

## For a Polyatomic Crystal

(108)

must consider the atomic form factor, along with the geometric structure factor, to describe diffraction

$$\Rightarrow S_{\mathbf{K}} = \sum_{j=1}^n f_j(\mathbf{K}) e^{i\mathbf{K} \cdot \mathbf{d}_j}$$

$$f_j(\mathbf{K}) = \frac{1}{e} \int d\vec{r} e^{i\mathbf{K} \cdot \vec{r}} \rho_j(\vec{r})$$

= a measure of the scattering "power" of the  $j^{\text{th}}$  atom  
 $\rho_j(\vec{r})$  is the charge density in the unit cell

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Classical calculation of  $f_j(\mathbf{K})$

let  $\alpha$  be the angle between  $\mathbf{K}$  and  $\vec{r}$

$$\Rightarrow f_j(\mathbf{K}) = \frac{1}{e} \int dr r^2 e^{iKr \cos \alpha} \rho_j(r) \sin \alpha d\alpha$$

$$d\vec{r} = 2\pi r^2 dr \sin \alpha d\alpha$$

$$= -2\pi r^2 dr d(\cos \alpha)$$

$$= \frac{2\pi}{e} \int dr r^2 e^{iKr \cos \alpha} \rho_j(r) d(\cos \alpha)$$

$d(\cos \alpha)$  ranges from  $-1 \rightarrow 1$

~~$$= \frac{1}{e} \int dr r^2 e^{iKr} \rho_j(r)$$~~

$$\begin{aligned}
 f_j(\vec{K}) &= \int d\vec{r} \rho_j(\vec{r}) e^{i\vec{K}\cdot\vec{r}} \\
 &= \frac{2\pi}{e} \int dr r^2 \rho_j(r) \int_{-1}^1 e^{iKr(\cos\alpha)} d(\cos\alpha) \\
 &= \frac{2\pi}{e} \int dr r^2 \rho_j(r) \frac{e^{iKr} - e^{-iKr}}{iKr} \\
 &= \frac{4\pi}{e} \int dr r^2 \rho_j(r) \frac{e^{iKr} - e^{-iKr}}{2iKr}
 \end{aligned}$$

$$f_j(\vec{K}) = \frac{4\pi}{e} \int dr r^2 \rho_j(r) \frac{\sin Kr}{Kr}$$

Interpretation

Suppose all the electron density was concentrated at  $r=0$

$\Rightarrow$  only  $Kr=0$  would contribute to the integrand

$$\Rightarrow \lim_{Kr \rightarrow 0} \frac{\sin Kr}{Kr} = \lim_{Kr \rightarrow 0} \frac{\cos Kr}{1} = 1$$

$$\Rightarrow f_j(\vec{K}) = \frac{4\pi}{e} \int dr r^2 \rho_j(r) = \frac{Q_{total}}{e} = Z,$$

$Z = \# \text{ of atomic electrons}$

$\Rightarrow f_j(\vec{K}) = \frac{\text{radiation amplitude scattered by actual electron distribution on an atom}}{\text{radiation amplitude scattered by one electron localized at a point}}$

# Practical Effects of the Atomic Form Factor (110)

Pt. #1: atomic form factors for ~~atoms~~ atoms (ions) in solids agree <sup>very</sup> closely with theoretical free atom values

Pt. #2: form factors are approximately proportional to the number of atomic electrons of the ion

⇒ two different ions of about the same number of electrons will have about the same  $f_j(\vec{K})$

example: KCl (rock salt structure)

K = atomic # 19

Cl = atomic # 17

but in KCl → K → K<sup>+</sup> & Cl → Cl<sup>-</sup>

⇒ K<sup>+</sup> has 18 electrons

Cl<sup>-</sup> has 18 electrons

⇒  $f_{K^+}(\vec{K}) \approx f_{Cl^-}(\vec{K})$  } almost identical atomic form factors (ionic)

Therefore, for KCl, it's like the rocksalt structure but with nearly identical scatterings from both  $K^+$  and  $Cl^-$

(111)

rocksalt: fcc + 2-atom basis

reciprocal lattice is bcc with

$$\vec{K} = \sum n_i \vec{b}_i$$

$$= \frac{4\pi}{a} \left[ \nu_1 \hat{x} + \nu_2 \hat{y} + \nu_3 \hat{z} \right]$$

$$\nu_i = \frac{1}{2} (n_1 + n_2 + n_3) - n_i \quad \left| \quad \sum_{i=1}^3 \nu_i = \frac{1}{2} (n_1 + n_2 + n_3) \right.$$

(same as for diamond case)

One can show that

$$f_{ic} = \begin{cases} f_+ + f_- & \nu_i = \text{integers} \\ f_+ - f_- & \nu_i = \text{integers} + \frac{1}{2} \end{cases}$$

One finds then that certain diffraction points "vanish" when  $f_+ = f_-$

One therefore expects to find certain peaks "missing" from the KCl diffraction

On the other hand, KBr is quite different,

$$K : Z = 19$$

$$Br : Z = 35$$

For KBr, those certain peaks will be present

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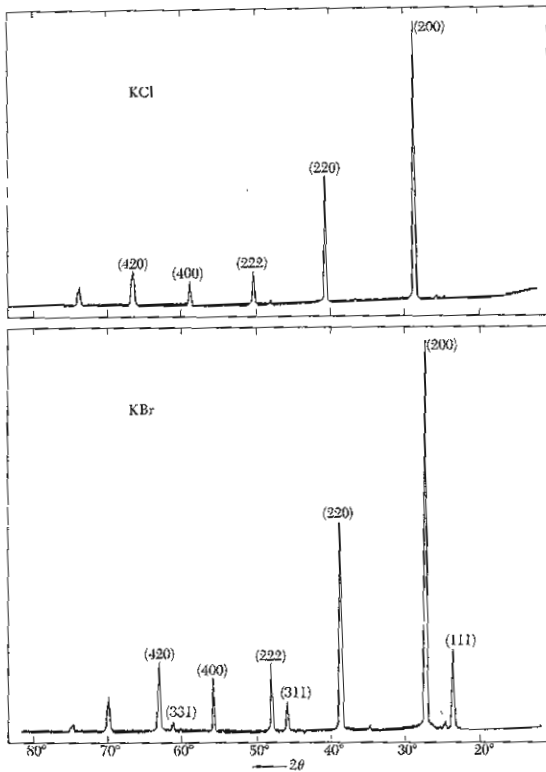


Figure 17 Comparison of x-ray reflections from KCl and KBr powders. In KCl the numbers of electrons of  $K^+$  and  $Cl^-$  ions are equal. The scattering amplitudes  $f(K^+)$  and  $f(Cl^-)$  are almost exactly equal, so that the crystal looks to x-rays as if it were a monatomic simple cubic lattice of lattice constant  $a/2$ . Only even integers occur in the reflection indices when these are based on a cubic lattice of lattice constant  $a$ . In KBr the form factor of  $Br^-$  is quite different than that of  $K^+$ , and all reflections of the fcc lattice are present. (Courtesy of R. van Nordstrand.)

- from Kittel, Intro. to Solid State Physics, Seventh Ed., p. 46