiments have been performed: a measurement of the integrated intensities with unpolarized neutrons including both magnetic and nuclear intensities, and a measurement with polarized neutrons determining for each reflexion the ratio γ between magnetic and nuclear amplitudes. The combination of these two measurements allowed a refinement of the thermal parameters which were found to be $B_{Nd}=0.12\pm0.02$ Å^2, $B_{Al}=0.40\pm0.02$ Å^2 and for the 400 reflexion, the nuclear amplitude of which being low and equal to

$$b_{Nd}\exp\left(-B_{Nd}\frac{\sin^2\theta}{\lambda^2}\right)-2b_{Al}\exp\left(-B_{Al}\frac{\sin^2\theta}{\lambda^2}\right),$$

provides an accurate measurement for this amplitude. Taking for aluminum $b_{Al}=0.3449\pm0.0009\times10^{-12}$ cm (Bacon, 1972) we found $b_{Nd}=0.769\pm0.005\times10^{-12}$ cm.

These two independent measurements based on different reference scattering lengths are in very good agreement and suggest the value: $b_{Nd}=0.769\pm0.005\times10^{-12}$ cm.

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Résultats cristallographiques de composés de la série des dibenzoates d'oligométhylène glycols.

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Preliminary crystallographic results are presented for a series of dibenzoates and *p*-substituted dibenzoates of oligomethylene glycols.

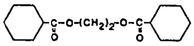
Les résultats d'études structurales, par diffraction de rayons X, de polyesters aliphatiques dérivés de l'éthylène glycol, triméthylène glycol et décaméthylène glycol (Fuller & Erickson, 1937; Fuller & Frosch, 1939 *a*, *b*; Fuller, Frosch & Pape, 1942), ou de polyesters aromatiques tels que le polyéthylène téréphtalate (Daubeny, Bunn & Brown, 1954) révèlent un raccourcissement systématique de la longueur de répétition de fibre par rapport à celle attendue pour une chaîne zig-zag complètement plane.

Si dans chacun des cas, une explication différente de ce raccourcissement est donnée en fonction même de la spécificité des différentes structures, il n'en reste pas moins que les distortions semblent concentrées sur la partie glycolique de la chaîne de polyesters.

Nous avons entrepris la recherche et l'étude de la structure cristalline de composés de la série des dibenzoates de glycol afin, d'examiner d'une part si un raccourcissement similaire à celui observé dans les chaînes de polyesters se

Tableau 1. *Données cristallographiques*

(I)



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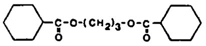

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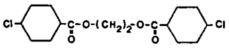

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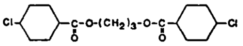

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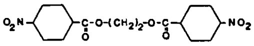

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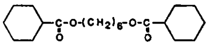

(I) Dibenzoate d'éthylène glycol
$C_{16}H_{14}O_4$, P.M. 270,28, P.F. 73 °C, $F(000)=142$,
orthorhombique, *Pbca*, $Z=8$,
$a=7{,}558$ (5), $b=21{,}834$ (7), $c=16{,}210$ (7) Å,
$V=2675{,}12$ Å^3, $d_{\text{mes}}=1{,}35$ g cm^{-3}, $d_{\text{cal}}=1{,}342$ g cm^{-3}

(II) Di-*p*-chlorobenzoate d'éthylène glycol
$C_{16}H_{12}O_4Cl_2$, P.M. 339,27, P.F. 140°C, $F(000)=174$,
monoclinique, *C*2/*c*, $Z=4$
$a=12{,}733$ (9), $b=9{,}522$ (8), $c=12{,}762$ (8) Å,
$\beta=100{\cdot}37$ (10)°, $V=1522$ Å^3,
$d_{\text{mes}}=1{,}48$ g cm^{-3}, $d_{\text{cal}}=1{,}452$ g cm^{-3}

(III) Di-*p*-nitrobenzoate d'éthylène glycol
$C_{16}H_{12}O_8N_2$, P.M. 360,3, P.F. 143 °C, $F(000)=186$,
monoclinique, *Cc*, $Z=8$,
$a=20{,}91$ (2), $b=21{,}34$ (2), $c=7{,}57$ (1) Å,
$\beta=105{,}0$ (3)°, $V=3247$ Å^3,
$d_{\text{mes}}=1{,}48$ g cm^{-3}, $d_{\text{cal}}=1{,}47$ g cm^{-3}

(IV) Dibenzoate de triméthylène glycol
$C_{17}H_{16}O_4$, P.M. 284,32, P.F. 59°C, $F(000)=150$,
orthorhombique, *Pbcn*, $Z=4$,
$a=11{,}17$ (2), $b=8{,}91$ (1), $c=14{,}82$ (2) Å,
$V=1475$ Å^3, $d_{\text{mes}}=1{,}30$ g cm^{-3}, $d_{\text{cal}}=1{,}29$ g cm^{-3}

(V) Di-*p*-chlorobenzoate de triméthylène glycol
$C_{17}H_{14}O_4Cl_2$, P.M. 353,30, P.F. 100°C, $F(000)=182$,
monoclinique, *C*2/*c*, $Z=4$,
$a=31{,}499$ (22), $b=4{,}530$ (3), $c=11{,}587$ (8) Å,
$\beta=95{,}37$ (10)°, $V=1646{,}1$ Å^3,
$d_{\text{mes}}=1{,}44$ g cm^{-3}, $d_{\text{cal}}=1{,}426$ g cm^{-3}

(VI) Dibenzoate d'hexaméthylène glycol
$C_{20}H_{22}O_4$, P.M. 326,39, P.F. 56°C, $F(000)=174$,
orthorhombique, *Pbca*, $Z=4$,
$a=8{,}73$ (1), $b=19{,}72$ (2), $c=10{,}61$ (1) Å,
$V=1827$ Å^3, $d_{\text{mes}}=1{,}20$ g cm^{-3}, $d_{\text{cal}}=1{,}17$ g cm^{-3}