differences of these values E for two neighboring elements also as a function of N, or of the atomic number Z, we obtain a curve with the same periodicity (Fig. 3).[4]
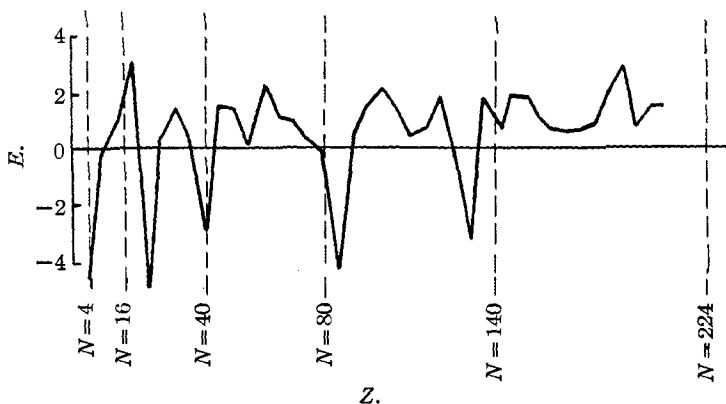

Fig. 3.—The relation between the value of E and the atomic number Z.

Nearly the same periodicity can be deduced theoretically from de Broglie's equation. This possibility will be discussed in another place.

[4] According to experimental data given by J. and W. Noddak, *Naturwiss.*, **18**, 757 (1930).

ALL UNION ELECTROTECHNICAL INSTITUTE   G. I. POKROWSKI
Moscow, U. S. S. R.

Molecular Rotation in Solid Sodium Nitrate

It was shown by Kracek and his co-workers,[1] that the gradual transition in sodium nitrate at 275° is accompanied by an important change of the intensities of the diffraction lines in the powder diagrams given by this substance. They conclude "that there is no serious objection to the hypothesis of molecular rotation as an explanation of the gradual transition in sodium nitrate," this conclusion being reached by a qualitative intensity discussion, the quantitative calculation of the rotating model presenting "a most interesting difficulty."

Now the scattering power of a ring model has been calculated by Coster[2] and by Kolkmeyer[3] with a view to the possibility of electron binding rings in diamond and by one of us[4] in testing electronic models of lithium. For the case of sodium nitrate we have now performed the intensity

[1] Kracek, Posnjak and Hendricks, THIS JOURNAL, **53**, 3339 (1931).
[2] Coster, *Verslag. Akad. Wetenschappen Amsterdam*, **28**, 391 (1919).
[3] Kolkmeyer, *ibid.*, **28**, 767 (1920).
[4] Bijvoet, *Rec. trav. chim.*, **42**, 874 (1923).

calculation along these lines and reached a fair interpretation of the observed intensities, which offers a strong affirmation of the model proposed.

The calculation of the scattering power of a ring of electrons (atoms) can be made in the following way. All points in the same lattice reflection plane have the same phase. A point at a distance d from this plane has a phase difference of $4\pi d \sin \theta/\lambda$ where θ represents the glancing angle.

Let the angle between the reflecting lattice plane and the plane containing the orbit of the N rotating electrons (atoms) be α and $d\varphi$ an element of the orbit containing $N(d\varphi/2\pi)$ electrons. The distance of this element to the lattice plane is then $\rho \sin \alpha \sin \varphi$ (ρ = radius of the orbit).

The diffracted amplitude is

$$\frac{N}{2\pi} e^{4\pi i d \sin \theta/\lambda} \, d\varphi$$

Integrating this over the circle we find the amplitude of the ring diffraction (phase compared with rays scattered by a point in the plane, $e.\ g.$, the center of the orbit)

$$\frac{N}{2\pi} \int_0^{2\pi} e^{4\pi i \rho \sin \alpha \sin \theta \sin \varphi/\lambda} \, d\varphi \; = \; N J_0 \left(4\pi \frac{\rho}{\lambda} \sin \alpha \sin \theta \right)$$

where $J_0(x)$ represents the Bessel function of the 0th order of the argument (x).

This calculation is based on the very probable supposition that there is no strict phase relation between the rotation in neighboring cells.

In the case of the rotating NO_3 group we substitute $N = 3F(O)$ where $F(O)$ is the atomic scattering factor for oxygenium. The phase is compared with that of the center of the orbit, the nitrogen atom.

We have calculated the intensities in the usual way on the basis of the equation $I = P \dfrac{1 + \cos^2 2\theta}{\cos \theta \sin^2 \theta} \, S^2$ with

$$S = \begin{cases} 2F(\mathrm{Na}) + 2F(\mathrm{N}) + 6F(\mathrm{O})\, I_0(x) & h+k+l = 4p \\ -2F(\mathrm{Na}) + 2F(\mathrm{N}) + 6F(\mathrm{O})\, I_0(x) & h+k+l = 2p \\ 0 & h+k+l \neq 2p \end{cases}$$

Here $I_0(x)$ represents the scattering power of a ring, x being equal to $4\pi\, (\rho/\lambda) \sin \theta \sin \alpha$; ρ, radius of the ring, and α the angle between reflecting and orbit plane.

The atomic scattering factors were taken according to James and Brindley.[5] For nitrogen the factor curve for neutral atoms was taken, as N^{+5} was found not to be in accordance with the observed intensities. For oxygenium also the factor for neutral atoms is used, which only slightly differs from that of O^{-2} and only for small diffraction angles.

Now it is the problem to ascertain whether it is possible to fix a value for ρ which gives good agreement between calculated and observed intensities. As the Bessel function has alternating positive and negative values, it is easy to limit this value. From the fact that $32\bar{1}$ is much stronger than the corresponding neighboring reflections, it follows that the value of ρ lies between 1.1 Å. and 1.65 Å. or between 2.4 Å. and 2.9 Å. The latter value

⁵ James and Brindley, Z. Krist., **78**, 470 (1931).

is at once excluded by 211, which is a very strong reflection. The intensities calculated with a radius $\rho = 1.15 \pm 0.05$ Å. are in very good agreement with the observed intensities (last columns, Table I). (In some films traces of reflections are reported exclusively due to oxygenium. This may be caused by uncertainty or unsteadiness of the temperature of the sample, the calculated density also indicating that the temperature of the diffracting layer is lower than that given by Kracek and his co-workers.)

TABLE I

hkl	sin θ	α	x	$J_0(x)^a$	$\frac{1}{2}\Sigma F(O)$	$\frac{1}{2}\Sigma F(N)$	$\frac{1}{2}\Sigma F(Na)$	$\frac{1}{2}S$	$\frac{1}{2}p$	Cont. fact.	I, calcd.	I, obs.
110	0.127	62°	1.61	+0.45	19.95	5.4	−8.85	5.55	3	252	2.3	3.2
211	.161	44°	1.62	+0.44	18.0	4.8	+8.7	21.6	3	150	21.0	>10
222	.170	0°	0.00	+1.00	17.55	4.7	−8.6	13.65	1	134	2.5	2.5
1̄10	.197	90°	2.86	−0.21	15.9	4.2	+8.2	9.1	3	100	2.5	3.4
210	.214	66°	2.84	−0.20	0.0	0.0	0.0	0.0	6	80	0.0	<0.5
200	.234	75°	3.26	−0.33	14.4	3.8	−7.7	8.65	3	67	1.5	2.4
220	.254	62°	3.24	−0.33	13.65	3.55	+7.4	6.4	3	60	0.7 }	
332	.254	25°	1.56	+0.48	13.65	3.55	+7.4	17.5	3	60	5.5 }	7.7
321	.260	48°	2.78	−0.18	13.5	3.5	−7.3	6.25	6	55	1.3	2.2
2̄10	.302	63°	3.88	−0.40	0.0	0.0	0.0	0.0	3	42	0.0	<0.5
2̄11	.306	47°	3.24	−0.33	11.25	2.95	−6.6	7.35	3	40	0.7	1.2
433	.316	20°	1.56	+0.48	11.1	2.9	−6.45	2.25	3	38	0.0	...
310	.322	78°	4.56	−0.31	10.95	2.85	+6.4	5.85	6	36	0.7 }	
422	.322	44°	3.25	−0.33	10.95	2.85	+6.4	5.65	3	36	0.4 }	1.1
432	.323	35°	2.67	−0.13	0.0	0.0	0.0	0.0	6	36	0.0	...
320	.332	64°	4.33	−0.36	0.0	0.0	0.0	0.0	6	33	0.0	<0.5
2̄11	.341	26°	2.16	+0.13	10.35	2.7	+6.1	10.15	3	31	0.9 }	
444	.341	0°	0.00	+1.00	10.35	2.7	+6.1	19.15	1	31	1.1 }	1.2
421	.361	56°	4.33	−0.36	0.0	0.0	0.0	0.0	6	28	0.0	...
442	.364	37°	3.16	−0.31	9.7	2.55	−5.75	6.2	3	27	0.3	...
431	.377	53°	4.38	−0.35	9.3	2.45	+5.6	4.8	6	25	0.4	0.5
330	.382	62°	4.88	−0.22	9.15	2.45	−5.5	5.05	3	25	0.2	...
2̄20	.394	90°	5.71	+0.06	8.8	2.35	+5.3	8.15	3	23	0.4 }	0.5
543	.394	28°	2.69	−0.14	8.8	2.35	+5.3	6.4	6	23	0.6 }	to 1.0
3̄10	.408	81°	5.83	+0.10	8.55	2.25	−5.15	2.05	6	22	0.0	...
532	.413	45°	4.24	−0.37	8.3	2.25	−5.1	6.0	6	20	0.4	...
554	.422	15°	1.58	+0.47	8.1	2.2	−4.95	1.05	3	19	0.0	...
32̄1	.425	74°	5.88	+0.12	8.1	2.2	+4.95	8.15	6	19	0.8	1.1
420	.428	66°	5.67	+0.05	8.1	2.2	−5.0	2.4	6	16	0.0	...
542	.443	40°	4.12	−0.39	0.0	0.0	0.0	0.0	6	16	0.0	...
2̄22	.466	82°	6.70	+0.29	7.4	2.1	−4.3	0.0	3	16	0.0	...
400	.469	75°	6.40	+0.24	7.2	2.1	+4.3	8.0	3	16	0.3 }	
521	.469	60°	5.80	+0.09	7.2	2.1	+4.3	6.95	6	16	0.5 }	1.1

^{a} Jahnke, "Emde Funktionentafeln."

The calculated radius is somewhat smaller than that expected from the parameter value $\frac{1}{4}$ of the non-rotating oxygenium atoms, which corresponds to a distance of 1.26 Å. between nitrogen and oxygenium.

From optical data, however, a distance is calculated of 1.15 Å.[6] and even of 1.09 Å.[7]

[6] Zachariasen cited from V. M. Goldschmidt, *Geochem. V.*, **2**, 66 (1926).
[7] W. L. Bragg, *Proc. Roy. Soc.* (London), A106, 356 (1924).

J. M. BIJVOET   J. A. A. KETELAAR
GEOLOGICAL INSTITUTE   LAB. FOR GEN. AND INORGANIC CHEMISTRY
UNIVERSITY OF AMSTERDAM   UNIVERSITY OF AMSTERDAM
AMSTERDAM, HOLLAND
RECEIVED DECEMBER 11, 1931
PUBLISHED FEBRUARY 5, 1932

POLYMERIZATION REACTIONS UNDER HIGH PRESSURE. II. THE MECHANISM OF THE REACTION

BY J. B. CONANT AND W. R. PETERSON

Unsaturated hydrocarbons and certain aliphatic aldehydes are polymerized at room temperature by the application of very high pressure (3000–12,000 atm.)[1] In the case of isoprene the product is rubber-like; in the case of *n*-butyraldehyde the final polymer is a hard solid which reverts to the original aldehyde on standing at room temperature and atmospheric pressure. The previous work[1] showed that peroxides and ozonides were effective catalysts for both types of polymerization. However, it was concluded that peroxide catalysis was not essential since a sample of isoprene distilled in nitrogen and compressed without exposure to air polymerized at a rate only slightly less than that of material freshly distilled in air. The results of the experiments recorded in this paper have led us to revise this conclusion. We are now strongly inclined to the opinion that peroxide catalysis is essential to the polymerization and the effect of increased pressure is only to accelerate the catalytic reaction.

The evidence that peroxide catalysis is essential to the pressure polymerization of isoprene is as follows. Peroxides and ozonides have a strong positive catalytic action. Freshly distilled isoprene polymerizes at a rate only one-fifth to one-tenth of that of isoprene which has stood in the air for some days. This increased tendency to polymerize on standing is almost certainly due to the formation of peroxides from the dissolved oxygen. If peroxides (or dissolved oxygen which will form a peroxide) are essential to the polymerization, we must assume that when the isoprene was distilled in nitrogen some trace of oxygen or volatile peroxides was in the distillate. We have now strong evidence for this assumption since we have found that by adding hexaphenylethane (which reacts rapidly with oxygen) to isoprene in nitrogen and distilling, the rate of polymeriza-

[1] THIS JOURNAL, **52**, 1659 (1930).