

用比值法指标化X光粉晶衍射 低级晶系 $d(A)$ 值

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一、前言

自从德拜(Debye), 谢尔(Scherrer)于1916年首先发明粉晶照相以来, 一直被广泛应用于科学研究、生产实践, 对于矿物研究与鉴定起了极其重要的作用。粉晶照相法虽有其局限性, 如: 线条的重合, 低级晶系图谱复杂等, 但却有其优点, 如: 操作简单, 强度可靠, 不受单晶的限制等, 则是别的方法所不及的。迄今照相技术, 计算方法, 鉴定手段等仍在继续不断地得到有关研究人员的改进。

过去, 粉末法总是在其它方法(旋转法, 迴摆法, 魏森堡法)的基础上, 首先求出晶胞参数, 然后再指标化。对高、中级晶系(等轴、四方、三方、六方晶系), 可在定出 a, c 之前直接指标化, 但对于低级晶系(斜方、单斜、三斜晶系)一直没有通用的简单方法。等轴晶系用图解或解析法都比较简单, 三方、六方、四方晶系也可采用解析或图解法, 但线条在一些地区过分密集, 不易分解(Bjurström, Hull, Davey, Bunn...)^{[5][8]}。

对于斜方晶系矿物, 赫斯(Hesse)^[9], 李卜森(Lipson)^[11]首先提出解析法。1949年伊藤(T. Ito)^[10]提出包括单斜, 三斜晶系的指标化方法, 虽然理论上正确, 但在实际应用中如何正确地选择开头的三个 Q 值($Q_{100}=d^{*2}_{100}, Q_{010}=d^{*2}_{010}$ 及 $Q_{001}=d^{*2}_{001}$)却是困难的。一般情况下, 开始的三条线很少是

$d_{100}, d_{010}, d_{001}$ 。如果开始的三条线的 hkl 限于0、1、2(3以上暂除外), 则其不同的组合就有26($3 \times 3 \times 3 - 1 = 26$)种之多。选定的 Q 是否正确, 往往要经过一段计算, 才能发现。近年来计算技术突飞猛进, 快速准确, 故可编制程序进行指标化; 也可按 $b/a, c/a$ 一定的间隔利用计算机预先计算 Q_{hkl} 的比值, 采取适当的编排, 便于查对, 以利于指标化。考虑我国目前计算机还不普及, 后一种办法较为现实。

本文主要目的是探索斜方晶系和单斜晶系矿物在没有单晶、且晶系不明的情况下, 求其晶面指标以及晶胞常数。同时, 还可检查粉晶 $d(A)$ 值和晶胞常数的精度、线条的重叠、 $d(A)$ 值与晶胞常数是否一致等。如某些线条测量有错误, 经过计算就可判定。作者曾在1964年计算过不同晶系矿物共二十多个, 发现两晶体的 $b/a, c/a$ 愈接近, 则其 $d^{*2}_{hkl}(\equiv Q_{hkl})$ 的比值亦愈接近, 这表明有可能解决上面提出的问题。

二、原理及计算

在等轴晶系中($a=b=c, \alpha=\beta=\gamma=90^\circ$)

$$d_{hkl} = a / \sqrt{h^2 + k^2 + l^2}$$

$$d^{*2}_{hkl} = a^2 / h^2 + k^2 + l^2$$

$$\text{或 } d^{*2}_{hkl} = a^{*2} (h^2 + k^2 + l^2)$$

$$d^{*2}_{(hkl)_n} / d^{*2}_{(hkl)_m} = \frac{d^{*2} (h^2 + k^2 + l^2)_n}{d^{*2} (h^2 + k^2 + l^2)_m}$$

$$= \frac{h_n^2 + k_n^2 + l_n^2}{h_m^2 + k_m^2 + l_m^2}$$

$$= \frac{q}{p} \dots \dots \dots (1)$$

p, q 为正整数, 除一些不可能的数值, 如: 7, 15, 23, ……等以外, 对于等轴晶系矿物来说, 如果 $d(A)$ 值的误差不大, 只需用第一个 d_{hkl}^{*2} 除其后的其它 d_{hkl}^{*2} , 然后求这些分子、分母的共同最大公约数 (M. C. F.), 即可求定 a (M. C. F. = a^{*2} , 如果 h, k, l 三者本身无公约数)。

对于四方晶系矿物:

$$\frac{1}{d_{hkl}^{*2}} = \frac{1}{a^2} (h^2 + k^2) + \frac{1}{c^2} l^2,$$

如: $l=0$, 则 $d_{hko}^{*2} = a^{*2} (h^2 + k^2)$

$$d_{(hko)n}^{*2} / d_{(hko)m}^{*2} = h_n^2 + k_n^2 / h_m^2 + k_m^2$$

$$= \frac{q}{p} \dots \dots \dots (2)$$

此关系同等轴晶系中 $d_{hoo}^{*2}, d_{oko}^{*2}$ 及 d_{hko}^{*2} 之比, p, q 分别为 1, 2, 4, 5, 8, 9, ……注意 $q/p=2$ 只能在等轴, 四方晶系中出现。求定 $a, b (=a)$ 后, 再求 c 。

对于三方、六方晶系:

$$d_{hkl}^{*2} = \frac{4}{3a^2} (h^2 + hk + k^2) + \frac{1}{c^2} l^2$$

如: $l=0$,

$$d_{hko}^{*2} = \frac{4}{3} a^{*2} (h^2 + hk + k^2),$$

$$d_{hkn}^{*2} / d_{hkm}^{*2} = h_n^2 + h_n k_n + k_n^2 / h_m^2 + h_m k_m + k_m^2$$

$$= \frac{q}{p} \dots \dots \dots (3)$$

p, q 分别等于 1, 3, 4, 7, 9, 12, ……。

注意 p, q 值与四方晶系的差别。

以任何 d_{hkl}^{*2} 除 $d_{h2k2l}^{*2}, d_{h3k3l}^{*2}$ ……其值等于 4, 9, 16, …… (n^2)。还须注意一些数值, 如: 1, 4, 9, 13, 16, ……在 (1), (2), (3) 式中都可有; 另一些数值, 如: 2, 3, 5, 8, 10, ……只在 (1), (2)

式中能有; 还有一些数值, 如: 7, 11, 14, ……只一种 (1, 2, 3) 能有, 其它数值 (如: 15, 23, 47, 55, ……), 在 (1), (2), (3) 式中都不允许出现。

对于斜方晶系:

$$d_{hkl}^{*2} = \frac{\lambda^2}{4a^2} h^2 + \frac{\lambda^2}{4b^2} k^2 + \frac{\lambda^2}{4c^2} l^2$$

$$= \frac{\lambda^2}{4} \left(\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \right)$$

$$d_{hkl}^{*2} \cdot a^2 = \frac{\lambda^2}{4} \left[h^2 + k^2 / (b/a)^2 + l^2 / (c/a)^2 \right]$$

$$\therefore d_{(hkl)n}^{*2} / d_{(hkl)m}^{*2} = \frac{h_n^2 + k_n^2 / (b/a)^2 + l_n^2 / (c/a)^2}{h_m^2 + k_m^2 / (b/a)^2 + l_m^2 / (c/a)^2} \dots \dots (4)$$

在斜方晶系中 a, b, c 可以互换, 取 $a < b < c$ 。如果需要, 求定 a, b, c 后可再调换复原。

对于单斜晶系, $\beta \neq 90^\circ$, 只 a, c 可以互换。如 $a < c$, b 与 a, c 可有以下三种关系:

(1) $b > a, b < c$;

(2) $b > a$ 及 c ;

(3) $b < a$ 及 c 。

$$d_{hkl} = \frac{1}{\sqrt{\frac{h^2}{a^2} + \frac{l^2}{c^2} - \frac{2hl \cos \beta}{ac} + \frac{k^2}{b^2}}}$$

$$d_{hkl}^{*2} \cdot a^2 = \frac{1}{\sin^2 \beta} \left[h^2 + l^2 / (c/a)^2 - \frac{2hl \cos \beta}{(c/a)} \right] + \frac{k^2}{(b/a)^2}$$

$$\therefore \frac{d_{hkn}^{*2} h_n k_n l_n}{d_{hkm}^{*2} h_m k_m l_m} = \frac{\frac{1}{\sin^2 \beta} \left[h_n^2 + l_n^2 / (c/a)^2 - \frac{2h_n l_n \cos \beta}{c/a} \right] + \frac{k_n^2}{(b/a)^2}}{\frac{1}{\sin^2 \beta} \left[h_m^2 + l_m^2 / (c/a)^2 - \frac{2h_m l_m \cos \beta}{c/a} \right] + \frac{k_m^2}{(b/a)^2}} \dots \dots (5)$$

在同一晶体中, β 、 b/a 、 c/a 均为常数。

如: $k_m = 0, k_n = 0$

则:

$$\frac{d_{(hkl)n}^{*2}}{d_{(hkl)m}^{*2}} = \frac{h_n^2 + l_n^2 / (c/a)^2 - 2h_n l_n \cos \beta / (c/a)}{h_m^2 + l_m^2 / (c/a)^2 - 2h_m l_m \cos \beta / (c/a)}$$

与斜方晶系比较, 由于 $\beta > 90^\circ$,

$$d_{101} < d_{10\bar{1}}, \quad \frac{1}{2}(d_{101} + d_{10\bar{1}})$$

等于斜方晶系中 d_{101} (设: 斜方、单斜晶系中 a , c 分别相等, 即 $a_o = a_m, c_o = c_m, a_o, c_o$ 为斜方晶系中的 a, c ; a_m, c_m 为单斜晶系的 a, c)。

据1800个矿物的统计, $\beta > 120^\circ$ 的只有十余个; $b/a, c/a$ 大于3或小于1/3有七十余个; 粉晶 $d(A)$ 值前10条线出现的指数一般为0、1、2, 大于3的较少。这些连同在斜方晶系中的情况, 对如何系统计算 d_{hkl}^{*2} 划定范围, 很有帮助。

d_{hkl}^{*2} 的比值, 按大小顺序排列, 每值之后均附 $b/a, c/a$ 的坐标, 这些计算值和对数表一样便于查对。1980年李容枝、何伟生两同志曾用小型计算机试算了60个斜方晶系已知 $b/a, c/a$ 的矿物的 d_{hkl}^{*2} 比值, 发现 b/a ($=A$)、 c/a ($=C$) 最接近的几个矿物 (如: $A=0.904, C=0.780$ 和 $A=0.904, C=0.784$) 其比值仍然有明显的差别。这足以证明以上设想是可行的。全部的斜方晶系和单斜晶系的矿物 (β 也按一定间隔考虑) 需要作专门的计算、排列。可先计算已知矿物, 再按一定间隔插入未知和可能为新矿物的 A 和 C 。同样, 也可由 A, C 的最大, 最小端向外扩大, 以增加应用的范围。

对于三斜晶系矿物尚缺少一般的解法, 只有在特殊的情况下才能用比值法求解 (见下例):

$$d_{hkl}^{*2} = h^2 a^{*2} + k^2 b^{*2} + l^2 c^{*2} + 2hka^*b^* \cos \gamma^* + 2klb^*c^* \cos \alpha^* + 2hla^*c^* \cos \beta^*$$

代入: $a^* = bcsin\alpha/V, b^* = casin\beta/V,$

$c^* = absin\gamma/V,$

$\cos \alpha^* = \cos \beta \cdot \cos \gamma - \cos \alpha / \sin \beta \cdot \sin \gamma,$

$\cos \beta^* = \cos \gamma \cdot \cos \alpha - \cos \beta / \sin \gamma \cdot \sin \alpha,$

$\cos \gamma^* = \cos \alpha \cdot \cos \beta - \cos \gamma / \sin \alpha \cdot \sin \beta.$

$v = abc(1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2\cos \alpha \cdot \cos \beta \cdot \cos \gamma)^{\frac{1}{2}}$

设: $hsin\alpha/a = x, ksin\beta/b = y,$

$lsin\gamma/c = z.$

$u = 2hk(\cos \alpha \cdot \cos \beta - \cos \gamma)ab,$

$v = 2kl(\cos \beta \cdot \cos \gamma - \cos \alpha)/bc,$

$w = 2hl(\cos \alpha \cdot \cos \gamma - \cos \beta)/ac.$

在同一晶带内一些特殊的指数, 如:

$d_{hkl}^{*2}, d_{okl}^{*2}, d_{hko}^{*2}$ 两两相加或相减, 其和或差的比值能消去 x, y, z 或 u, v, w 。例如:

$$d_{101}^{*2} + d_{10\bar{1}}^{*2} = 2(x^2 + z^2), \text{ 消去 } \frac{2hl}{ac}$$

$$(\cos \gamma \cdot \cos \alpha - \cos \beta) \dots \dots \dots (1)$$

$$d_{201}^{*2} + d_{20\bar{1}}^{*2} = 5(x^2 + z^2), \text{ 消去 } \frac{2hl}{ac}$$

$$(\cos \gamma \cdot \cos \alpha - \cos \beta) \dots \dots \dots (2)$$

$$d_{102}^{*2} + d_{10\bar{2}}^{*2} = 5(x^2 + z^2), \text{ 消去 } \frac{2hl}{ac}$$

$$(\cos \gamma \cdot \cos \alpha - \cos \beta) \dots \dots \dots (2)$$

$$d_{103}^{*2} + d_{10\bar{3}}^{*2} = 10(x^2 + z^2), \text{ 消去 } \frac{2hl}{ac}$$

$$(\cos \gamma \cdot \cos \alpha - \cos \beta) \dots \dots \dots (3)$$

$$d_{301}^{*2} + d_{30\bar{1}}^{*2} = 10(x^2 + z^2), \text{ 消去 } \frac{2hl}{ac}$$

$$(\cos \gamma \cdot \cos \alpha - \cos \beta) \dots \dots \dots (3)$$

$$d_{203}^{*2} + d_{20\bar{3}}^{*2} = 13(x^2 + z^2), \text{ 消去 } \frac{2hl}{ac}$$

$$(\cos \gamma \cdot \cos \alpha - \cos \beta) \dots \dots \dots (4)$$

$$d_{302}^{*2} + d_{30\bar{2}}^{*2} = 13(x^2 + z^2), \text{ 消去 } \frac{2hl}{ac}$$

$$(\cos \gamma \cdot \cos \alpha - \cos \beta) \dots \dots \dots (4)$$

上式(1):(2):(3):(4)=2:5:10:13, 如相减可消去 $(x^2 + z^2)$, 则(1):(2):(3):(4)=1:2:3:6。同样, 可以求 d_{hko}^{*2} 及 d_{okl}^{*2} 特殊晶面指数和之比。

对于 d^{*2}_{hkl} 是否能用同法处理,尚未做试算。很明显,这种(指三斜晶系)办法,有局限性,只能在特殊情况下才能求定指标。如矿物为三斜晶系,但不知晶胞常数,可先求每线的平方倒数,然后两两相加减,并观察分析其比值。

在以上各晶系中都可以在 $d(A)$ 值中先观察有无整数倍关系,其关系也可能为 d_{hkl} 与 d_{2h2k2l} ,.....等,而不一定是 d_{h00} , d_{2h00}

或 d_{hko} 与 d_{2h2k0} 等关系。

三、计算实例

采用比值法,作者于60年代曾计算过二十多个矿物的 d^{*2}_{hkl} 比值,1980年李、何两同志又计算60个斜方晶系矿物的 d^{*2}_{hkl} 比值以求其指数,现就不同的晶系各选一例通过计算,拟合实测 $d(A)$ (以 d^{*2}_{hkl} 表示)与计算的比值,以达到指标化的目的。

黄铁矿 d^{*2}_{hkl} 比值计算表

表1

线条编号	$d(A)$	I	d^{*2}_{hkl}	指数	线条编号	$d(A)$	I	d^{*2}_{hkl}	指数
1	3.080	84	0.1054	(111)	11	1.238	14	0.6523	(331)
2	2.673	100	0.1400	(200)	12	1.204	6	0.6897	(420)
3	2.394	60	0.1744	(210)	13	1.175	5	0.7246	(421)
4	2.186	48	0.2092	(211)	14	1.148	3	0.7590	(332)
5	1.896	34	0.2783	(220)	15	1.100	17	0.8264	(242)
6	1.618	55	0.3820	(311)	16	—	—	—	(150)
7	1.550	17	0.4162	(222)	17	1.038	55	0.9273	(333)
8	1.490	17	0.4505	(230)	18	1.002	—	0.9964	(520)
9	1.436	22	0.4849	(231)	19	0.986	—	1.029	(521)
10	—	—	—	(400)					

1. 黄铁矿 Pyrite FeS_2 等轴晶系

以第一个 d^{*2}_{hkl} 去除其以后的 d^{*2}_{hkl} ,即:

0.1400, 0.1744, 0.2092, 0.2783, 0.3820, 0.4162, 0.4505, 0.4849, 0.6523, 0.6897, 0.7246, 0.7590, 0.8264, 0.9273, 0.9964, 1.029除以0.1054,为:

$0.1400/0.1054 = 0.0350 \times 4 / 0.0351 \times 3 = 4/3$
 $0.1744/0.1054 = 0.0349 \times 5 / 0.0351 \times 3 = 5/3$
 $0.2092/0.1054 = 0.0349 \times 6 / 0.0351 \times 3 = 6/3$
 $0.2783/0.1054 = 0.0348 \times 8 / 0.0351 \times 3 = 8/3$
 $0.3820/0.1054 = 0.0347 \times 11 / 0.0351 \times 3 = 11/3$
 $0.4162/0.1054 = 0.0346 \times 12 / 0.0351 \times 3 = 12/3$
 $0.4505/0.1054 = 0.0347 \times 13 / 0.0351 \times 3 = 13/3$
 $0.4849/0.1054 = 0.0346 \times 14 / 0.0351 \times 3 = 14/3$
 $0.6523/0.1054 = 0.0343 \times 19 / 0.0351 \times 3 = 19/3$
 $0.6897/0.1054 = 0.0345 \times 20 / 0.0351 \times 3 = 20/3$
 $0.7246/0.1054 = 0.0345 \times 21 / 0.0351 \times 3 = 21/3$
 $0.7590/0.1054 = 0.0345 \times 22 / 0.0351 \times 3 = 22/3$

$0.8264/0.1054 = 0.0345 \times 24 / 0.0351 \times 3 = 24/3$
 $0.9273/0.1054 = 0.0344 \times 27 / 0.0351 \times 3 = 27/3$
 $0.9964/0.1054 = 0.0344 \times 29 / 0.0351 \times 3 = 29/3$
 $1.029 / 0.1054 = 0.0340 \times 30 / 0.0351 \times 3 = 30/3$

取最后四个M. C. F 的平均数,

为: $\frac{0.0345 + 0.0340 + 2 \times 0.0344}{4}$

$= 0.0345 = a^{*2} \therefore a = 5.399 \text{ \AA}$,

指标化后晶面指数见表1。

2. 铝硅钡石 Cymrite $Ba-AlSi_3(O_8OH)$

六方晶系

$d^{*2}_{h_2k_2l_2}, d^{*2}_{h_3k_3l_3}, d^{*2}_{h_4k_4l_4}, \dots, / d^{*2}_{h_1k_1l_1}$
 $d^{*2}_{h_3k_3l_3}, d^{*2}_{h_4k_4l_4}, \dots, / d^{*2}_{h_2k_2l_2}$

等的比值如下:

$0.04726, 0.06410, 0.1149, 0.1402,$
 $0.1514, 0.1563, 0.1858, 0.1993, 0.2047,$
 $0.2246, 0.2525, \dots, 0.8327$ 除以0.01686,
 $0.06410, 0.1149, 0.1402, 0.1514,$

0.1563, 0.1858, 0.1993, 0.2047, 0.2246 0.5557**, 0.5704, 0.6080**, 0.6211,
 0.2525, 0.2712, 0.2925, 0.3147, 0.3440, 0.6546, 0.6728, 0.6873, 0.7497**, 0.7571,
 0.3937, 0.4083, 0.4195**, 0.4640, 0.4742 0.7886, 0.8327除以0.04726, …………….

铝硅钨石 d_{hkl}^{*2} 比值计算表

表 2

线条编号	强度	$d(\text{\AA})$	$d^*(\text{\AA}^{-1})$	d_{hkl}^{*2}	线条编号	强度	$d(\text{\AA})$	$d^*(\text{\AA}^{-1})$	d_{hkl}^{*2}
1	st (强)	7.7	0.1299	0.01686	17	mw	1.595	0.6269	0.3930
2	vw (很弱)	4.6	0.2174	0.04726	18	w	1.565	0.6389	0.4083
3	vet (很强)	3.95	0.2532	0.06410	19	w	1.544	0.6477	0.4195
4	vst	2.95	0.3390	0.1149	20	w	1.468	0.6811	0.4640
5	sl	2.67	0.3745	0.1402	21	vw	1.452	0.6887	0.4742
6	vw	2.57	0.3891	0.1514	22	vw	1.341	0.7458	0.5557
7	vw	2.53	0.3953	0.1563	23	vw	1.324	0.7554	0.5704
8	w (弱)	2.32	0.4310	0.1858	24	w	1.283	0.7794	0.6080
9	m (中等)	2.24	0.4464	0.1993	25	vw	1.269	0.7879	0.6211
10	m	2.21	0.4525	0.2047	26	vw	1.236	0.8092	0.6546
11	vw	2.11	0.4739	0.2246	27	vw	1.219	0.8206	0.6728
12	w	1.99	0.5025	0.2525	28	vw	1.206	0.8295	0.6873
13	mw	1.92	0.5208	0.2712	29	w	1.155	0.8658	0.7497
14	m	1.849	0.5409	0.2925	30	vw	1.149	0.8704	0.7571
15	vw	1.783	0.5608	0.3147	31	vw	1.126	0.8884	0.7886
16	mw	1.705	0.5866	0.3440	32	vw	1.096	0.9119	0.8327

以 d_{hkl}^{*2} 去除第5, 8, 19, 22, 24, 7²则第一线的指数可能为(0001),
 及29线条的 d_{hkl}^{*2} 分别等于3, 4, 9, 12, 13
 及16;

$$c^* = \frac{1}{7.67} = 0.1304$$

第5线 $0.04726 \times 3 - 0.1402$
 $= +0.00158.$

第8线 $0.04726 \times 4 - 0.1858$
 $= +0.00320.$

第19线 $0.04726 \times 9 - 0.4195$
 $= +0.0059.$

第22线 $0.04726 \times 12 - 0.5557$
 $= +0.0114.$

第24线 $0.04726 \times 13 - 0.6080$
 $= +0.006$

第29线 $0.04726 \times 16 - 0.7497$
 $= +0.007.$

故 $d^* = 0.0467$ (0.04726的校正数),

$$d^* = 0.2161, \text{则 } a^* = 0.1876.$$

第二线的指数为 $10\bar{1}0$, 第一线 d_{hkl}^{*2} 与
 第6, 13, 32线 d_{hkl}^{*2} 之比分别接近 3^2 , 4^2 ,

则3, 4, 7, 9, 10—18, 19—21, 23,
 25—28, 30—32各线的指数为(括号内前面
 的数字为计算的, 后面的数字是测量的):

$$10\bar{1}1 \quad (0.2525 - 0.2520),$$

$$10\bar{1}2 \quad (0.3390 - 0.3370),$$

$$11\bar{2}1 \quad (0.3968 - 0.3968),$$

$$10\bar{1}3 \quad (0.4464 - 0.4450),$$

$$20\bar{2}1 \quad (0.4525 - 0.4500),$$

$$20\bar{2}2 \quad (0.5025 - 0.5000),$$

$$11\bar{2}4^{**} \quad (0.5409 - 0.5350),$$

$$10\bar{1}4 \quad (0.5608 - 0.5650),$$

$$21\bar{3}1 \quad (0.5862 - 0.5800),$$

$$21\bar{3}2 \quad (0.6272 - 0.6150), (?)$$

$$11\bar{2}4 \quad (0.6269 - 0.6400),$$

$$10\bar{1}5 \quad (0.6793 - 0.6850),$$

** 指5, 8, 19, 22, 24, 29线条
 注: $11\bar{2}4^{**}$ 可能是 $11\bar{2}3$ (?)

2133	(0.6887 - 0.6939) ,
3033	(0.7554 - 0.7450) ,
3141	(0.7880 - 0.7900) ,
1016	(0.8092 - 0.8050) ,
3142	(0.8206 - 0.8300) ,
3034	(0.8300 - 0.8250) ,
2135	(0.8704 - 0.8600) ,
2026	(0.8885 - 0.8850) .

3. 锂铍石 Liberite, $\text{Li}_2\text{BeSiO}_4$ [26] 是我国发现的新矿物, 前后曾两次测量晶胞常数, 单斜晶系, $\beta = 90^\circ 20'$, 故用斜方晶系公式计算误差不大。粉晶共有70条线, 现只算前面的20条线。

以第一条线的 d^{*2}_{hkl} 除其后的 d^{*2}_{hkl} , 由

此求出的 b/a , c/a 对其余的50条线亦能进行指标。线条的指标本当通过 d^{*2}_{hkl} 的比值查得, 为便于说明问题, 先给出指数; 确定 b/a , c/a 的上、下限; 变换 b/a , c/a 值; b/a 由1.046至1.060分三段, 每级中 c/a 值有: 低 (1.295, 1.296) 中 (1.297, 1.298)、高 (1.299, 1.300) 三种, 其中也包括两套晶胞常数, 藉以证明 b/a , c/a 的变换与 d^{*2}_{hkl} 比值的联系。

表3为锂铍石的 d^{*2}_{hkl} 比值 (实测和计算的):

$$Q_c = d^{*2}_{hkl} \text{ 计算值 (用 } b/a = A \text{ 和 } c/a = C \text{ 值)}.$$

$$Q_o = \text{实测 } d(A) \text{ 的平方倒数值}.$$

锂铍石实测 d^{*2}_{hkl} 比值计算表

表3(a)

线条编号	$d(A)$	$1/I_o$	d^{*2}_{hkl}	$d^{*2}_{(hkl)n}/d^{*2}_{(hkl)m}$ (实测值)	hkl	线条编号	$d(A)$	$1/I_o$	d^{*2}_{hkl}	$d^{*2}_{(hkl)n}/d^{*2}_{(hkl)m}$ (实测值)	hkl
1	4.93	4	0.04115	—	010	11	2.185	7	0.2095	5.092	120
2	3.82	10	0.06854	1.666	011	12	2.125	2	0.2220	5.384	210
3	3.71	10	0.07266	1.766	101	13	2.060	5	0.2356	5.727	121
4	3.40	7	0.08651	2.103	110	14	2.005	4	0.2488	6.048	211
5	3.05	4	0.1075	2.613	002	15	1.920	4	0.2712	6.596	022
6	2.97	6	0.1134	2.756	111	16	1.890	1	0.2799	6.804	013
7	2.59	10	0.1491	3.624	012	17	1.865	7	0.2875	6.988	103
8	2.47	9	0.1639	3.984	020	18	1.777	4	0.3168	7.698	122
9	2.35	9	0.1811	4.401	200	19	1.745	8	0.3284	7.982	113
10	2.27	9	0.1941	4.718	112	20	1.700	6	0.3460	8.410	220

通过表3(b)的计算, 证明矿物的 b/a , c/a 相等或相近, 则其 d^{*2}_{hkl} 的比值也相等或相近。

表3(b)第16次计算 $\Sigma(Q_c - Q_o)$ 的最小值 = 0.252, 由 $(Q_c - Q_o)$ 的统计和其 (+), (-) 的多少与分布, 看出晶胞常数与 $d(A)$ 值测量精度只达到 ± 0.01 ($\pm 1\%$), 但也足以说明 b/a , c/a 与 d^{*2}_{hkl} 比值的联系。此外, 表中也指出一些线条测量发生较大的误差, 如: 第7、12、13、16、17, 特别是第16条线的

误差最大。此外, 还应当指出在计算中一般取5位数字, 到小数点后第4位, 但有少数只计算到小数点后第3位。还有, 由于 b/a , c/a 在开始 (3和4次) 和最后 (23, 24, 25次) 选取的数值与实测相差过大, 故在计算中出现一些异常, 例如表3(b)的脚注(2)中4.840出现在4.716之上等等。

四、讨 论

1. 误差的表现形式为 x/y , 如 x 的误差

表 3(b)
锂 铍 石 d_{hk}^{*2} (计算值) 比值 计算表

计算次数	1		2		3		4		5	
	$a = 4.703^{(1)}$ $b = 4.945$ $c = 6.110$ $b/a = 1.051$ $c/a = 1.299$ $d_{hk}^{*2} / d_{hk}^{*2}$	$Q_c - Q_o$	$a = 4.676$ $b = 4.910$ $c = 6.059$ $b/a = 1.050$ $c/a = 1.295$ $d_{hk}^{*2} / d_{hk}^{*2}$	$Q_c - Q_o$	$b/a = 1.0$ $c/a = 1.2$ d_{hk}^{*2} 比值	$Q_c - Q_o$	$b/a = 1.1$ $c/a = 1.3$ d_{hk}^{*2} 比值	$Q_c - Q_o$	$b/a = 1.046$ $b/c = 1.295$ d_{hk}^{*2} 比值	$Q_c - Q_o$
线号										
1	—	—	—	—	—	—	—	—	—	—
2	1.655	-0.011	1.657	-0.009	1.694	+0.028	1.716	+0.050	1.652	-0.014
3	1.759	-0.007	1.760	-0.006	1.694	+0.028	1.926	+0.160	1.740	-0.026
4	2.105	+0.002	2.103	0	2.000	-0.103	2.210	+0.107	2.094	-0.009
5	2.619	+0.006	2.630	+0.017	2.778 ⁽²⁾	+0.165	2.864	+0.251	2.610	-0.003
6	2.759	+0.003	2.760	+0.004	2.694	-0.062	2.926	+0.170	2.747	-0.009
7	3.619	-0.005	3.630	+0.006	3.778	+0.154	3.864	+0.240	3.610	-0.014
8	4.000	+0.016	4.000	+0.016	4.000	+0.016	4.000	+0.016	4.000	+0.016
9	4.418	+0.016	4.410	+0.008	4.000	-0.402	4.840 ⁽²⁾	+0.438	4.376	-0.026
10	4.723	+0.005	4.732	+0.014	4.694	-0.024	4.716	-0.002	4.704	-0.014
11	5.103	+0.011	5.103	+0.011	5.000	-0.092	5.210	+0.118	5.094	+0.002
12	5.418	+0.034	5.410	+0.026	5.000	-0.384	5.840	+0.456	5.376	-0.008
13	5.758	+0.031	5.760	+0.033	5.6944	-0.033	5.926	+0.199	5.747	+0.020
14	6.073	+0.025	6.067	+0.010	5.6944	-0.354	6.556	+0.508	6.029	-0.019
15	6.618	+0.023	6.630	+0.035	6.778	+0.183	6.864	+0.269	6.610	+0.015
16	6.893	+0.089	6.917	+0.113	7.2500	+0.446	7.444	+0.640	6.872	+0.068
17	6.998	+0.010	7.020	+0.032	7.2500	+0.262	7.654	+0.666	6.968	-0.022
18	7.722	+0.024	7.732	+0.034	7.778	+0.080	8.074	+0.376	7.704	+0.006
19	7.997	+0.015	8.020	+0.038	8.2500	+0.268	8.654	+0.672	7.966	-0.016
20	8.417	+0.007	8.410	0	8.0000	-0.410	8.840	+0.430	8.376	-0.034
Σ		0.340		0.412		3.494		5.768		0.341

(1) 1、2表示两套晶胞常数为手算的比值结果，3、4为 $b/a, c/a$ 的上、下限。

(2) 由于 $b/a, c/a$ 选定距实际很远，因此出现此种不合理情况。

续表 3(b)

计算次数		6			7			8			9			10		
线号	Q_{hkl} 比值与 Q_e-Q_o	$b/a=1.046$ $c/a=1.297$ $d_{(hkl)m}^2/d_{(hkl)m}^2$		Q_e-Q_o	$b/a=1.046$ $c/a=1.298$ $d_{(hkl)m}^2/d_{(hkl)m}^2$		Q_e-Q_o	$b/a=1.047$ $c/a=1.296$ d_{hkl}^2 比值		Q_e-Q_o	$b/a=1.047$ $c/a=1.297$ d_{hkl}^2 比值		Q_e-Q_o	$b/a=1.047$ $c/a=1.298$ d_{hkl}^2 比值		Q_e-Q_o
		$d_{(hkl)m}^2/d_{(hkl)m}^2$		Q_e-Q_o	$d_{(hkl)m}^2/d_{(hkl)m}^2$		Q_e-Q_o	d_{hkl}^2 比值		Q_e-Q_o	d_{hkl}^2 比值		Q_e-Q_o	d_{hkl}^2 比值		Q_e-Q_o
1	—	—		—	—		—	—		—	—		—	—		—
2	1.6503	1.6494		-0.0157	1.6494		-0.0166	1.653		-0.013	1.652		-0.014	1.65		-0.015
3	1.7446	1.7436		-0.0214	1.7436		-0.0224	1.749		-0.017	1.748		-0.018	1.757		-0.009
4	2.0942	2.0942		-0.0088	2.0942		-0.0088	2.096		-0.007	2.096		-0.007	2.096		-0.007
5	2.6015	2.5976		-0.0115	2.5976		-0.0154	2.610		-0.002	2.607		-0.006	2.602		-0.011
6	2.7446	2.7436		-0.0114	2.7436		-0.0124	2.749		-0.007	2.748		-0.008	2.757		+0.003
7	3.6015	3.5976		-0.0225	3.5976		-0.0264	3.610		-0.014	3.607		-0.017	3.602		-0.022
8	4.000	4.0000		+0.0160	4.0000		+0.0160	4.000		+0.016	4.000		+0.016	4.000		+0.016
9	4.3768	4.3768		-0.0242	4.3768		-0.0242	4.385		-0.017	4.385		-0.017	4.385		-0.017
10	4.6358	4.6318		+0.0822	4.6918		-0.0262	4.706		-0.012	4.703		-0.015	4.719		+0.001
11	5.094	5.0942		+0.0022	5.0942		+0.0022	5.096		+0.004	5.096		+0.004	5.096		+0.004
12	5.3768	5.3768		-0.0072	5.3768		-0.0072	5.385		+0.001	5.385		+0.001	5.385		+0.001
13	5.7446	5.7436		+0.0176	5.7436		+0.0166	5.749		+0.022	5.748		+0.021	5.757		+0.032
14	6.0272	6.0262		-0.0208	6.0262		-0.0218	6.038		-0.010	6.037		-0.011	6.055		+0.007
15	6.6015	6.5976		+0.0065	6.5976		+0.0026	6.610		+0.015	6.607		+0.012	6.603		+0.008
16	6.8535	6.8447		+0.0495	6.8447		+0.0407	6.873		+0.069	6.866		+0.062	6.856		+0.052
17	6.9478	6.9389		-0.0401	6.9389		-0.0490	6.969		-0.019	6.992		+0.004	6.952		-0.036
18	7.6958	7.6918		-0.0022	7.6918		-0.0062	7.707		+0.009	7.703		+0.005	7.719		+0.021
19	7.9478	7.9389		-0.0342	7.9389		-0.0431	7.969		-0.013	7.962		-0.020	7.952		-0.030
20	8.3768	8.3768		-0.0332	8.3768		-0.0332	8.385		-0.025	8.385		-0.025	8.385		-0.025
Σ				0.4272			0.3910			0.292			0.305			0.317

续表 3(b)

计算次数 线号	11		12		13		14		15	
	$b/a = 1.048$ $c/a = 1.296$ d_{hk}^{*2} 比值	$Q_c - Q_o$	$b/a = 1.048$ $c/a = 1.297$ d_{hk}^{*2} 比值	$Q_c - Q_o$	$b/a = 1.048$ $c/a = 1.298$ d_{hk}^{*2} 比值	$Q_c - Q_o$	$b/a = 1.049$ $c/a = 1.296$ d_{hk}^{*2} 比值	$Q_c - Q_o$	$b/a = 1.049$ $c/a = 1.297$ d_{hk}^{*2} 比值	$Q_c - Q_o$
1	—	—	—	—	—	—	—	—	—	—
2	1.654	-0.012	1.653	-0.013	1.652	-0.014	1.655	-0.011	1.656	-0.010
3	1.753	-0.013	1.751	-0.015	1.750	-0.016	1.766	0	1.755	-0.011
4	2.100	-0.003	2.098	-0.005	2.098	-0.005	2.100	-0.003	2.102	-0.001
5	2.616	+0.003	2.612	-0.001	2.607	-0.006	2.620	+0.007	2.617	+0.004
6	2.753	-0.003	2.751	-0.005	2.750	-0.006	2.766	+0.010	2.755	-0.001
7	3.616	-0.008	3.612	-0.012	3.607	-0.077	3.620	-0.004	3.617	-0.007
8	4.000	+0.016	4.000	+0.016	4.000	+0.016	4.000	+0.016	4.000	+0.016
9	4.396	-0.006	4.393	-0.009	4.393	-0.009	4.401	-0.001	4.401	-0.001
10	4.715	-0.003	4.710	-0.008	4.706	-0.012	4.741	+0.022	4.717	-0.001
11	5.099	+0.007	5.098	+0.006	5.098	+0.006	5.100	+0.008	5.100	+0.008
12	5.396	+0.012	5.393	+0.009	5.393	+0.009	5.401	+0.017	5.401	+0.017
13	5.753	+0.026	5.751	+0.024	5.750	+0.023	5.766	+0.039	5.761	+0.034
14	6.050	+0.002	6.046	-0.002	6.045	-0.003	6.077	+0.029	6.056	+0.008
15	6.616	+0.021	6.612	+0.017	6.607	+0.012	6.620	+0.025	6.817	+0.022
16	6.887	+0.083	6.876	+0.072	6.866	+0.062	6.895	+0.091	6.888	+0.084
17	6.986	-0.002	6.975	-0.013	7.000	+0.012	7.026	+0.038	6.988	0
18	7.715	+0.017	7.710	+0.012	7.706	+0.008	7.741	+0.043	7.717	+0.019
19	7.986	+0.004	7.975	-0.007	7.965	-0.017	8.026	+0.044	7.989	+0.007
20	8.396	-0.014	8.393	-0.017	8.391	-0.019	8.401	-0.009	8.401	-0.009
Σ		0.255		0.263		0.343		0.417		0.260

续表 3(b)

计算次测	16		17		18		19		20	
	Q_{hkl} 比值 与 Q_c-Q_0	Q_c-Q_0	$b/a=1.050$ $c/a=1.298$ $d_{hkl}^2/d_{(hkl)m}^2$ 比值	Q_c-Q_0	$b/a=1.050$ $c/a=1.299$ $d_{hkl}^2/d_{(hkl)m}^2$ 比值	Q_c-Q_0	$b/a=1.050$ $c/a=1.300$ $d_{hkl}^2/d_{(hkl)m}^2$ 比值	Q_c-Q_0	$b/a=1.051$ $c/a=1.298$ d_{hkl}^2 比值	Q_c-Q_0
线号										
1	—	—	—	—	—	—	—	—	—	—
2	1.653	-0.013	1.6543	-0.0117	1.654	-0.012	1.6523	-0.0137	1.656	-0.010
3	1.753	-0.013	1.7568	+0.0092	1.756	-0.010	1.7549	-0.0111	1.760	-0.006
4	2.100	-0.003	2.1025	-0.0005	2.103	0	2.1025	-0.0005	2.105	+0.002
5	2.612	-0.001	2.6174	+0.0044	2.614	+0.001	2.6094	-0.0036	2.622	+0.009
6	2.753	-0.003	2.7568	+0.0008	2.756	0	2.7549	-0.0011	2.760	+0.004
7	3.612	-0.012	3.6174	-0.0065	3.614	-0.010	3.6094	-0.0146	3.622	-0.002
8	4.000	+0.016	4.0000	+0.0160	4.000	+0.016	4.0000	+0.0160	4.000	+0.016
9	4.401	-0.001	4.4101	+0.0091	4.410	+0.008	4.4101	+0.0091	4.418	+0.016
10	4.712	-0.006	4.7199	+0.0019	4.654	-0.064	4.7120	-0.0060	4.727	+0.009
11	5.100	+0.008	5.1025	+0.0105	5.103	+0.011	5.1025	+0.0105	5.103	+0.011
12	5.401	+0.017	5.4101	+0.0261	5.410	+0.026	5.4101	+0.0261	5.418	+0.034
13	5.753	+0.026	5.7568	+0.0298	5.756	+0.029	5.7549	+0.0279	5.759	+0.032
14	6.054	+0.006	6.0644	+0.0164	6.064	+0.016	6.0525	+0.0045	6.074	+0.026
15	6.612	+0.017	6.6174	+0.0224	6.614	+0.019	6.6094	+0.0144	6.621	+0.026
16	6.877	+0.073	6.8891	+0.0851	6.882	+0.078	6.8713	+0.0673	6.900	+0.090
17	6.978	-0.010	6.9917	+0.0037	6.984	-0.004	6.9738	-0.0142	7.005	+0.17
18	7.712	+0.014	7.7199	+0.0219	7.717	+0.019	7.7120	+0.0140	7.725	+0.027
19	7.978	-0.004	7.9917	+0.0097	7.984	+0.002	7.9738	-0.0082	8.005	+0.023
20	8.401	-0.009	8.4101	+0.0001	8.410	0	8.4101	+0.0001	8.417	+0.007
Σ		0.252		0.2859		0.325		0.2629		0.367

续表 3(b)

计算次数		21		22		23		24		25	
线号	$\frac{Q_{hk1}}{Q_0-Q_0}$ 比值与 Q_0-Q_0	$b/a=1.051$ $c/a=1.299$ $d_{(hkl)/m}^{+2}$	Q_0-Q_0	$b/a=1.051$ $c/a=1.300$ d_{hk}^{+2} 比值	Q_0-Q_0	$b/a=1.060$ $c/a=1.296$ $d_{(hkl)/m}^{+2}$	Q_0-Q_0	$b/a=1.060$ $c/a=1.298$ $d_{(hkl)/m}^{+2}$	Q_0-Q_0	$b/a=1.060$ $c/a=1.300$ $d_{(hkl)/m}^{+2}$	Q_0-Q_0
1											
2	1.6578	-0.0082	-0.012	1.654	+0.003	1.669	+0.003	1.6663	+0.0003	1.6649	-0.0011
3	1.7591	-0.0069	-0.008	1.758	+0.026	1.792	+0.026	1.7906	+0.0246	1.7886	+0.0228
4	2.1046	+0.0016	+0.002	2.105	+0.021	2.124	+0.021	2.1237	+0.0207	2.1237	+0.0207
5	2.6183	+0.0053	+0.001	2.614	+0.062	2.675	+0.062	2.6677	+0.0547	2.6596	+0.0466
6	2.7591	+0.0031	+0.002	2.758	+0.036	2.792	+0.036	2.7906	+0.0346	2.7886	+0.0326
7	3.6183	-0.0057	-0.010	3.614	+0.051	3.675	+0.051	3.6677	+0.0437	3.6590	+0.0356
8	4.000	+0.0160	+0.016	4.000	+0.016	4.006	+0.016	4.0000	+0.0160	4.0000	+0.0160
9	4.4184	+0.0173	+0.016	4.418	+0.092	4.494	+0.092	4.4948	+0.0983	4.4948	+0.0938
10	4.7229	+0.0049	+0.001	4.719	+0.081	4.799	+0.081	4.7914	+0.0734	4.7833	+0.0653
11	5.1046	+0.0126	+0.013	5.105	+0.050	5.124	+0.050	5.1237	+0.0317	5.1237	+0.0311
12	5.4184	+0.0344	+0.034	5.418	+0.110	5.494	+0.110	5.4948	+0.1108	5.4948	+0.1108
13	5.7591	+0.0321	+0.031	5.758	+0.066	5.793	+0.066	5.7906	+0.0636	5.7886	+0.0616
14	6.0730	+0.0250	+0.024	6.072	+0.115	6.163	+0.115	6.1618	+0.1138	6.1597	+0.1117
15	6.6183	+0.0233	+0.019	6.614	+0.081	6.676	+0.081	6.6677	+0.0727	6.6596	+0.0646
16	6.8913	+0.0873	+0.079	6.883	+0.217	7.021	+0.217	7.0023	+0.1983	6.9841	+0.1801
17	6.9959	+0.0077	-0.001	6.987	+0.156	7.144	+0.156	7.1260	+0.1380	7.1028	+0.1138
18	7.7229	+0.0249	+0.021	7.719	+0.101	7.799	+0.101	7.7914	+0.0934	7.7833	+0.0853
19	7.9959	+0.0139	+0.005	7.987	+0.162	8.144	+0.162	8.1260	+0.1440	8.1078	+0.1258
20	8.4184	+0.0084	+0.008	8.418	+0.084	8.494	+0.084	8.4948	+0.0848	8.4948	+0.0848
Σ		0.3386	0.303		1.530		1.530		1.4174		1.3039

为 $\pm \Delta x$, y 的误差为 $\pm \Delta y$ 。

则: $x/y = \frac{x \pm \Delta x}{y \pm \Delta y}$, 相对误差为

$\pm 100 \left(\frac{\Delta x}{x} + \frac{\Delta y}{y} \right) \%$, 晶胞常数和 $d(A)$

值一般最好保证精度到小数点后第三位, 在布拉格低角度也要保证到小数点后第二位数

2. 如果某一矿物的粉晶衍射有 n 条线, 理论上作 $(n-1) + (n-2) + (n-3) + \dots + 1$ 次 d_{hkl}^* 的除法, 而实际只对开头的 10—20 条线作 2—3 次除法就够了。

3. 另一例子是硅镁石(humite), 斜方晶系, $b/a=2.023$, $b/c=4.376$, 在 ASTM 卡片上有标星, 表示指标化精度高, 但经过大量的计算(计算量大于锂铍石)证明其 $b/a=2.032$ $b/c=4.409$ 与 $b(A)$ 值 (d_{hkl}^{*2} 之比值)拟合最佳, 说明实际的 $b(A)$ 较给出的 $b(A)$ 稍高, 或 a 、 c 比给出的稍低或兼而有之。

4. 以上 b/a , c/a 可变为常用的 $a:b:c$ ($a/b:1:c/b$)。

5. 对单斜晶系: β 由 $90^\circ, 91^\circ, 92^\circ, \dots, 120^\circ$ 递增, 计算方法同斜方晶系。以 1° 递增, 从理论上单斜晶系的计算量为斜方晶系的 30 倍, 但实际较此倍数小, 因为 $\sin 90^\circ \rightarrow \sin 100^\circ$, 如按 1° 递增, 其差均在小数点后第三位 ($0.00x$), 而 $0.00x$ 是我们要求 $d(A)$ 的最高精度, 因此, 单单由 β 角在 $90^\circ-100^\circ$ 范围内引起的数值变化不大。所以, 实际计算工作量肯定可以大大缩减, 而所用的计算方法与斜方晶系完全相同。考虑除 $\sin \beta$ 外尚有 $\cos \beta$ 的影响, β 由 $90^\circ \rightarrow 120^\circ$ 对 $\cos \beta$ 的变化较 $\sin \beta$ 大。如有需要 β 可以 0.5° 递增, 此可经过试算加以确定。

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TO INDEX X-RAY POWDER DIFFRACTION LINES OF LOWER SYMMETRICAL SYSTEMS (ORTHORHOMBIC, MONOCLINIC) BY MEANS OF THE RATIO METHOD

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Abstract

To index X-ray powder diffraction lines of an unknown crystal is, in general, based on the known cell constants, or on the high symmetry of crystals. The constants and λ in the d-calculating formula can be cancelled by the ratio method. The experimental $d(\text{\AA})$ -values are expressed by the reciprocals of the squares of the $d(\text{\AA})$ -values, i. e. d^{*2}_{hkl} . By dividing the rear d^{*2}_{hkl} 's, by those of the first, second, third etc., in the order of the initial descending $d(\text{\AA})$ -values we acquire the ratio values.

In order to reduce the calculation, we take first ten or twenty lines in diffraction patterns and take three dividings with the 1st, 2nd and 3rd d^{*2}_{hkl} as divisors.

For isometric crystals, there is a maximum common factor (M. C. F.) in the ratio $d^{*2}_{(hkl)_n}/d^{*2}_{(hkl)_m}$, i. e. $a^{*2}(=d^{*2}_{100})$. For tetragonal, trigonal or hexagonal crystals, the ratios of d^{*2}_{h00} , d^{*2}_{0k0} and d^{*2}_{h00} are either the same as

those in isometric or showing some particular values, c can be found after the determination of a and b . For orthorhombic,

$$d^{*2}_{(hkl)_n}/d^{*2}_{(hkl)_m} = h_n^2 + k_n^2/(b/a)^2 + l_n^2/(c/a)^2 / [h_m^2 + k_m^2/(b/a)^2 + l_m^2/(c/a)^2]$$

and for monoclinic,

$$d^{*2}_{(hkl)_n}/d^{*2}_{(hkl)_m} = 1/\sin^2\beta [h_n^2 + l_n^2/(c/a)^2 - 2h_n l_n \cos\beta/(c/a)] + \\ k_n^2/(b/a)^2 / [1/\sin^2\beta [h_m^2 + l_m^2/(c/a)^2 - 2h_m l_m \cos\beta/(c/a)] + k_m^2/(b/a)^2]$$

Calculations of the ratios show that the more the approach of b/a 's and c/a 's of two crystals, the more the approach of their respective ratios of the d^{*2}_{hkl} 's. The essential of the method is to find the $b/a(=A)$ and $c/a(=C)$ from the given $d(\text{\AA})$ -values by calculating and comparing the ratios of the $d^{*2}_{hkl}(Q_{hkl})$. These ratios are arranged systematically with A, C as coordinates in order to facilitate the locating of A & C of an unknown. Sixty orthorhombic minerals of known A & C were calculated and the ratios of the nearest A and C may be discriminated, as in $A=0.904, C=0.780$ & $A=0.904, C=0.784$, $A=0.8919, C=0.354$ & $A=0.983, C=0.355$ and hence the method is practicable. The same and high reliabilities of both a, b, c and $d(\text{\AA})$ -values are necessary. The accuracy of calculations depends on that of a, b, c and $d(\text{\AA})$ -values, found experimentally. For monoclinic crystals the angle varies from 90° to 120° .