

The Scherrer equation versus the 'Debye-Scherrer equation'

To the Editor — X-ray diffraction is a convenient method for determining the mean size of single-crystal nanoparticles or crystallites in nanocrystalline bulk materials. The first scientist to investigate the effect of limited particle size on X-ray diffraction patterns was Paul Scherrer, who published his results in a paper that included what became known as the Scherrer equation¹. However, it seems to us that this equation is often erroneously referred to as the 'Debye-Scherrer equation'. (Indeed, strictly speaking, there is no Debye-Scherrer equation.) We would, therefore, like to recall some relevant historical facts to illuminate the origins of the Scherrer equation, and to assist authors in citing the appropriate equations and references in future work.

Between 1915 and 1917 Scherrer and his PhD supervisor, Peter Debye, worked together at the University of Göttingen to develop methods^{2,3} for analysing crystal structures using samples of fine powder. Their motivation was to avoid the problem of growing the large single crystals that were needed to use the methods developed by Max von Laue and the Braggs (William Henry and his son William Lawrence), and to facilitate the cumbersome data evaluation processes associated with these methods³. Their method, which was independently developed around the same time by Albert Hull⁴ at the General Electric Research Laboratory, became known as the Debye-Scherrer method. After Scherrer received his doctorate in 1916 (for a thesis on the Faraday effect of the hydrogen molecule), he continued to work on powder X-ray diffraction, publishing his landmark paper on the effect of crystallite size on the width of X-ray diffraction peaks in 1918.

Scherrer derived his equation for the ideal condition of a perfectly parallel,

infinitely narrow and monochromatic X-ray beam incident on a monodisperse powder of cube-shaped crystallites¹. The equation is $D_{hkl} = K\lambda/(B_{hkl}\cos\theta)$, where D_{hkl} is the crystallite size in the direction perpendicular to the lattice planes, hkl are the Miller indices of the planes being analysed, K is a numerical factor frequently referred to as the crystallite-shape factor⁵, λ is the wavelength of the X-rays, B_{hkl} is the width (full-width at half-maximum) of the X-ray diffraction peak in radians and θ is the Bragg angle. In addition to depending on the crystallite shape, the numerical factor K also depends on the definitions of the average crystallite size (for example, if the cube root of the crystallite volume is used instead of the definition above) and the width (for example, if the integral line width is used, as in von Laue's derivation of Scherrer's formula^{5,6}, rather than the full-width at half-maximum, which is usually easier to obtain from experimental data). The structure of the formula is not affected by these definitions, but the numerical value of K may change appreciably^{5,7}. Using the above definition of D_{hkl} , and in the absence of detailed shape information, $K = 0.9$ is a good approximation^{5,8}.

All improvements to Scherrer's original equation have essentially been refinements to K arising from more detailed analysis of the instrumental and non-instrumental factors that lead to broadening of the diffraction peak, such as experimental resolution, the shape and size distributions of the crystallites, and the effects of microstrain and defects^{5,7-9}. It is important to note that Scherrer's equation can only be applied for average sizes up to about 100–200 nm (depending on the instrument, sample and signal-to-noise ratio), because diffraction-peak broadening decreases with increasing crystallite size and it becomes

difficult to separate the peak broadening due to crystallite size from the broadening due to other factors.

When the Swiss Institute for Nuclear Research and the Federal Institute for Reactor Research were merged in 1988, the new institute was named the Paul Scherrer Institute, in recognition of his outstanding contributions to science. Debye is remembered, for example, through the Debye equations that describe frequency-dependent effects in dielectric materials, and also for the Debye theory of the specific heat capacity of solids. We hope that this correspondence will (where necessary) stimulate those working in the field to review the basic physics involved, to note the various factors that contribute to the broadening of X-ray diffraction peaks, to be aware of the practical limitations in applying Scherrer's equation and, of course, to cite Scherrer's 1918 paper where appropriate.

References

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