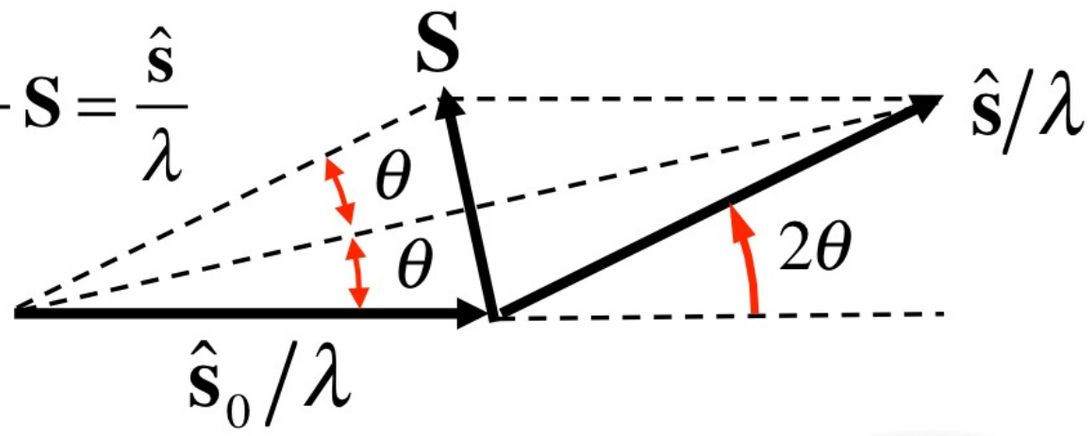
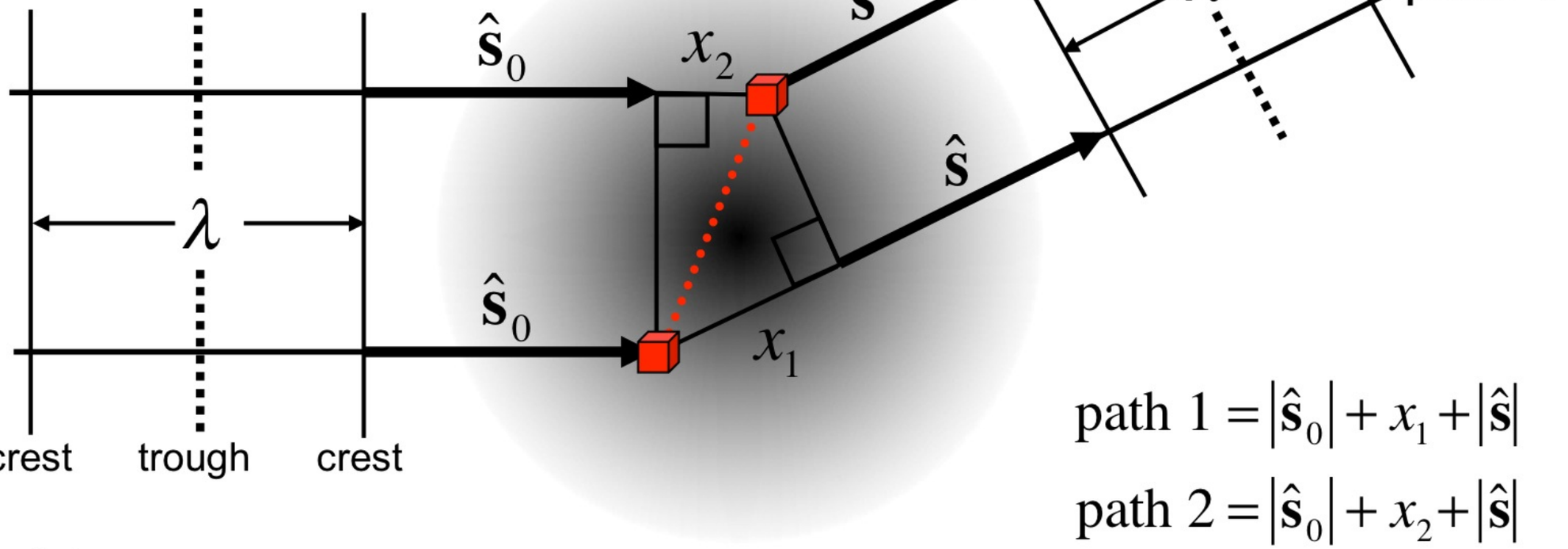
X-ray scattering by different volume elements of an atomic electron density distribution

θ Bragg angle

2θ scattering angle

$$\frac{\hat{\mathbf{s}}_0}{\lambda} + \mathbf{S} = \frac{\hat{\mathbf{s}}}{\lambda}$$





$$\left|\hat{\mathbf{s}}_0\right| = \left|\hat{\mathbf{s}}\right| = 1$$

$$\hat{\mathbf{s}}_0 \bullet \hat{\mathbf{s}} = \cos 2\theta$$

$$\mathbf{S} = \frac{\hat{\mathbf{s}} - \hat{\mathbf{s}}_0}{\lambda}, \qquad |\mathbf{S}| = 2\left(\frac{\sin\theta}{\lambda}\right)$$

$$\text{path } 1 = \left|\hat{\mathbf{s}}_0\right| + x_1 + \left|\hat{\mathbf{s}}\right|$$

$$\text{path } 2 = \left|\hat{\mathbf{s}}_0\right| + x_2 + \left|\hat{\mathbf{s}}\right|$$

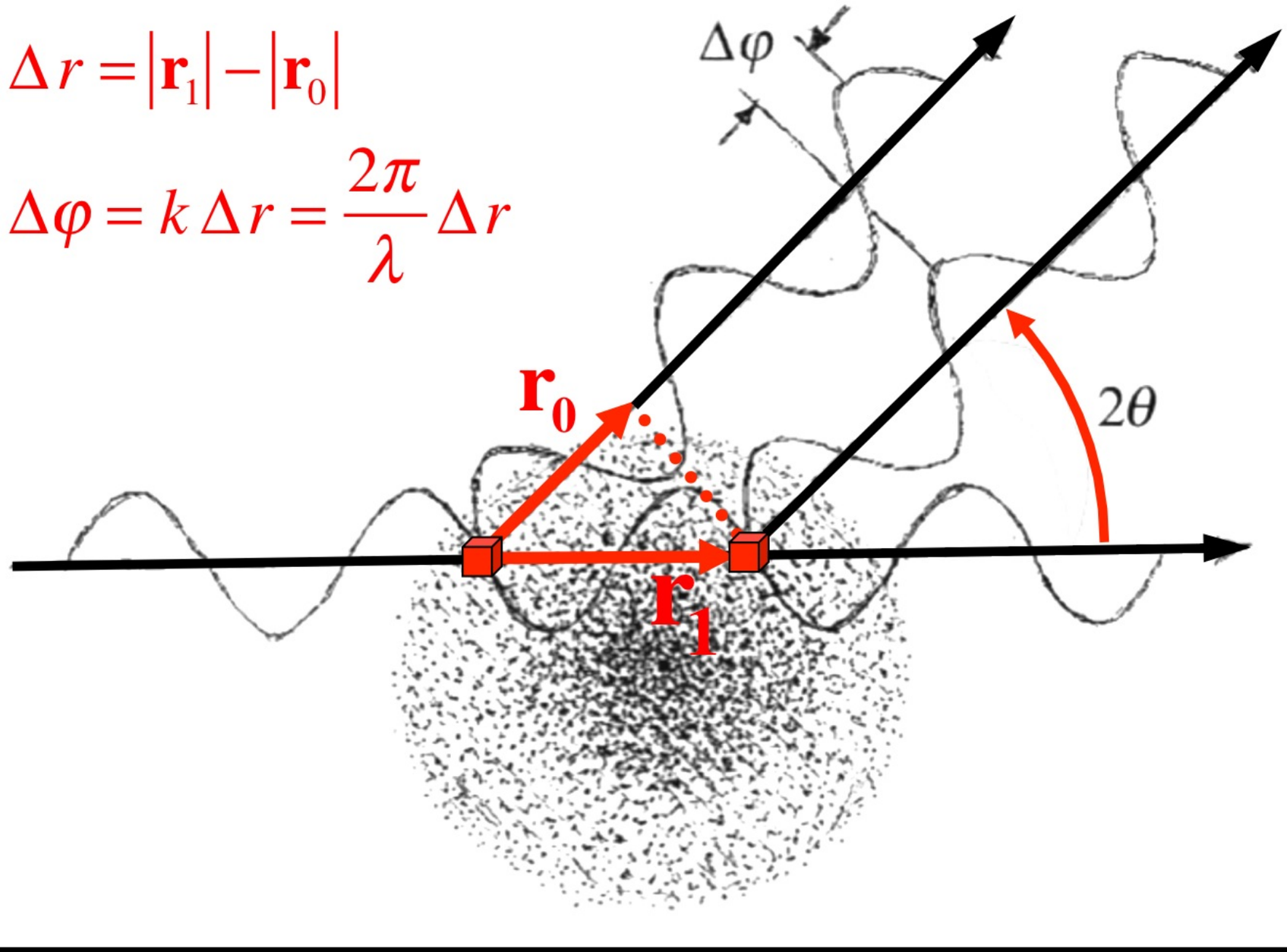
$$\text{path } 2 - \text{path } 1 = x_2 - x_1 = \Delta x$$

$$\Delta\varphi = k\Delta x = \frac{2\pi}{\lambda}\Delta x$$

Phase differences due to scattering from different volume elements of an atomic electron density distribution

$$\Delta r = |\mathbf{r}_1| - |\mathbf{r}_0|$$

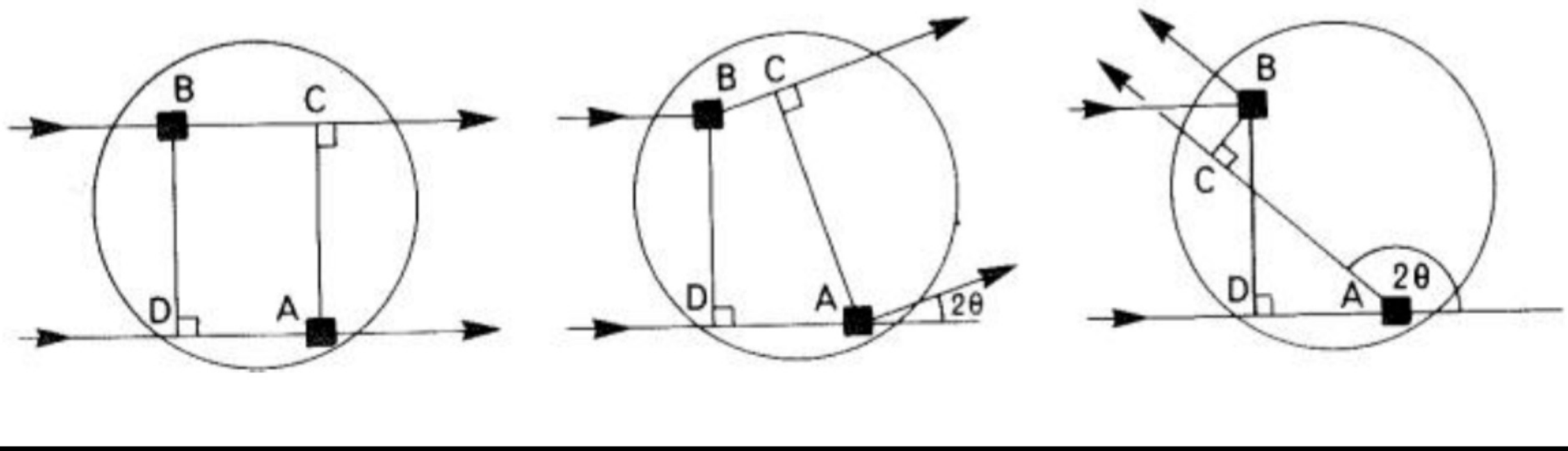
$$\Delta\varphi = k\,\Delta r = \frac{2\pi}{\lambda}\Delta r$$



Since X-ray wavelengths are comparable to atomic diameters, interference effects due to the differences in path lengths to and from each volume element of the atomic electron density distribution are responsible for the approximately Gaussian falloff of atomic scattering factors with increasing scattering angle.

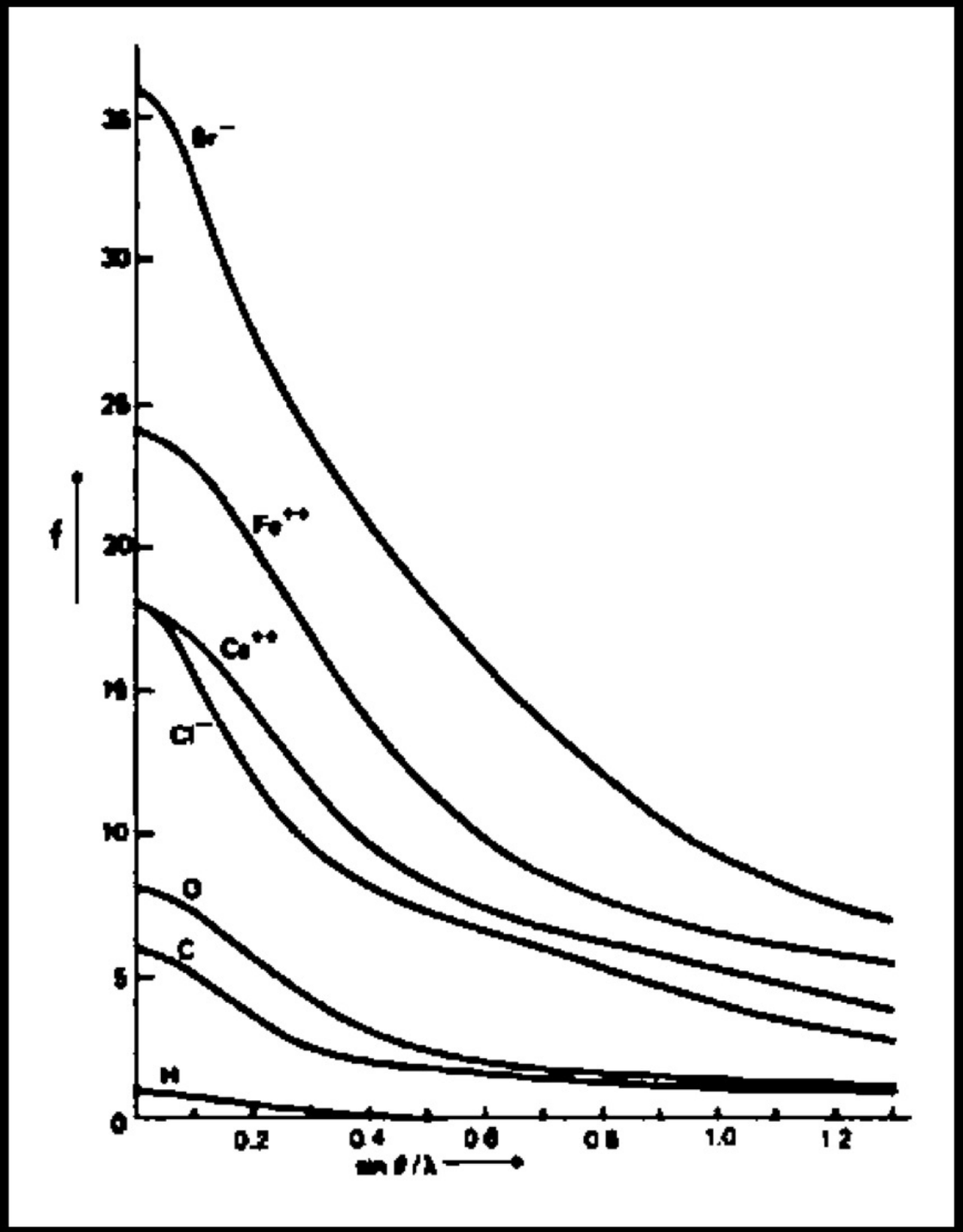
Figure adapted from Harold P. Klug and Leroy E. Alexander (1974). X-Ray Diffraction Procedures for Polycrystalline and Amorphous Materials. New York: John Wiley.

Scattering factor *versus* scattering angle



The higher the scattering angle,
the greater the difference between wave path lengths
the greater the destructive wave interference,
the greater the scattering factor fall-off with scattering angle

Scattering factor *versus* scattering angle



The atomic scattering factor $f_a(S)$ is roughly proportional to the atomic number Z_a.

At $S = (\sin\theta)/\lambda = 0$, $f_a(0) = Z_a$

http://www.xtal.iqfr.csic.es/Cristalografia/archivos_05/fac_scat3.jpg

Atomic Scattering Factors for X-rays

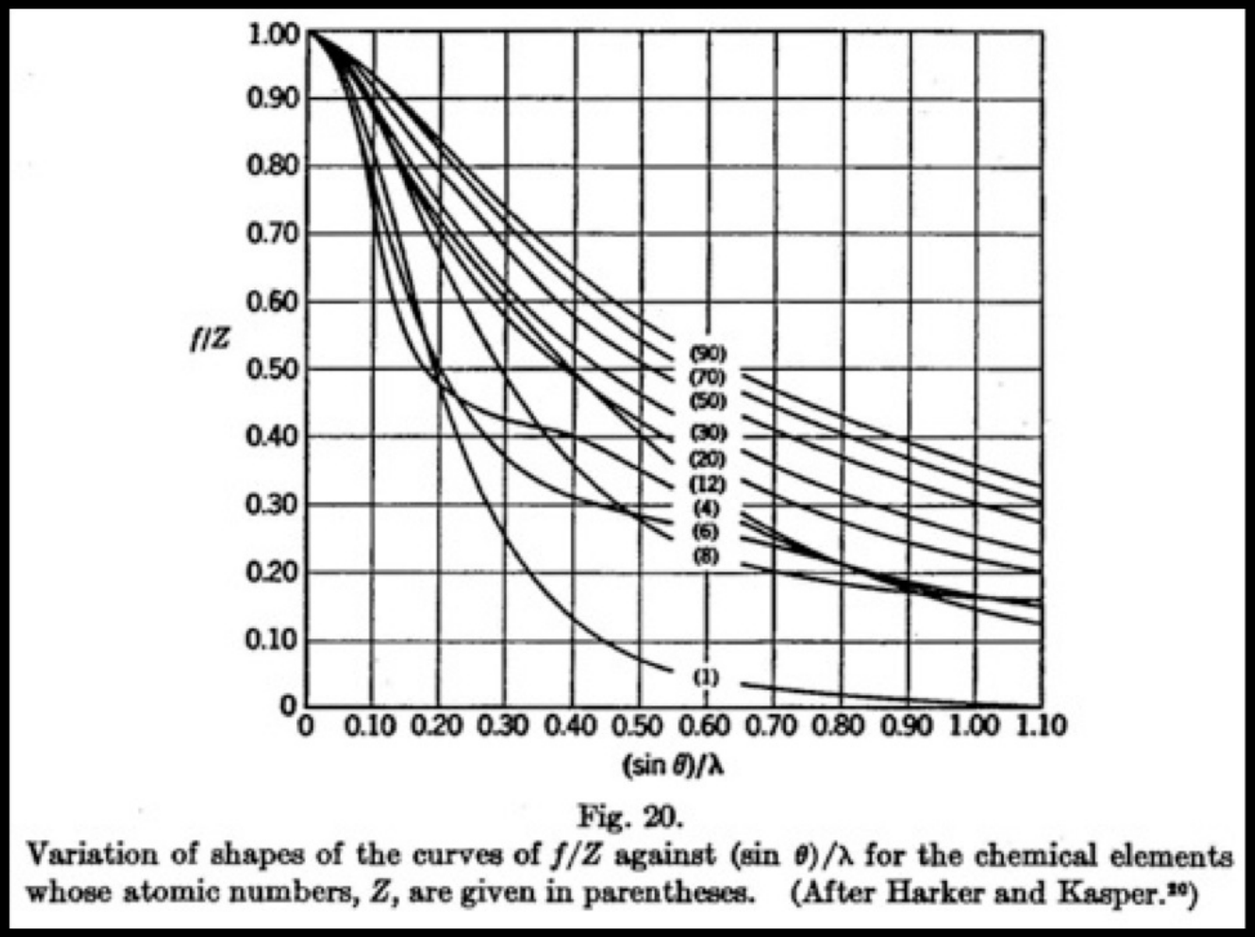


Fig. 20.
Variation of shapes of the curves of f/Z against $(\sin\theta)/\lambda$ for the chemical elements whose atomic numbers, Z, are given in parentheses. (After Harker and Kasper.[20])

Buerger (1960).

The "humps" or ripples in the f-curves for Z = 6 and Z = 4 occur because the $_4$Be $2s^2$ L-valence shell is filled and the $_6$C $2s^22p^2$ L-valence shell is half-filled. When a valence shell is filled or half-filled there is a slight real-space expansion of the outer, valence-shell electron density $\rho_v(r)$ and therefore a reciprocal-space contraction of the low-angle, valence-shell scattering factor curve $f_v(S) = \mathcal{F}^{-1}\left[\rho_v(r)\right]$.

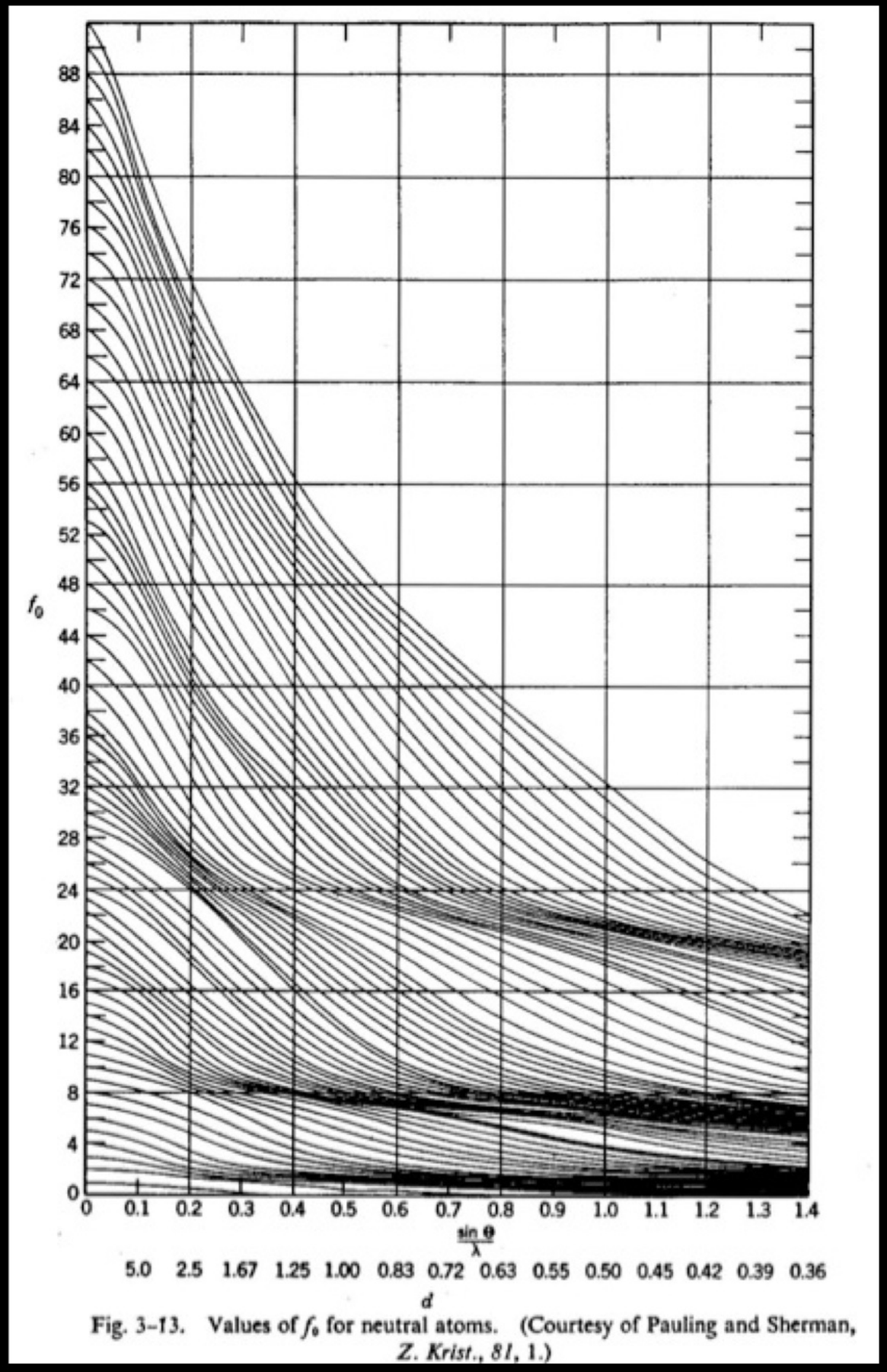
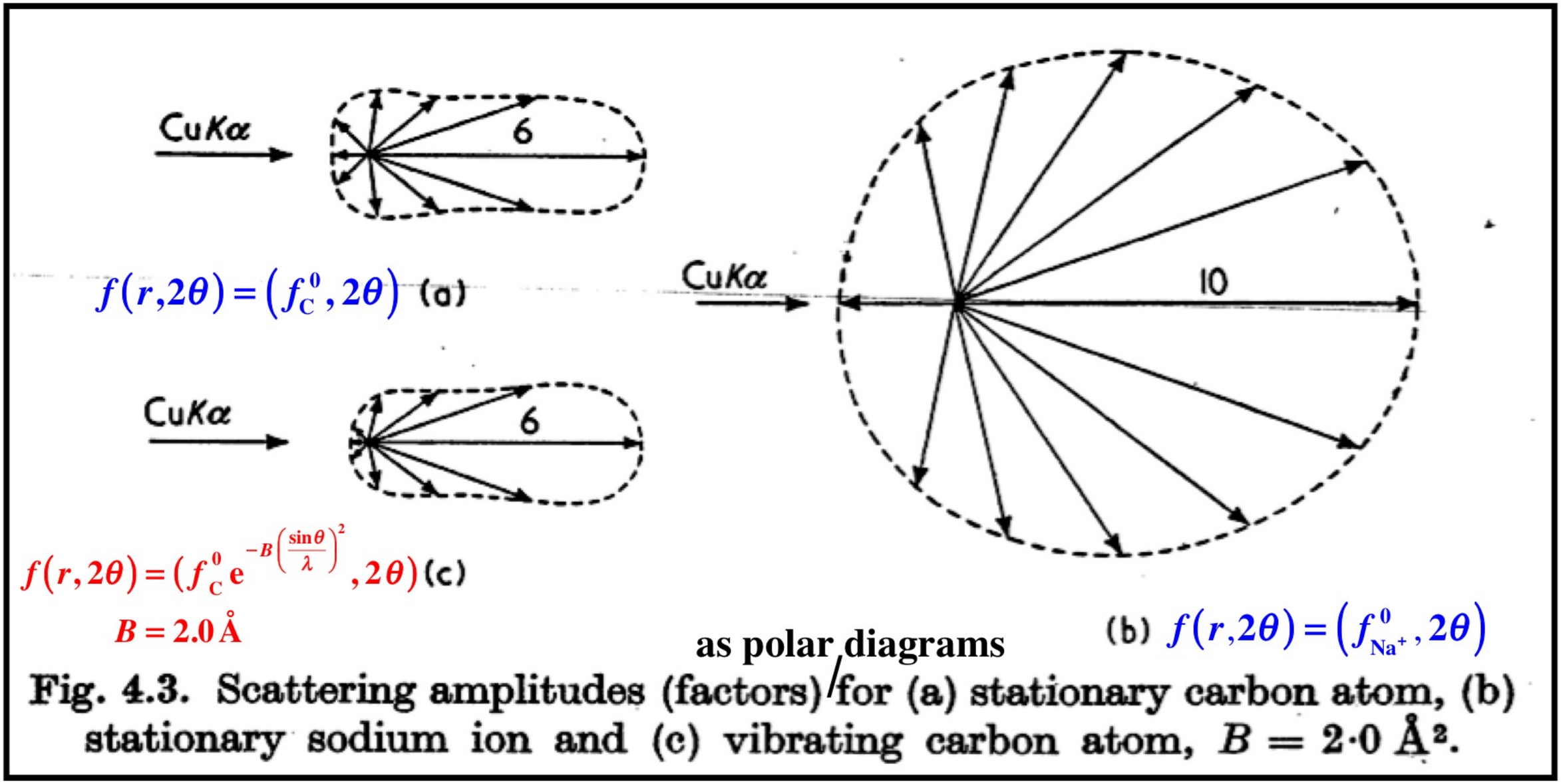


Fig. 3–13. Values of f_0 for neutral atoms. (Courtesy of Pauling and Sherman, *Z. Krist.*, *81*, 1.)

Klug & Alexander (1974).

Polar Plots of Atomic X-ray Scattering Factors versus scattering angle



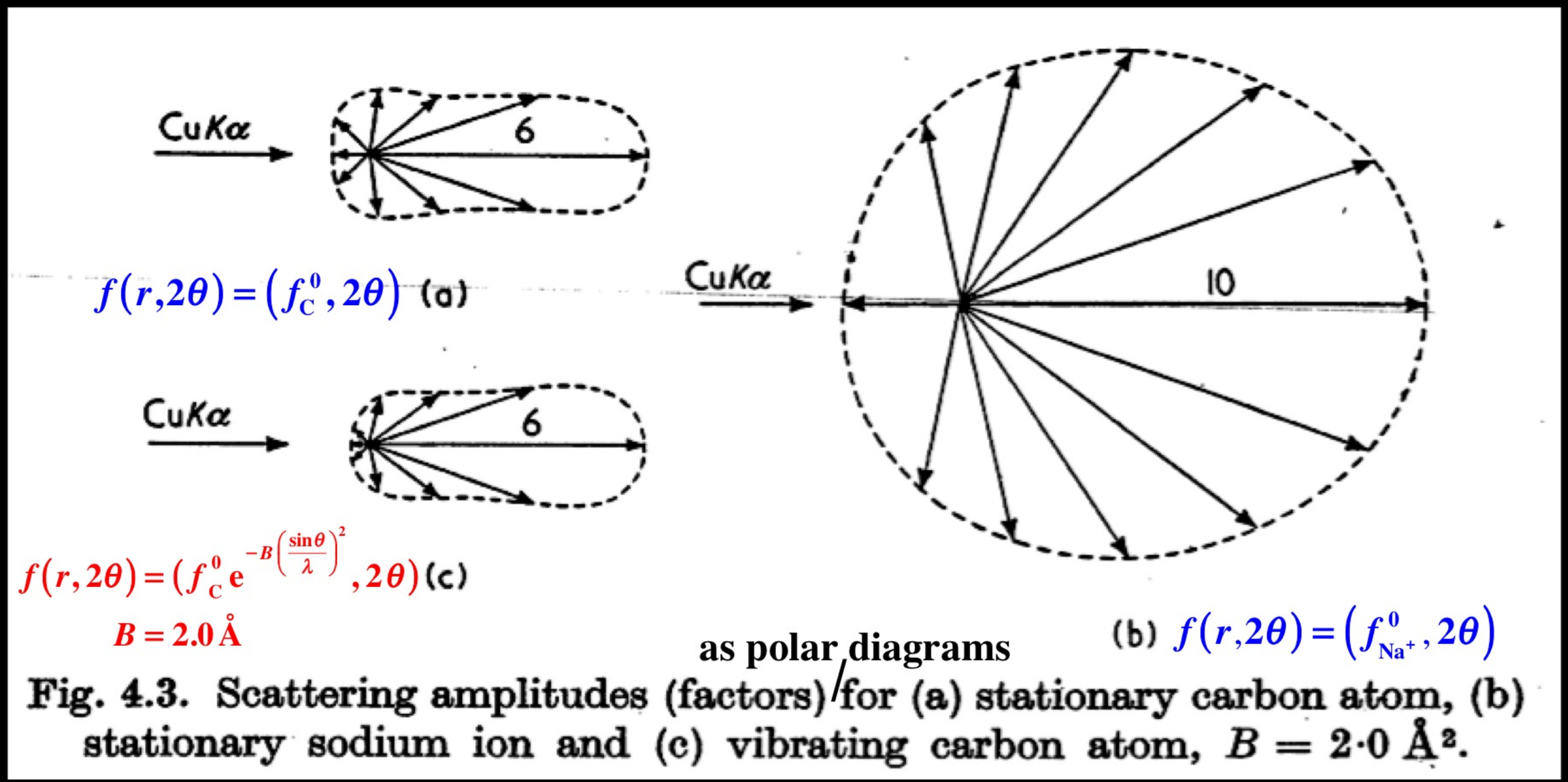
as polar diagrams

Fig. 4.3. Scattering amplitudes (factors) for (a) stationary carbon atom, (b) stationary sodium ion and (c) vibrating carbon atom, $B = 2{\cdot}0$ Å^2.

Due to interference effects among waves scattered from different volume elements of the atomic electron density distribution, the amplitude of scattering decreases with increasing scattering angle.

S.C. Nyburg (1961). X-Ray Analysis of Organic Structures. New York: Academic Press.

Polar Plots of Atomic X-ray Scattering Factors versus scattering angle



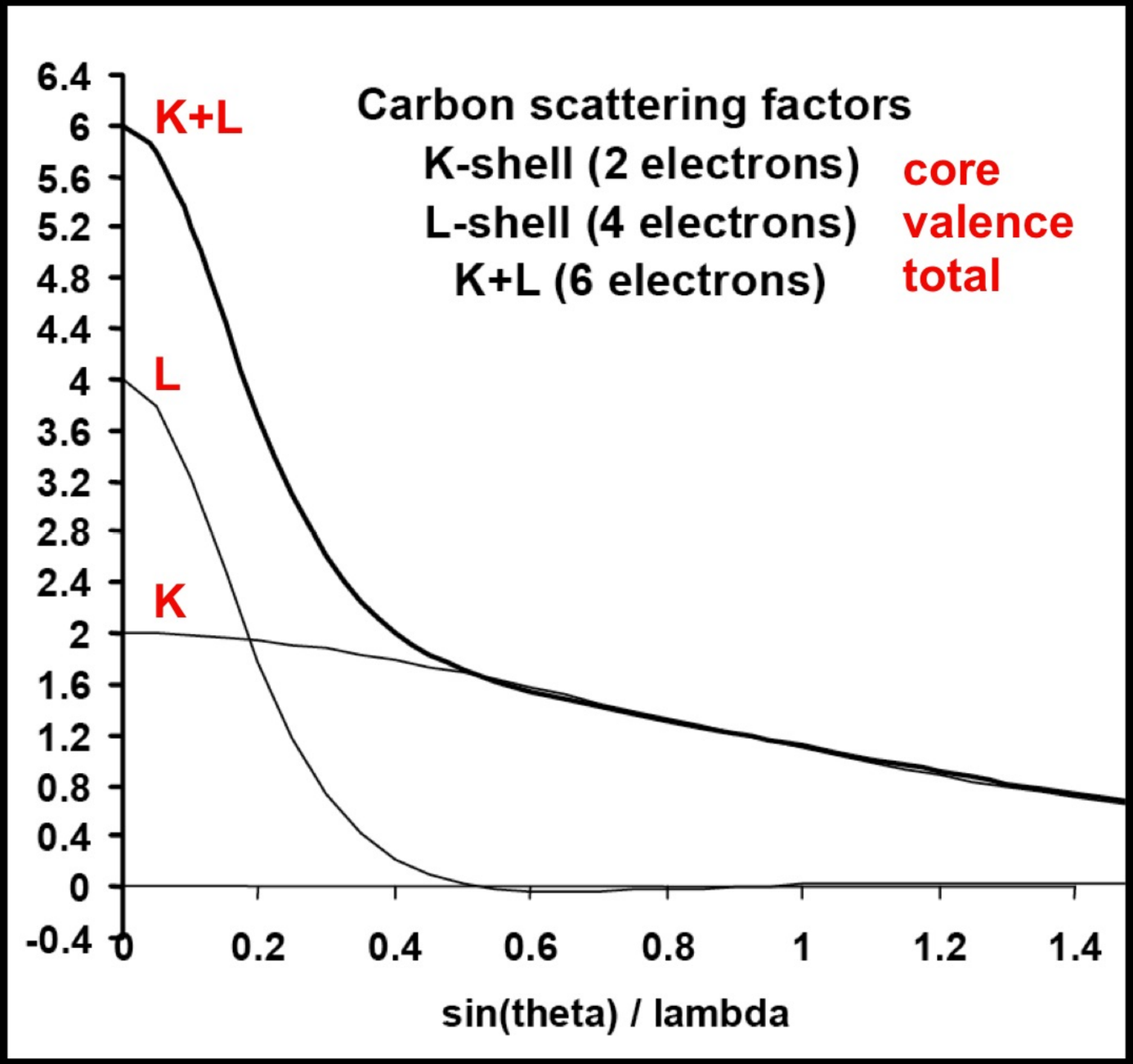
as polar diagrams

Fig. 4.3. Scattering amplitudes (factors) for (a) stationary carbon atom, (b) stationary sodium ion and (c) vibrating carbon atom, $B = 2{\cdot}0$ Å^2.

Due to interference effects among waves scattered from different volume elements of the atomic electron density distribution, the amplitude of scattering decreases with increasing scattering angle.

S.C. Nyburg (1961). X-Ray Analysis of Organic Structures. New York: Academic Press.

Carbon atom scattering from different electron shells



For carbon, the four-electron valence shell (L-shell) scattering is negligible for $(\sin\theta)/\lambda > 0.5$ Å^{-1}, $d_{min} < 1$ Å .

The two-electron inner shell (K-shell) scattering extends well beyond $(\sin\theta)/\lambda = 1.4$ Å^{-1} , $d_{min} < 0.36$ Å .

Radial electron density and scattering factor curves for K^+ [Ar] $1s^2 2s^2 2p^6 3s^2 3p^6$ subshells

$U(r) = 4\pi r^2 |R(r)|^2$ subshell curves

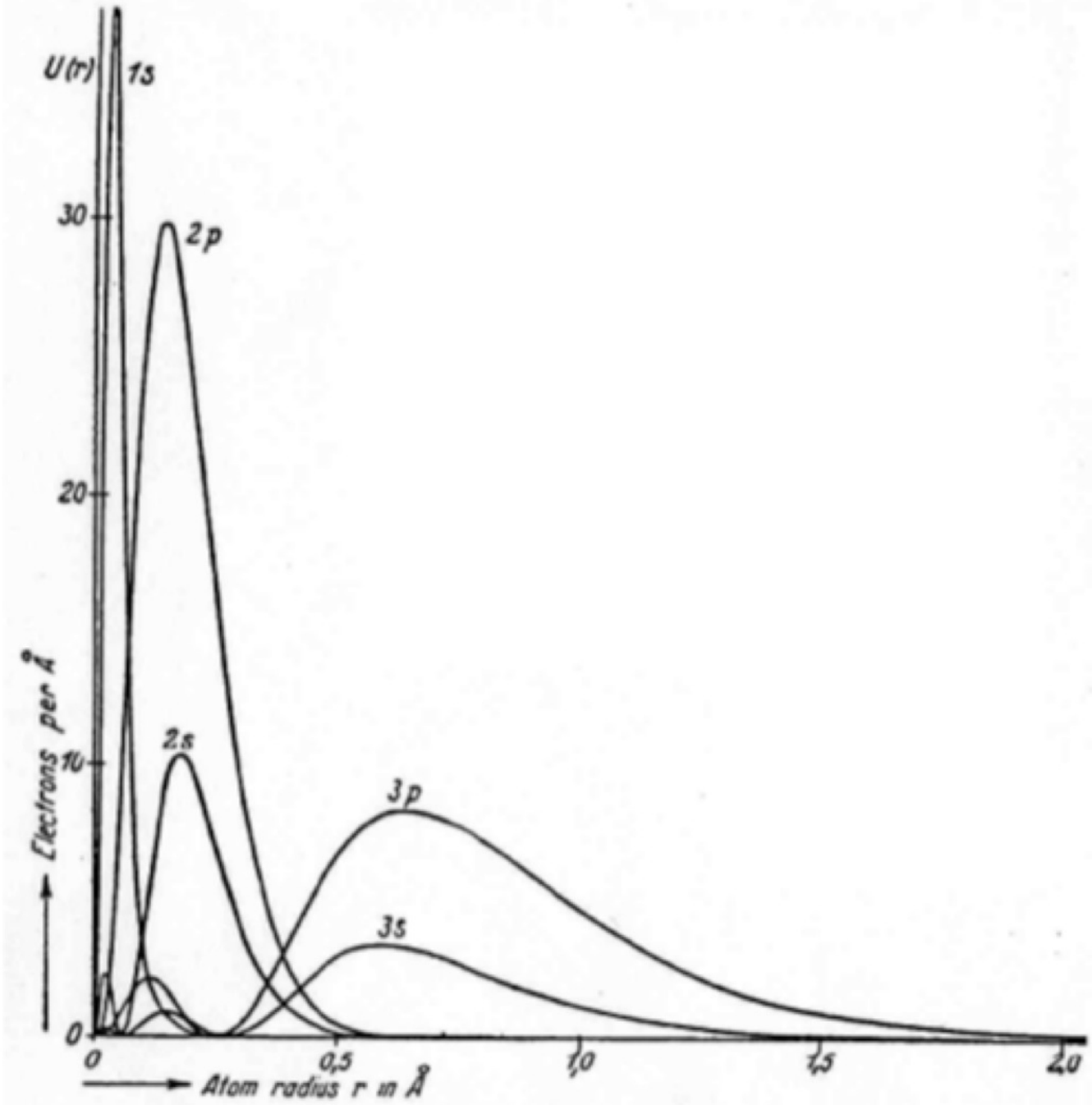


FIG. 43. Radial charge distribution for the different electron groups of K^+
(James, *Ergebnisse der technischen Röntgenkunde*, vol. III, 1933)

$f(S) = \int_0^\infty U(r) \frac{\sin(2\pi Sr)}{2\pi Sr} dr$ subshell curves

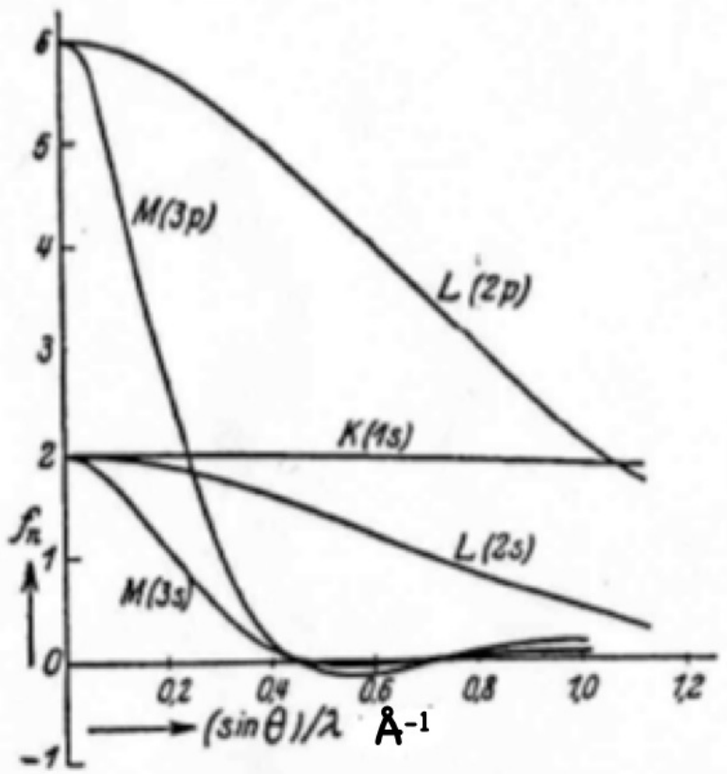


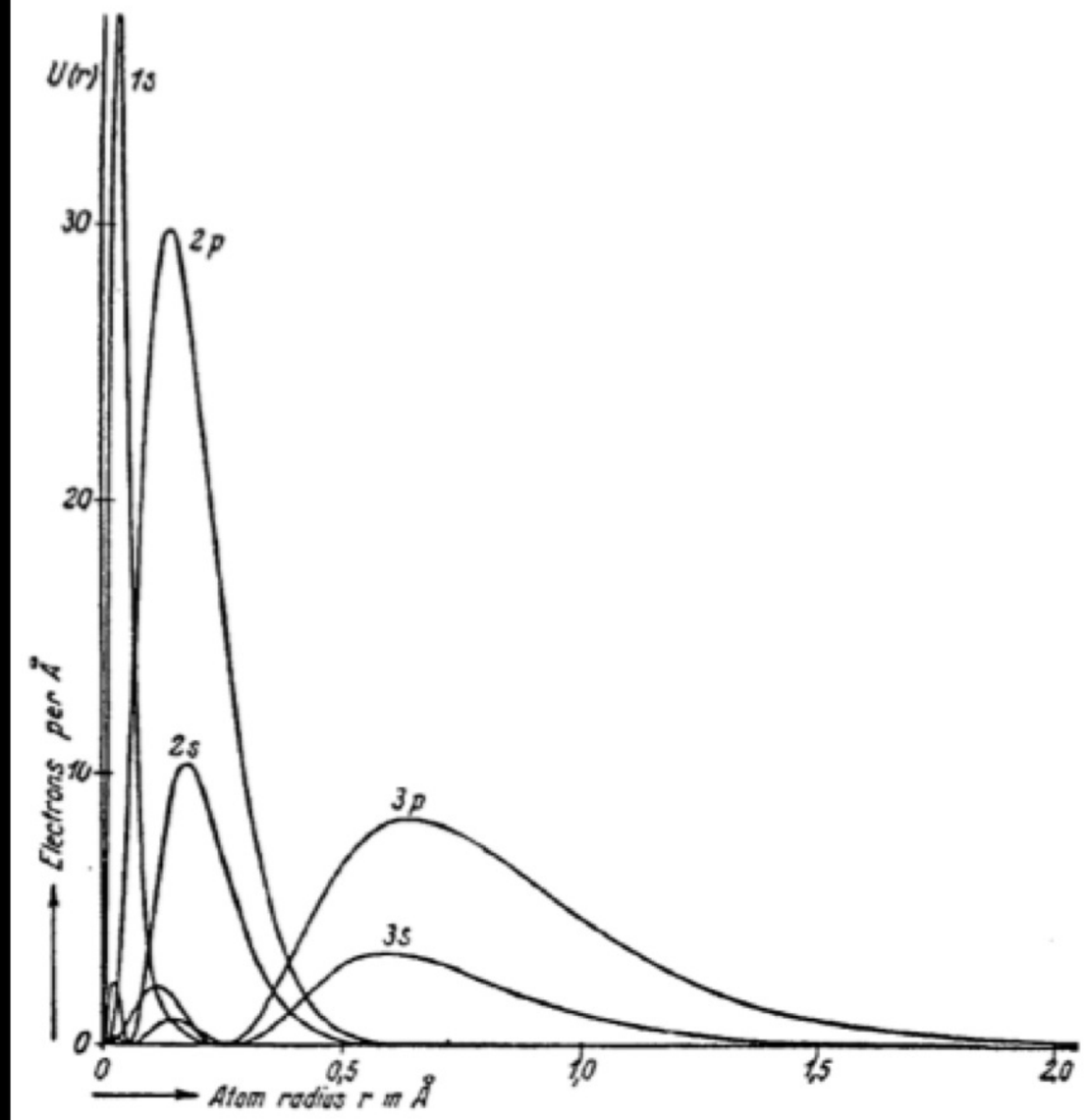
FIG. 48. *f*-curves for the individual electron groups of K^+
(James, *Ergebnisse der technischen Röntgenkunde*, vol. III, 1933)

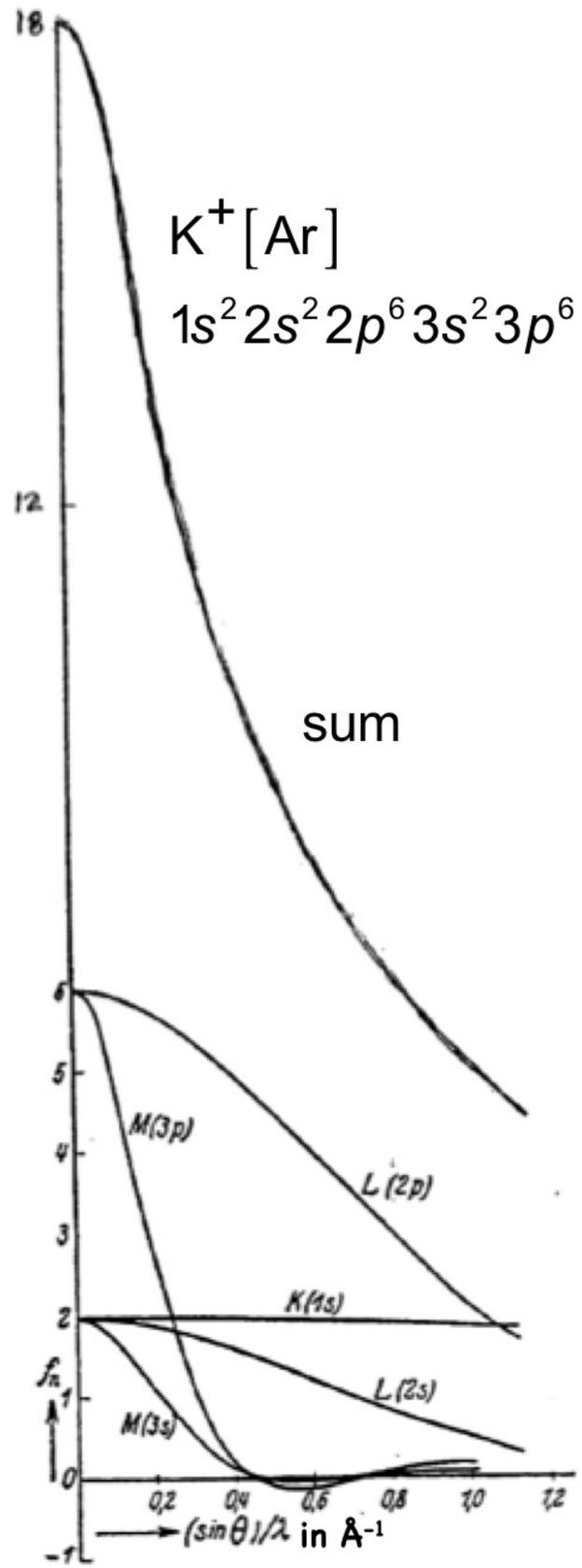
Figures copied from R.W. James, (1982). The *Optical Principles of the Diffraction of X-Rays.* Woodbridge, Connecticut: Ox Bow Press.

Radial electron density and scattering factor curves

$$f(S) = \mathcal{F}^{-1}\left[\rho(r)\right]$$

$$\begin{cases} \rho(r) = 4\pi r^2 \left|R(r)\right|^2 \\ f(S) = \int_0^\infty \rho(r)\dfrac{\sin(2\pi Sr)}{2\pi Sr}\,\mathrm{d}r \end{cases}$$





Figures copied and adapted from James (1982).

Tables of Atomic Scattering Factors

Table 2.2 A, p. 72, vol. IV, ITXC

TABLE 2.2A

Mean Atomic Scattering Factors in Electrons for Free Atoms and Chemically Significant Ions

Element Z Method†	H 1 HF	H^{-1} 1 HF	He 2 RHF	Li 3 RHF	Li^{+1} 3 RHF	Be 4 RHF	Be^{+2} 4 RHF
$(\sin\theta)/\lambda$							
0.00	1.000	2.000	2.000	3.000	2.000	4.000	2.000
.01	.998	1.986	1.998	2.986	1.999	3.987	2.000
.02	.991	1.946	1.993	2.947	1.997	3.950	1.999
.03	.980	1.883	1.984	2.884	1.994	3.889	1.997
.04	.966	1.802	1.972	2.802	1.990	3.807	1.995
.05	.947	1.708	1.957	2.708	1.984	3.707	1.992
.06	.925	1.606	1.939	2.606	1.977	3.592	1.988
.07	.900	1.501	1.917	2.502	1.968	3.468	1.983
.08	.872	1.396	1.893	2.400	1.959	3.336	1.978
.09	.842	1.293	1.866	2.304	1.948	3.201	1.973
.10	.811	1.195	1.837	2.215	1.936	3.065	1.966
.11	.778	1.102	1.806	2.135	1.923	2.932	1.959
.12	.744	1.014	1.772	2.065	1.909	2.804	1.952
.13	.710	.933	1.737	2.004	1.894	2.683	1.944
.14	.676	.858	1.701	1.950	1.878	2.569	1.935
.15	.641	.789	1.663	1.904	1.861	2.463	1.925
.16	.608	.725	1.624	1.863	1.843	2.365	1.915
.17	.574	.667	1.584	1.828	1.824	2.277	1.905
.18	.542	.613	1.543	1.796	1.804	2.197	1.894
.19	.511	.565	1.502	1.768	1.784	2.125	1.882
.20	.481	.520	1.460	1.742	1.762	2.060	1.870

$$\left(\frac{\sin\theta}{\lambda}\right)_{\max} = \frac{1}{\lambda} = \begin{cases} 1.41\ \text{Å}^{-1} \text{ for Mo K}\alpha \\ 0.65\ \text{Å}^{-1} \text{ for Cu K}\alpha \end{cases}$$

HF = nonrelativisitic Hartree-Fock Calculation
RHF = relativistic Hartree-Fock Calculation
DS = Dirac-Slater Calculation
SDS = Stewart, Davidson & Simpson Calculation

Analytical Approximation for the Scattering Factors

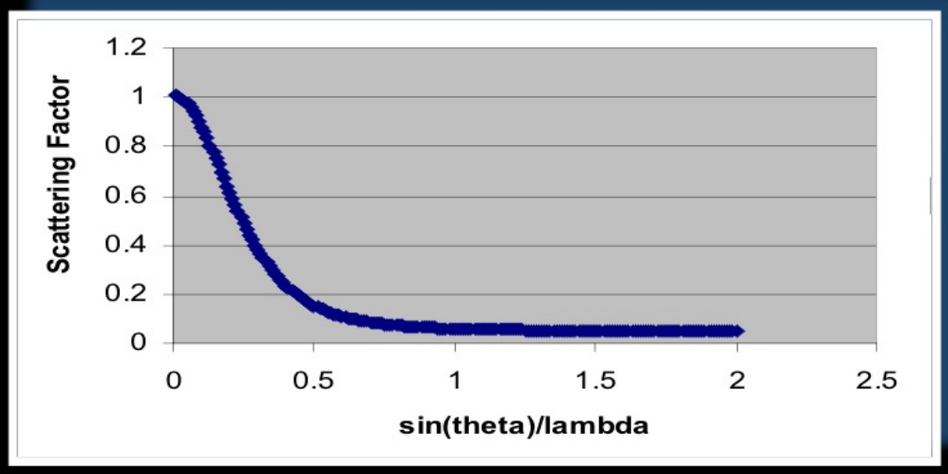
Table 2.2B, p. 99, vol. IV, ITXC.

TABLE 2.2B

Coefficients for Analytical Approximation to the Scattering Factors of Table 2.2A

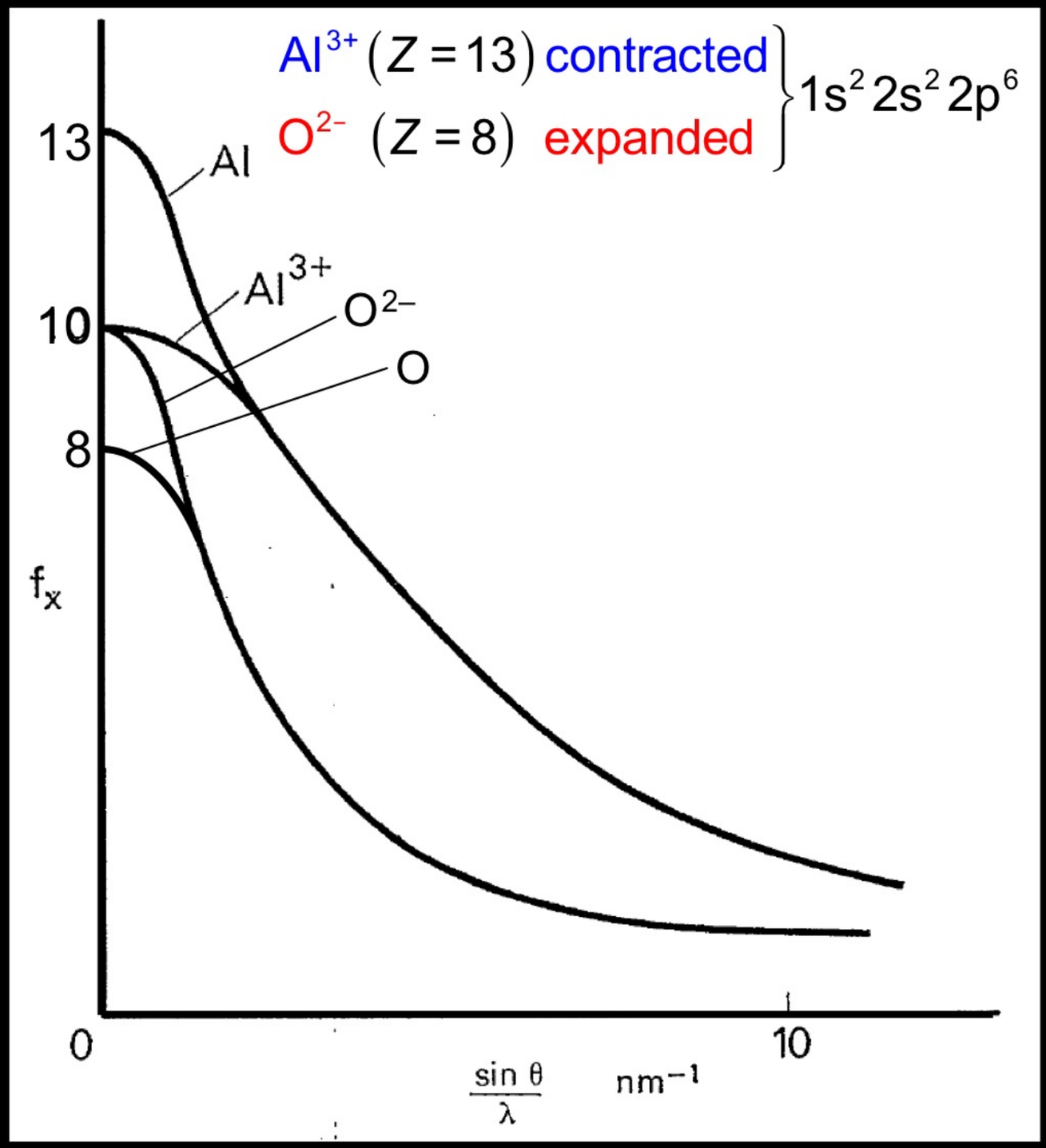
		a_1	b_1	a_2	b_2	a_3	b_3	a_4	b_4	c	Maximum Error	$\frac{\sin\theta}{\lambda}$	Mean Error
H	SDS	0.493002	10.5109	0.322912	26.1257	0.140191	3.14236	0.040810	57.7997	0.003038	0.000	0.00	0.000
H	HF	0.489918	20.6593	0.262003	7.74039	0.196767	49.5519	0.049879	2.20159	0.001305	0.000	0.17	0.000
H^{-1}	HF	0.897661	53.1368	0.565616	15.1870	0.415815	186.576	0.116973	3.56709	0.002389	0.002	0.09	0.001
He	RHF	0.873400	9.10370	0.630900	3.35680	0.311200	22.9276	0.178000	0.982100	0.006400	0.001	1.01	0.000
Li	RHF	1.12820	3.95460	0.750800	1.05240	0.617500	85.3905	0.465300	168.261	0.037700	0.005	2.00	0.001
Li^{+1}	RHF	0.696800	4.62370	0.788800	1.95570	0.341400	0.631600	0.156300	10.0953	0.016700	0.001	1.78	0.000
Be	RHF	1.59190	43.6427	1.12780	1.86230	0.539100	103.483	0.702900	0.542000	0.038500	0.003	0.56	0.001
Be^{+2}	RHF	6.26030	0.002700	0.884900	0.831300	0.799300	2.27580	0.164700	5.11460	-6.1092	0.001	1.97	0.000
B	RHF	2.05450	23.2185	1.33260	1.02100	1.09790	60.3498	0.706800	0.140300	-0.19320	0.002	0.75	0.001
C	RHF	2.31000	20.8439	1.02000	10.2075	1.58860	0.568700	0.865000	51.6512	0.215600	0.006	2.00	0.001
C_{val}	HF	2.26069	22.6907	1.56165	0.656665	1.05075	9.75618	0.839259	55.5949	0.286977	0.001	0.16	0.000
N	RHF	12.2126	0.005700	3.13220	9.89330	2.01250	28.9975	1.16630	0.582600	-11.529	0.007	0.11	0.002
O	RHF	3.04850	13.2771	2.28680	5.70110	1.54630	0.323900	0.867000	32.9089	0.250800	0.001	0.22	0.000
O^{-1}	HF	4.19160	12.8573	1.63969	4.17236	1.52673	47.0179	-20.307	-0.01404	21.9412	0.011	1.50	0.004
F	RHF	3.53920	10.2825	2.64120	4.29440	1.51700	0.261500	1.02430	26.1476	0.277600	0.001	0.01	0.000
F^{-1}	HF	3.63220	5.27756	3.51057	14.7353	1.26064	0.442258	0.940706	47.3437	0.653396	0.003	0.09	0.001
Ne	RHF	3.95530	8.40420	3.11250	3.42620	1.45460	0.230600	1.12510	21.7184	0.351500	0.002	0.25	0.001
Na	RHF	4.76260	3.28500	3.17360	8.84220	1.26740	0.313600	1.11280	129.424	0.676000	0.009	0.13	0.002
Na^{+1}	RHF	3.25650	2.66710	3.93620	6.11530	1.39980	0.200100	1.00320	14.0390	0.404000	0.001	0.70	0.000
Mg	RHF	5.42040	2.82750	2.17350	79.2611	1.22690	0.380800	2.30730	7.19370	0.858400	0.015	0.08	0.003

$$f\left(\frac{\sin\theta}{\lambda}\right) = \sum_{i=1}^{4} a_i \exp\left(-b_i \frac{\sin^2\theta}{\lambda^2}\right) + c$$



For cations $\rho(r)$ contracts and $f(S)$ expands.

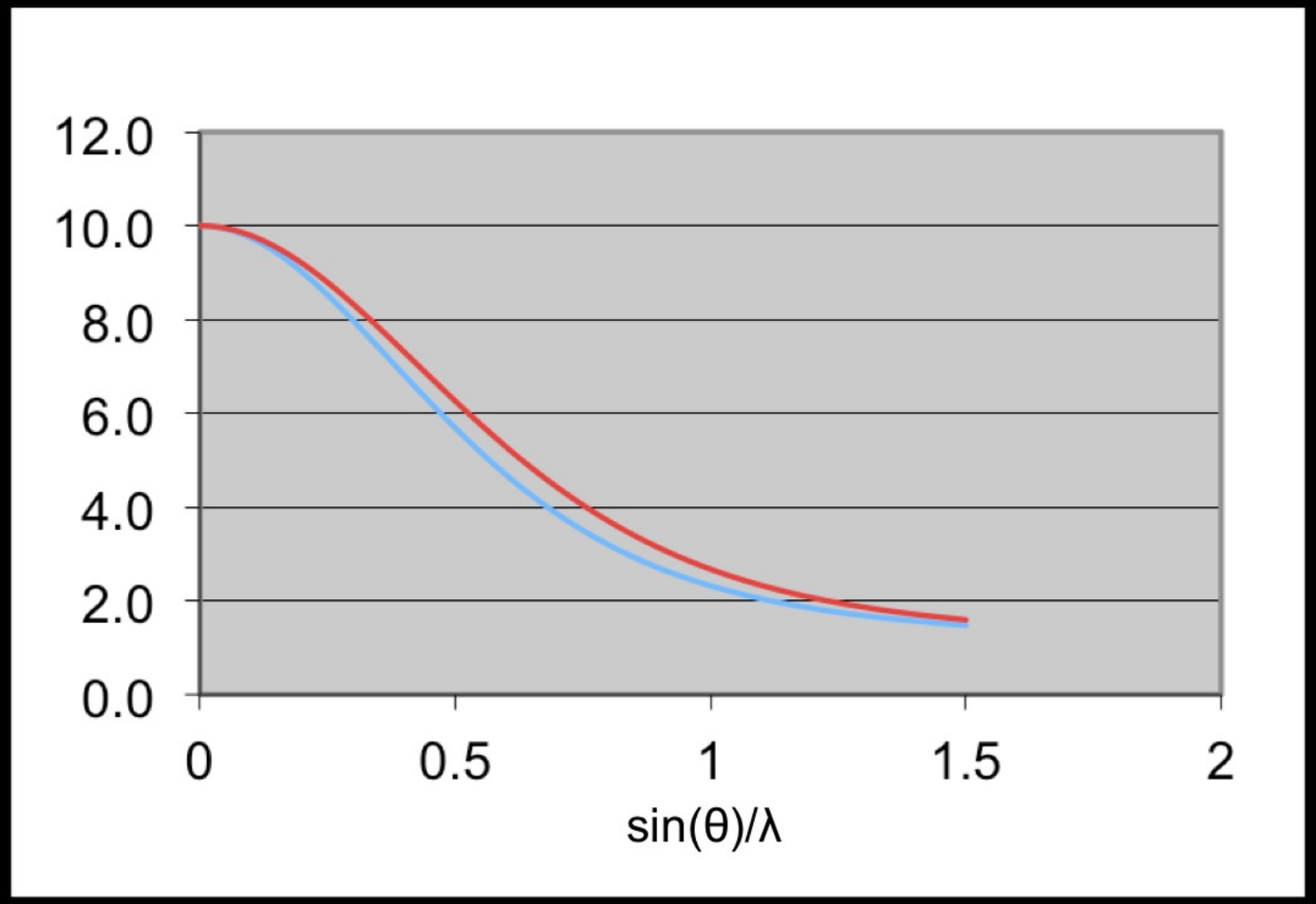
For anions $\rho(r)$ expands and $f(S)$ contracts.



C.J. Ball (1971). An introduction to the theory of diffraction. New York: Pergamon Press.

Scattering factors for Al^{3+} versus Si^{4+}

isoelectronic
Al^{3+} ion
Si^{4+} ion
$[Ar]1s^22s^22p^6$



The Al^{3+} and Si^{4+} scattering factors are nearly identical!

It is very difficult to distinguish between Al^{3+} and Si^{4+} with X-rays!

X-ray diffraction is not always a good elemental analysis technique.
It determines only electron density, NOT atomic identity!

Debye-Waller Factors

$$
\left\{
\begin{aligned}
F_{\mathbf{h}} &= \sum_{a=1}^{N} f_a(\mathbf{h})\, D_a(\mathbf{h}) \exp\left(2\pi i \mathbf{h}\bullet\langle \mathbf{r}_a \rangle\right) \\
D_a(\mathbf{h}) &= \mathcal{F}^{-1}\left[p(\mathbf{u}_a)\right], \qquad \mathbf{u}_a = \mathbf{r}_a - \langle \mathbf{r}_a \rangle \\
& \qquad\qquad\qquad\qquad 0 \le |\mathbf{h}| < \infty \\
f_a(\mathbf{h}) &= \mathcal{F}^{-1}\left[\rho_a(\mathbf{r})\right] \qquad\qquad Z_a \ge f_a > 0 \\
D_a(\mathbf{h}) &= \mathcal{F}^{-1}\left[p(\mathbf{u}_a)\right] \qquad\qquad 1 \ge D_a > 0 \\
f_a(\mathbf{h})\, D_a(\mathbf{h}) &= \mathcal{F}^{-1}\left[\rho_a(\mathbf{r}) * p(\mathbf{u}_a)\right]
\end{aligned}
\right\}
$$

If the *distribution of atomic displacements due to thermal vibration, and possibly also disorder,* is *Gaussian* (as indeed it is for harmonic vibration), then

$$
D_a(\mathbf{h}) = \exp\left[-2\pi^2 \left\langle \left(\mathbf{u}_a \bullet \mathbf{h}\right)^2 \right\rangle\right] = \exp\left[-2\pi^2 \left\langle \left(\mathbf{u}_a \bullet \frac{\mathbf{h}}{|\mathbf{h}|}\right)^2 |\mathbf{h}|^2 \right\rangle\right] = \exp\left(-2\pi^2 \frac{\langle u_a^2 \rangle_{\mathbf{h}}}{d_{\mathbf{h}}^2}\right),
$$

where

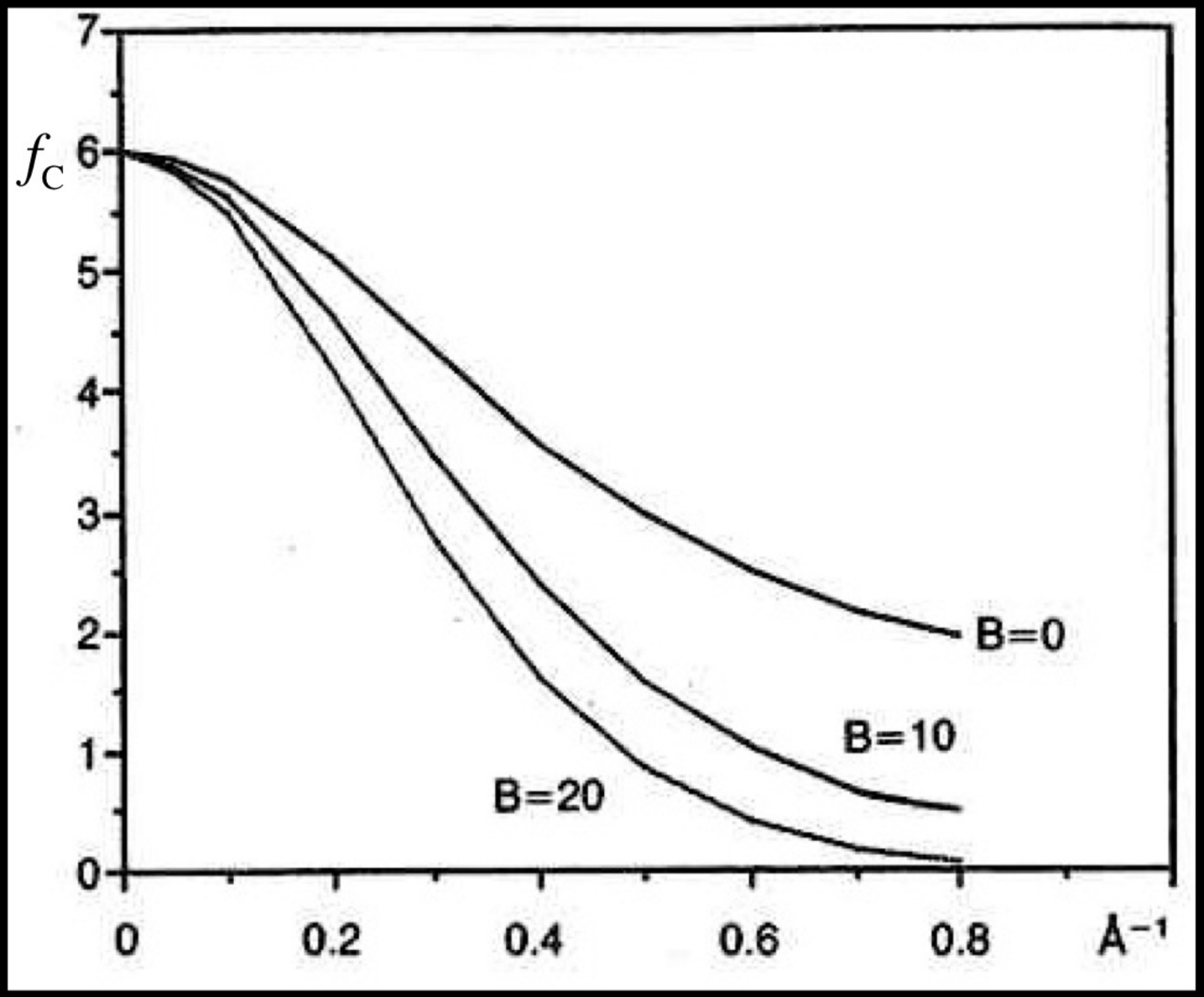
$$
|\mathbf{h}| = \frac{1}{d_{hkl}} = 2\left(\frac{\sin\theta_{hkl}}{\lambda}\right),
$$

and $\langle u_a^2 \rangle_{\mathbf{h}}$ is the mean-square value of the displacement of atom a projected onto the direction of the reciprocal lattice vector $\mathbf{h}$, i.e., the mean-square displacement of atom a perpendicular to the diffracting planes hkl. If the displacements are isotropic, the Debye-Waller parameter is commonly denoted by B_a such that

$$
D_a(\mathbf{h}) = \exp\left[-B_a\left(\frac{\sin\theta_{hkl}}{\lambda}\right)^2\right], \qquad B_a = 8\pi^2 \langle u_a^2 \rangle .
$$

Carbon atom scattering factors attenuated by the Debye-Waller factor

Direct-space smearing, i.e., expansion of ρ (r) results in reciprocal-space contraction of f (S).



$$f_C = f_C^0 \exp\left[-B\left(\frac{\sin\theta}{\lambda}\right)^2\right]$$

$B = 8\pi^2\langle u^2\rangle$	$\langle u^2\rangle$	$\langle u^2\rangle^{1/2}$
10 Å^2	0.13 Å^2	0.36 Å
20	0.25	0.50

$$8\pi^2 \approx 80$$

$$d^* = \frac{1}{d} = 2\left(\frac{\sin\theta}{\lambda}\right)$$