

In particular, the two sets of values quoted by Huggins & Sakamoto (1957) were derived using two differing and arbitrarily selected (Huggins, 1956) values for the repulsion exponent  $\rho$ . We have found not only different values for  $\rho$  but also that each compound has its own characteristic value for the exponent.

	$\rho$ (Huggins & Sakamoto)	$\rho$ (present work)
MgO	0.400	0.333
CaO	0.400	0.333
BaO	0.400	0.333

We have further calculated the lattice energy of barium oxide by an equation similar to that of Born & Landé (1918) but employing an exponential form for the repulsion term (Pauling, 1928) and using the values of  $r_0$  and  $\beta$  from Table 2. This leads to the result  $U(r_0) = -753$  kg.cal./mole, very similar to that obtained with this equation using the inverse  $r^n$  repulsion expression (Morris, 1957).

It has been our experience that any modification of the Born-Landé equation (Ladd & Lee, 1958; Born & Mayer, 1932) so as to include the attractive potential energy terms represented by  $C/r^6$  and  $D/r^8$  always leads to a lower (more negative) value for the lattice energy. It seems unlikely then that this quantity for barium oxide can be greater than about  $-753$  kg.cal./mole.

Applying the Born-Haber cycle in the form,

$$\Delta H_f(\text{cryst.}) - \Delta H_f(\text{M}^{2+}\text{gas}) - \frac{1}{2}\text{D}(\text{O}_2) - \text{E}(\text{O}^{2-}) + 1.2 - U(r_0) = 0,$$

to the oxides of magnesium, calcium and barium we arrive at the value of  $179 \pm 8$  kg.cal./g.atom for the electron affinity,  $\text{E}(\text{O}^{2-})$ , taking the thermodynamic data from the compilation of Rossini *et al.* (1952). To complete the series of lattice energies of the alkaline earth oxides we have used data from the same source together with the mean value for  $\text{E}(\text{O}^{2-})$  just derived; these results are listed in Table 1.

The uncertainty in the calculated values of the lattice energies of MgO, CaO and BaO lies in the low accuracy with which their compressibilities have been measured (Weir, 1956; Bridgman, 1949). More reliable data would undoubtedly lead to a further refinement of these values.

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**A simple method for the determination of  $\partial^2\rho/\partial x^2$  at atomic positions.** By H. W. EHRLICH, *Chemistry Department, The University, Edinburgh, 9, Scotland*

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The value of  $\partial^2\rho/\partial x^2$  at atomic positions is required when assessing the accuracy of a structure determination or when determining the magnitude of a shift indicated by an ( $F_o - F_c$ ) map. In principle, the most reliable method

of deriving this quantity is from an  $F_o$  synthesis, but many refinements are now carried out by techniques not requiring such a summation. Furthermore, for a reliable determination of  $\partial^2\rho/\partial x^2$ , the Fourier synthesis must be

Table 1. Values of  $-\partial^2\rho/\partial x^2$  for various atoms for different values of  $a$ 

Three-dimensional atoms								
$a$	Point atom	U	I	C	C	C	H	H
	$Z=1$	$B=0$	$B=0$	$B=0$	$B=1.3$	$B=4.5$	$B=0$	$B=5.5 \text{ \AA}^2$
1.54 \AA	118	6060	3160	200	138	60.7	7.9	2.48
1.84	124	6250	3260	206	142	61.0	8.1	2.60
2.07	118	6080	3180	202	142	62.7	8.0	2.65
2.38	122	6190	3230	206	142	61.9	8.2	2.66
3.02	120	6140	3190	203	141	62.0	8.1	2.66
Two-dimensional atoms								
$a$	Point atom	U	I	C	C	C	H	H
	$Z=1$	$B=0$	$B=0$	$B=0$	$B=1.3$	$B=4.5$	$B=0$	$B=5.5 \text{ \AA}^2$
1.57 \AA	91.0	4700	2440	157	109	51.5	7.2	2.64
1.99	85.5	4550	2370	152	111	54.3	7.2	2.87
2.18	87.5	4580	2390	154	110	53.2	7.3	2.88
2.92	86.8	4550	2380	154	111	54.1	7.2	2.89
3.40	87.4	4580	2390	154	110	53.1	7.2	2.87

Table 2. Values of  $-\partial^2\rho/\partial x^2$  for three-dimensional atoms from two values of  $a$  for which  $n=81$ 

$a$	Point atom	C	C	C	C	C
	$Z=1$	$B=0.0$	$B=1.3$	$B=3.0$	$B=4.5$	$B=10.0 \text{ \AA}^2$
2.00 \AA	137	232	158	99	66.6	20.2
2.07	118	202	142	91	62.7	19.6

sampled at very fine intervals, and this adds to the tedium of the method.

An approximate value for the curvature is obtained from the assumption that the electron density near the centre of an atom closely resembles  $\rho = Z(p/\pi)^{3/2} \exp(-px^2)$  (Costain, 1941) which leads to the result  $\partial^2\rho/\partial x^2 = -2pZ(p/\pi)^{3/2}$  at the centre of the atom, where  $Z$  is the atomic number and  $p$  is usually between 3 and 5. Although  $p$  varies with the nature of the atom, its temperature factor and the range of the Fourier series, the mathematical relationship between these quantities is not a simple one.

The method described here for the determination of the curvature is based on the premise that the shape of an atom from a Fourier synthesis is independent of the size of the unit cell. This seems not unreasonable, as the quality of the image in an optical instrument is related to its resolving power, which is  $1.22\lambda/(2 \sin \theta_{\max.})$ , where  $\lambda$  is the wavelength of the radiation used. In X-ray diffraction work,  $\sin \theta_{\max.} = 1$  usually, and therefore the quality of the image is solely dependent on the wavelength of the radiation used.

Let us take a hypothetical cubic lattice with vectors of length  $a$ , and with one atom at the origin. The diffraction pattern will consist of spots with a  $\sin \theta$  value of  $(\lambda/2a)(h^2 + k^2 + l^2)^{1/2}$  whose intensities are proportional to  $f_{\sin \theta}^2$ , where  $f_{\sin \theta}$  is the value of the scattering factor for a particular value of  $\sin \theta$ . Thus the electron density

$$\rho = \frac{1}{V} \sum_h \sum_k \sum_l f_{\sin \theta} \cdot \cos 2\pi \left( \frac{hx}{a} + \frac{ky}{b} + \frac{lz}{c} \right)$$

and

$$\frac{\partial^2 \rho}{\partial x^2} = \frac{-4\pi^2}{a^2 V} \sum_h \sum_k \sum_l h^2 \cdot f_{\sin \theta} \cdot \cos 2\pi \left( \frac{hx}{a} + \frac{ky}{b} + \frac{lz}{c} \right),$$

which becomes

$$\frac{\partial^2 \rho}{\partial x^2} = \frac{-4\pi^2}{a^5} \sum_h \sum_k \sum_l h^2 \cdot f_{\sin \theta}$$

at the atomic centres.

Our choice of  $a$  is determined by several factors, viz.

- (1)  $a$  should be as small as possible to reduce the calculation to a minimum.
- (2)  $a$  must be chosen so as to avoid errors from overlap with  $\partial^2\rho/\partial x^2$  of adjacent atoms. Overlap errors arise when very broad atoms are involved or from series-terminating effects.
- (3) If we are using Cu  $K\alpha$  radiation with  $\lambda = 1.540 \text{ \AA}$ , and we choose  $a = 1.540 \text{ \AA}$ , then there will be a total of 33 reflexions (000,  $6 \times 100$ ,  $12 \times 110$ ,  $8 \times 111$ , and  $6 \times 200$ ). But if  $a = 1.539 \text{ \AA}$  there will only be 27 reflexions (no 200). Therefore in the expression above for the curvature,  $4\pi^2/a^5$  will change only slightly, whereas there will be a considerable change in  $\sum \sum \sum h^2 \cdot f_{\sin \theta}$ . Errors from this source are appreciable only when  $a$  is small, and again  $a$  must be carefully chosen to eliminate these. If  $n$  reflexions are possible, then the best choice for  $a$  is such that  $n$  reciprocal-lattice unit cells occupy the same volume as the limiting sphere, i.e.  $a^3 = 3n\lambda^3/(32\pi)$ .

The larger errors arise from (3) and errors from (2) only occur when the atom is very sharp or very diffuse. Table 1 lists some values of  $-\partial^2\rho/\partial x^2$  as calculated by this method for various values of  $a$ . These values have been chosen to satisfy the equation  $a^3 = 3n\lambda^3/(32\pi)$  (or  $a^2 = n\lambda^2/(4\pi)$  for the two-dimensional case).

The Table shows that consistent results are obtained by this method for different values of  $a$ , the only large discrepancies arising for small  $a$  with very diffuse atoms. This seems to support the premise that  $\partial^2\rho/\partial x^2$  is independent of  $a$ .

From the Table it is clear that adequate results are obtained for three-dimensional work using a hypothetical lattice with  $a = 1.54 \text{ \AA}$  and in the two-dimensional case with  $a = 1.99 \text{ \AA}$ . Except for very broad atoms this method gives answers which are accurate to within 2%.

As indicated above  $a$  must be carefully chosen to get the correct value for  $\partial^2\rho/\partial x^2$ ; in particular  $a$  should satisfy

the relationship  $a^3 = V = 3n\lambda^3/(32\pi)$  (or  $a^2 = A = n\lambda^2/(4\pi)$  in the two-dimensional case). This method then gives a theoretical value for the curvature of a particular atom with a known scattering factor, which may differ from the experimental value because the crystal unit-cell volume may not satisfy  $V = 3n\lambda^3/(32\pi)$ . The difference will be largest for a point atom, in which case  $\Sigma h^2 \cdot f_{\sin\theta} = Z\Sigma h^2$ , which is constant for constant  $n$ , while the coefficient  $4\pi^2/(a^2V)$  will vary with  $V$ . The error thus depends on how much  $V = a^3$  differs from  $3n\lambda^3/(32\pi)$ , and will be  $[(3n\lambda^3/32\pi V)^{5/3} - 1] \times 100\%$  (or  $[(n\lambda^2/4\pi A)^2 - 1] \times 100\%$  in two dimensions). With more diffuse atoms  $\Sigma h^2 \cdot f_{\sin\theta}$  will vary with  $V$  and partly compensate for this error. Thus the expressions above give the maximum error. Table 2 gives the values of  $-\partial^2\rho/\partial x^2$  as calculated from two values of  $a$  for which  $n = 81$ .  $a = 2.07 \text{ \AA}$  is the optimum value.

Hence using Cu  $K\alpha$  radiation the curvature may be calculated from the equation

$$\partial^2\rho/\partial x^2 = 9.12[f_{0.500} + 4f_{0.707} + 4f_{0.866} + 4f_{1.000}]$$

(corresponding to  $a = 1.54 \text{ \AA}$ ) for the three-dimensional case.

For diffuse atoms it is probably better to use

$$\partial^2\rho/\partial x^2 = 2.08[f_{0.372} + 4f_{0.526} + 4f_{0.645} + 4f_{0.744} + 20f_{0.832} + 24f_{0.911}]$$

(corresponding to  $a = 2.07 \text{ \AA}$ ).

The equation for two dimensions is

$$\partial^2\rho/\partial x^2 = 5.03[f_{0.386} + 2f_{0.547} + 4f_{0.774} + 10f_{0.865}]$$

(corresponding to  $a = 1.99 \text{ \AA}$ ).

This method of determining  $\partial^2\rho/\partial x^2$  is thus both rapid and reliable, and can easily be adapted for use with other wave lengths of X-radiation. By sampling the Fourier transform at such large intervals one might expect considerable errors, but it is also found that calculating  $\rho_{\max}$  using such wide meshes, remarkably good results are obtained.

### Reference

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### Erratum to Laue Obituary, *Acta Cryst.* (1960), 13, 513.

The verse from Kallimachos is, unfortunately, incorrectly quoted, and this will make it difficult to find it in

anthologies. Instead of ξφρησαν (they said) it should begin with εἰπέτης (someone said).

P. P. EWALD.

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*Announcements and other items of crystallographic interest will be published under this heading at the discretion of the Editorial Board. The notes (in duplicate) should be sent to the General Secretary of the International Union of Crystallography (D. W. Smits, Mathematisch Instituut, University of Groningen, Reitdiepskade 4, Groningen, The Netherlands).*

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### Crystallographic Data for Various Polymers

For purposes of ready reference a table listing currently available crystallographic data for a variety of crystal-

lizable polymers was compiled and has been published: R. L. Miller and L. E. Nielsen, *J. Polymer Sci.* 44, 391 (1960). Copies are available from the authors who would be pleased to receive further data and/or references for inclusion in the table and to receive any comments on it. Address: Robert L. Miller, Research Department, Plastics Division, Monsanto Chemical Company, Springfield 2, Mass., U. S. A.

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