

measured as a function of temperature (Sections 6-5 and 7-2), the thermal expansion coefficient of the specimen can be determined by x-ray diffraction.

- The intensities of the diffraction lines decrease.
- The intensity of the background scattering between lines increases.

The second and third effects are described below. Here we are usually interested not in intensity changes with temperature, but in variations in intensity with 2θ at constant temperature (usually room temperature).

Thermal agitation decreases the intensity of a diffracted beam because it has the effect of smearing out the lattice planes; atoms can be regarded as lying no longer on mathematical planes but rather in platelike regions of ill-defined thickness. Thus the reinforcement of waves scattered at the Bragg angle by various parallel planes, the reinforcement which is called a diffracted beam, is not as perfect as it is for a crystal with fixed atoms. This reinforcement requires that the path difference, which is a function of the plane spacing d , between waves scattered by adjacent planes be an integral number of wavelengths. Now the thickness of the platelike "planes" in which the vibrating atoms lie is, on the average, $2u$, where u is the average displacement of an atom from its mean position. Under these conditions reinforcement is no longer perfect, and it becomes more imperfect as the ratio u/d increases, i.e., as the temperature increases, since that increases u , or as θ increases, since high- θ reflections involve planes of low d value. Thus the intensity of a diffracted beam decreases as the temperature is raised, and, for a constant temperature, thermal vibration causes a greater decrease in the reflected intensity at high angles than at low angles. In intensity calculations we allow for this effect by introducing the *temperature factor* e^{-2M} , which is a number by which the calculated intensity is to be multiplied to allow for thermal vibration of the atoms. Qualitatively, we conclude that e^{-2M} decreases as 2θ increases. A method of calculating e^{-2M} when it is needed is outlined later, and Fig. 4-20 shows the result of such a calculation for iron.

The temperature effect and the previously discussed absorption effect in cylindrical specimens depend on angle in opposite ways and, to a first approximation, cancel each other in the Debye-Scherrer method. In back reflection, for

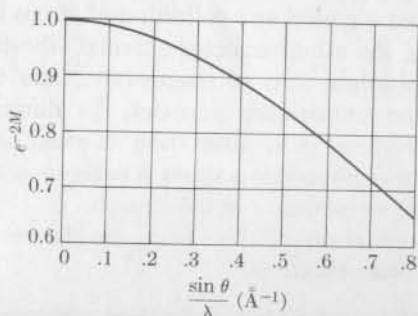


Fig. 4-20 Temperature factor e^{-2M} of iron at 20°C as a function of $(\sin \theta)/\lambda$.

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example, the intensity of a diffracted beam is decreased very little by absorption but very greatly by thermal agitation, while in the forward direction the reverse is true. The two effects do not exactly cancel one another at all angles; however, if the comparison of line intensities is restricted to lines not differing too greatly in θ values, the absorption and temperature effects can be safely ignored in the Debye-Scherrer method. This is a fortunate circumstance, since both of these effects are rather difficult to calculate exactly.

Theoretically, thermal vibration of the atoms causes a very slight increase in the breadth B , measured at half-maximum intensity, of the diffraction lines. However, this expected effect has never been detected [4.2], and diffraction lines are observed to be sharp right up to the melting point, but their maximum intensity gradually decreases.

It is also worth noting that the mean amplitude of atomic vibration is not a function of the temperature alone but depends also on the elastic constants of the crystal. At any given temperature, the less "stiff" the crystal, the greater the vibration amplitude u . This means that u is much greater at any one temperature for a soft, low-melting-point metal like lead than it is for, say, tungsten. Substances with low melting points have quite large values of u even at room temperature and therefore yield rather poor back-reflection photographs. For example, thermal atomic vibration in lead at 20°C reduces the intensity of the highest-angle line observed with Cu $K\alpha$ radiation (at about $161^\circ 2\theta$) to only 18 percent ($e^{-2M} = 0.18$) of the value for atoms at rest.

In only one application described in this book (Sec. 14-10) will we need any quantitative information about the temperature factor e^{-2M} , but it is convenient to describe the calculation here. Formally, we allow for the effect by defining f as the atomic scattering factor of an atom undergoing thermal vibration, f_0 as the same quantity for an atom at rest, and relating the two by

$$f = f_0 e^{-M}.$$

(The quantity f_0 is then the scattering factor as usually tabulated, for example in Appendix 12.) Because the intensity of any line depends on f^2 , calculated intensities must be multiplied by e^{-2M} to allow for thermal vibration. The quantity M depends on both the amplitude u of thermal vibration and the scattering angle 2θ :

$$M = 2\pi^2 \left(\frac{u^2}{d^2} \right) = 8\pi^2 \bar{u}^2 \left(\frac{\sin \theta}{\lambda} \right)^2 = B \left(\frac{\sin \theta}{\lambda} \right)^2 \quad (4-17)$$

where \bar{u}^2 is the mean square displacement of the atom in a direction normal to the reflecting planes. The exact calculation of \bar{u}^2 as a function of temperature is extremely difficult, which means that M or B is hard to determine accurately. Debye has given the following expression:

$$M = \frac{6h^2 T}{mk\Theta^2} \left[\phi(x) + \frac{x}{4} \right] \left(\frac{\sin \theta}{\lambda} \right)^2, \quad (4-18)$$

where h is Planck's constant, T the absolute temperature, m the mass of the vibrating atom, k Boltzmann's constant, Θ the Debye characteristic temperature of the substance

in $^{\circ}\text{K}$, $x = \Theta/T$, and $\phi(x)$ is a function tabulated, along with values of Θ , in Appendix 15. Because $m = A/N$, where A = atomic weight and N = Avogadro's number, the coefficient of the bracketed terms above becomes

$$\frac{6h^2T}{mk\Theta^2} = \frac{(6)(6.02 \times 10^{26})(6.63 \times 10^{-34})^2T}{A\Theta^2(1.38 \times 10^{-23})(10^{-20})} = \frac{1.15 \times 10^4 T}{A\Theta^2}$$

if λ is in angstroms. Equation (4-18) is approximate and applies only to elements with cubic crystal structure.

For thorough treatments of the effect of thermal vibration on the diffraction pattern, see James [G.7] and Warren [G.30].

The thermal vibration of atoms has another effect on diffraction patterns. Besides decreasing the intensity of diffraction lines, it causes some general coherent scattering in all directions. This is called *temperature-diffuse scattering*; it contributes only to the general background of the pattern and its intensity gradually increases with 2θ . Contrast between lines and background naturally suffers, so this effect is a very undesirable one, leading in extreme cases to diffraction lines in the back-reflection region scarcely distinguishable from the background. Figure 4-21 illustrates this effect. In (a) is shown an extremely hypothetical pattern (only three lines, equally spaced, equally strong, with no background whatever) for atoms at rest; in (b) the lines, decreased in intensity by the factor e^{-2M} , are superimposed on a background of thermal diffuse scattering.

In the phenomenon of temperature-diffuse scattering we have another example, beyond those alluded to in Sec. 3-7, of scattering at non-Bragg angles. Here again it is not surprising that such scattering should occur, since the displacement of atoms from their mean positions constitutes a kind of crystal imperfection and leads to a partial breakdown of the conditions necessary for perfect destructive interference between rays scattered at non-Bragg angles.

The effect of thermal vibration also illustrates what has been called "the approximate law of conservation of diffracted energy." This law states that the total energy diffracted by a particular specimen under particular experimental conditions is roughly constant. Therefore, anything done to alter the physical condition of the specimen does not alter the total amount of diffracted energy but

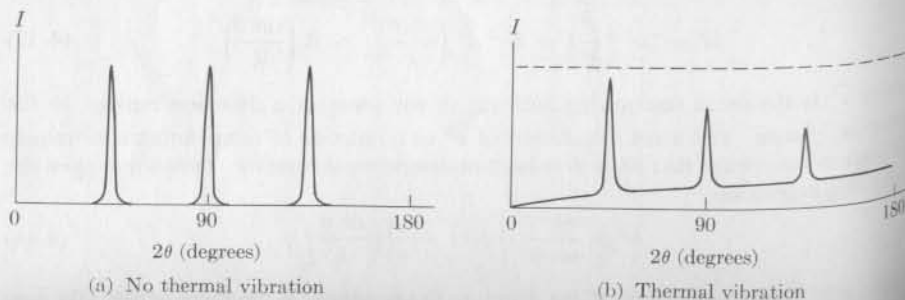


Fig. 4-21 Effect of thermal vibration of the atoms on a powder pattern. Very schematic.

only its distribution in space. This "law" is not at all rigorous, but it does prove helpful in considering many diffraction phenomena. For example, at low temperatures there is very little background scattering due to thermal agitation and the diffraction lines are relatively intense; if the specimen is now heated to a high temperature, the lines will become quite weak and the energy which is lost from the lines will appear in a spread-out form as temperature-diffuse scattering.

4-12 INTENSITIES OF POWDER PATTERN LINES

We are now in a position to gather together the factors discussed in preceding sections into an equation for the relative intensity of powder-pattern lines.

Debye-Scherrer Camera

$$\text{(Approximate)} \quad I = |F|^2 p \left(\frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} \right), \quad (4-19)$$

where I = relative integrated intensity (arbitrary units), F = structure factor, p = multiplicity factor, and θ = Bragg angle. The trigonometric terms in parentheses are the Lorentz-polarization factor. In arriving at this equation, we have omitted factors which are constant for all lines of the pattern. For example, all that is retained of the Thomson equation (Eq. 4-2) is the polarization factor $(1 + \cos^2 2\theta)$, with constant factors, such as the intensity of the incident beam and the charge and mass of the electron, omitted. The intensity of a diffraction line is also directly proportional to the irradiated volume of the specimen and inversely proportional to the camera radius, but these factors are again constant for all diffraction lines and may be neglected. Omission of the temperature and absorption factors means that Eq. (4-19) is valid only for lines fairly close together on the pattern; this latter restriction is not as serious as it may sound. Finally, it should be remembered that this equation gives the relative *integrated* intensity, i.e., the relative area under the curve of intensity vs. 2θ .

If an exact expression is required, the absorption factor $A(\theta)$ and the temperature factor e^{-2M} must be inserted:

$$\text{(Exact)} \quad I = |F|^2 p \left(\frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} \right) A(\theta) e^{-2M}. \quad (4-20)$$

Diffractometer

Here the absorption factor is independent of θ and so does not enter into the calculation of relative intensities. Equation (4-19) becomes still less precise, because there is no longer any approximate cancellation of the absorption and temperature factors. Equation (4-19) may still be used, for adjacent lines on the pattern, but the calculated intensity of the higher-angle line, relative to that of the lower-angle line, will always be somewhat too large because of the omission of the temperature factor.

The exact equation for the diffractometer is

$$\text{(Exact)} \quad I = |F|^2 p \left(\frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} \right) e^{-2M} \quad (4-21)$$

APPENDIX 15

DATA FOR CALCULATION OF THE TEMPERATURE FACTOR

Values of $\phi(x) = \frac{1}{x} \int_0^x \frac{\xi}{e^\xi - 1} d\xi$ as a Function of x

x	.0	.1	.2	.3	.4	.5	.6	.7	.8	.9
0	1.000	0.975	0.951	0.928	0.904	0.882	0.860	0.839	0.818	0.797
1	0.778	0.758	0.739	0.721	0.703	0.686	0.669	0.653	0.637	0.622
2	0.607	0.592	0.578	0.565	0.552	0.539	0.526	0.514	0.503	0.491
3	0.480	0.470	0.460	0.450	0.440	0.431	0.422	0.413	0.404	0.396
4	0.388	0.380	0.373	0.366	0.359	0.352	0.345	0.339	0.333	0.327
5	0.321	0.315	0.310	0.304	0.299	0.294	0.289	0.285	0.280	0.276
6	0.271	0.267	0.263	0.259	0.255	0.251	0.248	0.244	0.241	0.237

For x greater than 7, $\phi(x)$ is given to a good approximation by $(1.642/x)$. (From Vol. 2, p. 264 of [G.11]).

Debye Temperatures

$x = \frac{\Theta}{T}$

James [G.7, p. 221] gives the following values of the characteristic Debye temperature Θ for some cubic metals.

Metal	$\Theta(^{\circ}\text{K})$	Metal	$\Theta(^{\circ}\text{K})$
Al	390	Ta	245
Ca	230	Pb	88
Cu	320	Fe	430
Ag	210	Co	410
Au	175	Ni	400
Cr	485	Pd	275
Mo	380	Ir	285
W	310	Pt	230

APPENDIX 16

ATOMIC WEIGHTS Based on the assigned relative atomic mass of $^{12}\text{C} = 12$.

Element	Symbol	Atomic number	Atomic weight	Element	Symbol	Atomic number	Atomic weight
Actinium	Ac	89	(227)	Mercury	Hg	80	200.59
Aluminium	Al	13	26.9815	Molybdenum	Mo	42	95.94
Americium	Am	95	(243)	Neodymium	Nd	60	144.24
Antimony	Sb	51	121.75	Neon	Ne	10	20.179
Argon	Ar	18	39.948	Neptunium	Np	93	237.0482
Arsenic	As	33	74.9216	Nickel	Ni	28	58.71
Astatine	At	85	(210)	Niobium	Nb	41	92.9064
Barium	Ba	56	137.34	Nitrogen	N	7	14.0067
Berkelium	Bk	97	(247)	Nobelium	No	102	(254)
Beryllium	Be	4	9.01218	Osmium	Os	76	190.2
Bismuth	Bi	83	208.9806	Oxygen	O	8	15.9994
Boron	B	5	10.81	Palladium	Pd	46	106.4
Bromine	Br	35	79.904	Phosphorus	P	15	30.9738
Cadmium	Cd	48	112.40	Platinum	Pt	78	195.09
Calcium	Ca	20	40.08	Plutonium	Pu	94	(242)
Californium	Cf	98	(249)	Polonium	Po	84	(210)
Carbon	C	6	12.011	Potassium	K	19	39.102
Cerium	Ce	58	140.12	Praseodymium	Pr	59	140.9077
Cesium	Cs	55	132.9055	Promethium	Pm	61	(147)
Chlorine	Cl	17	35.453	Protactinium	Pa	91	231.0359
Chromium	Cr	24	51.996	Radium	Ra	88	226.0254
Cobalt	Co	27	58.9332	Radon	Rn	86	(222)
Copper	Cu	29	63.546	Rhenium	Re	75	186.2
Curium	Cm	96	(247)	Rhodium	Rh	45	102.9055
Dysprosium	Dy	66	162.50	Rubidium	Rb	37	85.4678
Einsteinium	Es	99	(254)	Ruthenium	Ru	44	101.07
Erbium	Er	68	167.26	Samarium	Sm	62	150.4
Europium	Eu	63	151.96	Scandium	Sc	21	44.9559
Fermium	Fm	100	(253)	Selenium	Se	34	78.96
Fluorine	F	9	18.9984	Silicon	Si	14	28.086
Francium	Fr	87	(223)	Silver	Ag	47	107.868
Gadolinium	Gd	64	157.25	Sodium	Na	11	22.9898
Gallium	Ga	31	69.72	Strontium	Sr	38	87.62
Germanium	Ge	32	72.59	Sulfur	S	16	32.06
Gold	Au	79	196.9665	Tantalum	Ta	73	180.9479
Hafnium	Hf	72	178.49	Technetium	Tc	43	98.9062
Helium	He	2	4.00260	Tellurium	Te	52	127.60
Holmium	Ho	67	164.9303	Terbium	Tb	65	158.9254
Hydrogen	H	1	1.0080	Thallium	Tl	81	204.37
Indium	In	49	114.82	Thorium	Th	90	232.0381
Iodine	I	53	126.9045	Thulium	Tm	69	168.9342
Iridium	Ir	77	192.22	Tin	Sn	50	118.69
Iron	Fe	26	55.847	Titanium	Ti	22	47.90
Krypton	Kr	36	83.80	Tungsten	W	74	183.85
Lanthanum	La	57	138.9055	Uranium	U	92	238.029
Lawrencium	Lr	103	(257)	Vanadium	V	23	50.9414
Lead	Pb	82	207.2	Xenon	Xe	54	131.30
Lithium	Li	3	6.941	Ytterbium	Yb	70	173.04
Lutetium	Lu	71	174.97	Yttrium	Y	39	88.9059
Magnesium	Mg	12	24.305	Zinc	Zn	30	65.37
Manganese	Mn	25	54.9380	Zirconium	Zr	40	91.22
Mendelevium	Md	101	(256)				

Values in parentheses represent the most stable known isotopes.