闪锌矿晶体的讨论

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1 结构

闪锌矿 ZnS 结构如图 1 所示，S 原子（绿色）位于 $000, 0\frac{1}{2}\frac{1}{2}, \frac{1}{2}0\frac{1}{2}, \frac{1}{2}\frac{1}{2}0$,Zn 原子（紫色）坐标 $\frac{1}{4}\frac{1}{4}\frac{1}{4}, \frac{1}{4}\frac{3}{4}\frac{3}{4}, \frac{3}{4}\frac{1}{4}\frac{3}{4}, \frac{3}{4}\frac{3}{4}\frac{1}{4}$

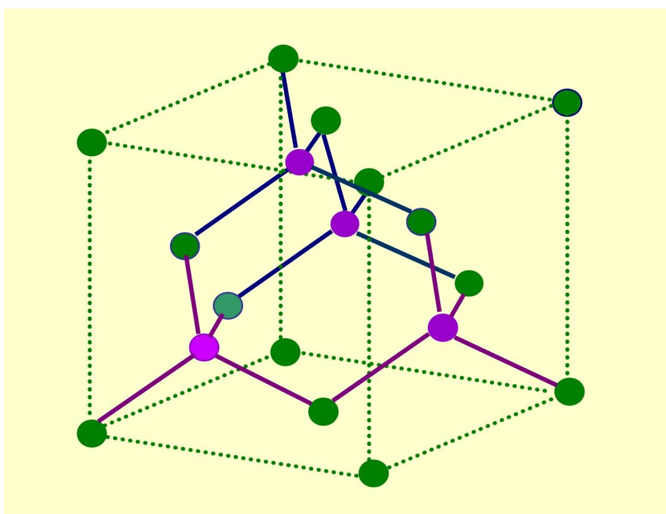


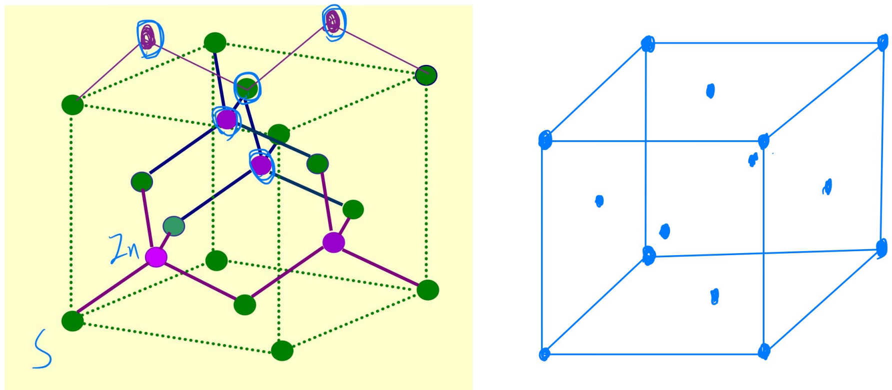
图 1: 闪锌矿结构

可以取如图 2 一个 S 原子连接四个 Zn 原子（由每个 Zn 与 4 个 S 相连，各占有 $\frac{1}{4}$）为一个基元，则可以等效于面心立方点阵。

闪锌矿的原胞如图 3，连接顶点 S 原子到两个邻近的面心得到原胞基矢。

$$\begin{cases} \vec{\alpha_1} = \frac{a}{2}\hat{x} + \frac{a}{2}\hat{y} \\ \vec{\alpha_2} = \frac{a}{2}\hat{x} + \frac{a}{2}\hat{z} \\ \vec{\alpha_3} = \frac{a}{2}\hat{y} + \frac{a}{2}\hat{z} \end{cases} \tag{1}$$

可见在一个原胞中，内部包含了一个 Zn 原子，其余的三个 Zn 原子在原胞外，且原胞八个顶点的 S 原子各占有 $\frac{1}{8}$，共有一个 Zn，一个 S。对应闪锌矿的化学组成 ZnS。其 Wigner-Seitz 原胞对应于体心立方的布里渊区，即为正菱形十二面体。



(a) 基元　　(b) 等效面心立方晶格

图 2: 基元选取

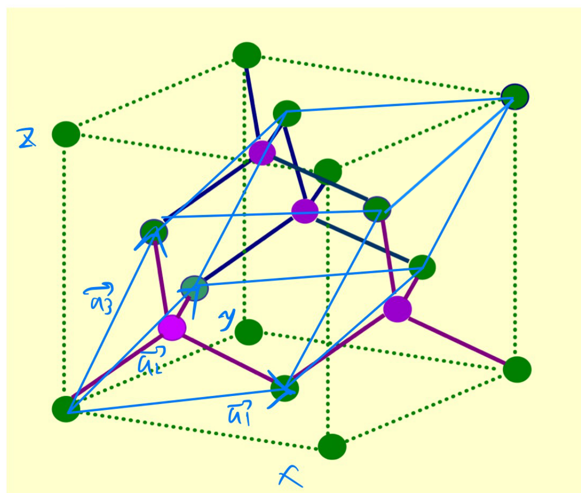


图 3: 原胞

1.1 对称性

首先对面面心的连线为二重旋转轴，同时也为四重旋转反演轴，共 3 条；体对角线为三重旋转轴，共 4 条；同时晶格表面的面对角线，与该面面心与对面面心连线轴构成的平面均为反映面，共有 6 个反映面。由此得到闪锌矿的点群为 T_d 点群。

闪锌矿由不同原子构成，其失去了金刚石原有的四度螺旋轴。

1.2 倒易点阵与布里渊区

由于基元组成的晶格为面心立方，其倒易点阵为边长为 $\frac{4\pi}{a}$ 的体心立方。倒格子基矢

$$\begin{cases} \vec{b_1} = \frac{2\pi}{a}(\hat{x} + \hat{y} - \hat{z}) \\ \vec{b_2} = \frac{2\pi}{a}(\hat{x} - \hat{y} + \hat{z}) \\ \vec{b_3} = \frac{2\pi}{a}(-\hat{x} + \hat{y} + \hat{z}) \end{cases} \tag{2}$$

对应的第一布里渊区为一个截角八面体如图4

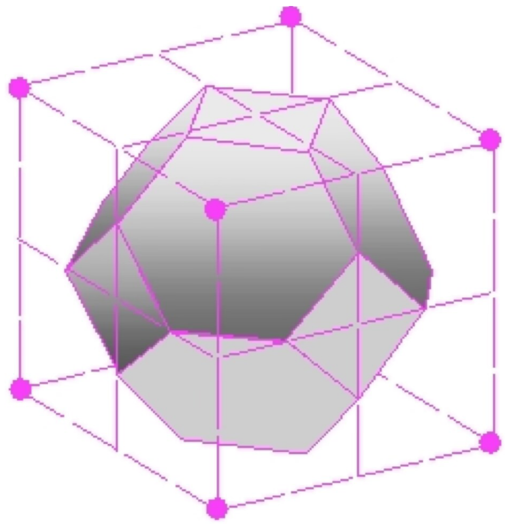


图 4: 第一布里渊区

如图 5 进一步可以推知第二布里渊区为该体心立方本身（次近邻点为紫色，为近邻晶格的体心），第三布里渊区仍为截角八面体（第三近邻点为绿色，为对角晶格的体心）。

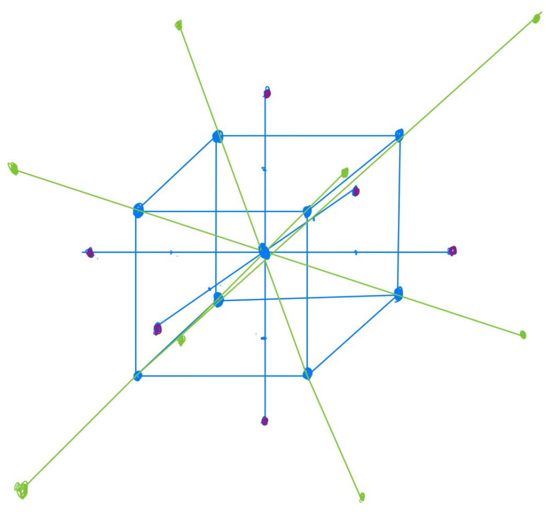


图 5: 第 2、3 **布里渊区**

1.3 晶体衍射

惯用晶胞中有 8 个原子，分别是 4 个 S 原子: 000，$\frac{1}{2}\frac{1}{2}0$，$\frac{1}{2}0\frac{1}{2}$，$0\frac{1}{2}\frac{1}{2}$ 和 4 个 Zn 原子:$\frac{1}{4}\frac{1}{4}\frac{1}{4}$，$\frac{3}{4}\frac{3}{4}\frac{1}{4}$，$\frac{1}{4}\frac{3}{4}\frac{3}{4}$，$\frac{3}{4}\frac{1}{4}\frac{3}{4}$，令 S 原子的原子散射因子为 f_a，Zn 原子的原子散射因子 f_b，对于波矢 $k = \frac{2\pi}{a}(H, K, L)$，则闪锌矿的几何结构因子

$$\begin{aligned}
F_{HKL} &= f_a[1 + \exp(i\pi(H+K)) + \exp(i\pi(K+L)) + \exp(i\pi(L+H))] \\
&\quad + f_b[\exp(i\frac{\pi}{2}(H+K+L)) + \exp(i\frac{\pi}{2}(3H+3K+L)) + \exp(i\frac{\pi}{2}(H+3K+3L)) + \exp(i\frac{\pi}{2}(3H+K+3L))] \\
&= (f_a + f_b \exp(i\frac{\pi}{2}(H+K+L)))[1 + \exp(i\pi(H+K)) + \exp(i\pi(K+L)) + \exp(i\pi(L+H))]
\end{aligned} \tag{3}$$

由此可见闪锌矿的几何结构因子类似于 2 个面心立方结构相差一定相位的线性组合。当 H,K,L 奇偶混杂时，$F_{HKL}=0$，衍射峰消失；当 H，K，L 全为奇数时，$|F_{HKL}|=4\sqrt{f_a^2+f_b^2}$；当 H,K,L 全部是偶数，且 H+K+L=4n(其中 n 为整数)时，达到极大值 $|F_{HKL}|=4(f_a+f_b)$。

2 晶体结合

ZnS 通过共价键结合，每个 Zn 原子和 S 原子的配位数都是 4，与金刚石类似，存在 sp^3 杂化。但是异类原子组成的晶体形成的共价键也包括离子键的成分。这里取 8 个惯用晶胞组成的大正方体，以该 8 个惯用晶胞共同的顶点为原点，在最接近的 Zn 与 S 原子的间距取为 1 的情况下，可得惯用晶胞正方体边长为 $a=\frac{4}{\sqrt{3}}$，可以计算 ZnS 的马德隆常数如下

$$\alpha=\frac{4}{1}+\frac{4}{3}+12\sqrt{\frac{3}{11}}+12\sqrt{\frac{3}{19}}-12\frac{\sqrt{3}}{2\sqrt{2}}-\frac{6}{2}\frac{\sqrt{3}}{4}-\frac{24}{2}\frac{1}{2\sqrt{2}}-\frac{12}{4}\frac{\sqrt{3}}{4\sqrt{2}}-\frac{8}{8}\frac{1}{4}=2.3097 \tag{4}$$

该计算结果与标准结果 1.638 相比存在一定差距。如果进一步提高所取的晶格范围，可以得到更加接近的结果。

3 晶格振荡

分别使用 l,m,n 编号原子的基矢 $\vec{a_1}=\frac{a}{2}(\hat{x}+\hat{z}),\vec{a_2}=\frac{a}{2}(\hat{x}+\hat{y}),\vec{a_3}=\frac{a}{2}(\hat{y}+\hat{z})$ 方向序号。取 S 原子与临近沿对角线方向的一个 Zn 原子为原胞，S 原子位于 1 位置，Zn 原子位于 2 位置。偏移格点的位移用 u^x,u^y,u^z 表示。

假设 S 与 S 原子间相互作用力系数为 A，Zn 与 Zn 原子之间相互作用系数为 B,S 与 Zn 之间的力相互作用系数为 C。S 原子质量 m，Zn 原子质量为 M。现在对第 (l_1,m_1,n_1) 与 (l_2,m_2,n_2) 的 S 原子和 Zn 原子作为原胞进行受力分析。

首先是 S 原子：

$$\begin{aligned}
m\ddot{u}^x_{l_1m_1n_1}=&-\frac{C}{3}(u^x_{l_1m_1n_1}+u^y_{l_1m_1n_1}+u^z_{l_1m_1n_1}-u^x_{l_2m_2n_2}-u^y_{l_2m_2n_2}-u^x_{l_2m_2n_2})\\
&-\frac{C}{3}(u^x_{l_1m_1n_1}-u^x_{l_2(m_2-1)n_2}+u^y_{l_1m_1n_1}-u^y_{l_2(m_2-1)n_2}-u^z_{l_1m_1n_1}+u^z_{l_2(m_2-1)n_2})\\
&-\frac{C}{3}(u^x_{l_1m_1n_1}-u^x_{l_2m_2(n_2-1)}-u^y_{l_1m_1n_1}+u^y_{l_2m_2(n_2-1)}-u^z_{l_1m_1n_1}+u^z_{l_2m_2(n_2-1)})\\
&-\frac{C}{3}(u^x_{l_1m_1n_1}-u^x_{(l_2-1)m_2n_2}-u^y_{l_1m_1n_1}+u^y_{(l_2-1)m_2n_2}+u^z_{l_1m_1n_1}-u^z_{(l_2-1)m_2n_2})\\
&+\frac{A}{2}\Big[(u^x_{(l_1+1)m_1n_1}-u^x_{l_1m_1n_1})+(u^x_{(l_1-1)m_1n_1}-u^x_{l_1m_1n_1})+(u^x_{l_1(m_1+1)n_1}-u^x_{l_1m_1n_1})+(u^x_{l_1(m_1-1)n_1}-u^x_{l_1m_1n_1})\\
&+(u^x_{(l_1+1)m_1(n_1-1)}-u^x_{l_1m_1n_1})+(u^x_{(l_1-1)m_1(n_1+1)}-u^x_{l_1m_1n_1})+(u^x_{l_1(m_1+1)(n_1-1)}-u^x_{l_1m_1n_1})+(u^x_{l_1(m_1-1)(n_1+1)}-u^x_{l_1m_1n_1})\\
&+(u^y_{l_1(m_1+1)n_1}-u^y_{l_1m_1n_1})+(u^y_{l_1(m_1-1)n_1}-u^y_{l_1m_1n_1})-(u^y_{(l_1+1)m_1(n_1-1)}-u^y_{l_1m_1n_1})-(u^y_{(l_1-1)m_1(n_1+1)}-u^y_{l_1m_1n_1})\\
&+(u^z_{(l_1+1)m_1n_1}-u^z_{l_1m_1n_1})+(u^z_{(l_1-1)m_1n_1}-u^z_{l_1m_1n_1})-(u^z_{l_1(m_1+1)(n_1-1)}-u^z_{l_1m_1n_1})-(u^z_{l_1(m_1-1)(n_1+1)}-u^z_{l_1m_1n_1})\Big]
\end{aligned} \tag{5}$$

$$
\begin{aligned}
m\ddot{u}^y_{l_1m_1n_1} = &-\frac{C}{3}(u^x_{l_1m_1n_1}+u^y_{l_1m_1n_1}+u^z_{l_1m_1n_1}-u^x_{l_2m_2n_2}-u^y_{l_2m_2n_2}-u^x_{l_2m_2n_2})\\
&-\frac{C}{3}(u^x_{l_1m_1n_1}-u^x_{l_2(m_2-1)n_2}+u^y_{l_1m_1n_1}-u^y_{l_2(m_2-1)n_2}-u^z_{l_1m_1n_1}+u^z_{l_2(m_2-1)n_2})\\
&+\frac{C}{3}(u^x_{l_1m_1n_1}-u^x_{l_2m_2(n_2-1)}-u^y_{l_1m_1n_1}+u^y_{l_2m_2(n_2-1)}-u^z_{l_1m_1n_1}+u^z_{l_2m_2(n_2-1)})\\
&+\frac{C}{3}(u^x_{l_1m_1n_1}-u^x_{(l_2-1)m_2n_2}-u^y_{l_1m_1n_1}+u^y_{(l_2-1)m_2n_2}+u^z_{l_1m_1n_1}-u^z_{(l_2-1)m_2n_2})\\
&+\frac{A}{2}\big[(u^y_{l_1m_1(n_1+1)}-u^y_{l_1m_1n_1})+(u^y_{l_1m_1(n_1-1)}-u^y_{l_1m_1n_1})+(u^y_{l_1(m_1+1)n_1}-u^y_{l_1m_1n_1})+(u^y_{l_1(m_1-1)n_1}-u^y_{l_1m_1n_1})\\
&+(u^y_{(l_1+1)m_1(n_1-1)}-u^y_{l_1m_1n_1})+(u^y_{(l_1-1)m_1(n_1+1)}-u^y_{l_1m_1n_1})+(u^y_{(l_1-1)(m_1+1)n_1}-u^y_{l_1m_1n_1})+(u^y_{(l_1+1)(m_1-1)n_1}-u^y_{l_1m_1n_1})\\
&+(u^x_{l_1(m_1+1)n_1}-u^x_{l_1m_1n_1})+(u^x_{l_1(m_1-1)n_1}-u^x_{l_1m_1n_1})-(u^x_{(l_1+1)m_1(n_1-1)}-u^x_{l_1m_1n_1})-(u^x_{(l_1-1)m_1(n_1+1)}-u^x_{l_1m_1n_1})\\
&+(u^z_{l_1m_1(n_1+1)}-u^z_{l_1m_1n_1})+(u^z_{l_1m_1(n_1-1)}-u^z_{l_1m_1n_1})-(u^z_{(l_1-1)(m_1+1)n_1}-u^z_{l_1m_1n_1})-(u^z_{(l_1+1)(m_1-1)n_1}-u^z_{l_1m_1n_1})\big]
\end{aligned}
\tag{6}
$$

$$
\begin{aligned}
m\ddot{u}^z_{l_1m_1n_1} = &-\frac{C}{3}(u^x_{l_1m_1n_1}+u^y_{l_1m_1n_1}+u^z_{l_1m_1n_1}-u^x_{l_2m_2n_2}-u^y_{l_2m_2n_2}-u^x_{l_2m_2n_2})\\
&+\frac{C}{3}(u^x_{l_1m_1n_1}-u^x_{l_2(m_2-1)n_2}+u^y_{l_1m_1n_1}-u^y_{l_2(m_2-1)n_2}-u^z_{l_1m_1n_1}+u^z_{l_2(m_2-1)n_2})\\
&+\frac{C}{3}(u^x_{l_1m_1n_1}-u^x_{l_2m_2(n_2-1)}-u^y_{l_1m_1n_1}+u^y_{l_2m_2(n_2-1)}-u^z_{l_1m_1n_1}+u^z_{l_2m_2(n_2-1)})\\
&-\frac{C}{3}(u^x_{l_1m_1n_1}-u^x_{(l_2-1)m_2n_2}-u^y_{l_1m_1n_1}+u^y_{(l_2-1)m_2n_2}+u^z_{l_1m_1n_1}-u^z_{(l_2-1)m_2n_2})\\
&+\frac{A}{2}\big[(u^z_{l_1m_1(n_1+1)}-u^z_{l_1m_1n_1})+(u^z_{l_1m_1(n_1-1)}-u^z_{l_1m_1n_1})+(u^z_{(l_1+1)m_1n_1}-u^z_{l_1m_1n_1})+(u^z_{(l_1-1)m_1n_1}-u^y_{l_1m_1n_1})\\
&+(u^z_{l_1(m_1+1)(n_1-1)}-u^z_{l_1m_1n_1})+(u^z_{l_1(m_1-1)(n_1+1)}-u^z_{l_1m_1n_1})+(u^z_{(l_1-1)(m_1+1)n_1}-u^z_{l_1m_1n_1})+(u^z_{(l_1+1)(m_1-1)n_1}-u^z_{l_1m_1n_1})\\
&+(u^x_{(l_1+1)m_1n_1}-u^x_{l_1m_1n_1})+(u^x_{(l_1-1)m_1n_1}-u^x_{l_1m_1n_1})-(u^x_{l_1(m_1-1)(n_1+1)}-u^x_{l_1m_1n_1})-(u^x_{l_1(m_1+1)(n_1-1)}-u^x_{l_1m_1n_1})\\
&+(u^y_{l_1m_1(n_1+1)}-u^y_{l_1m_1n_1})+(u^y_{l_1m_1(n_1-1)}-u^y_{l_1m_1n_1})-(u^y_{(l_1-1)(m_1+1)n_1}-u^y_{l_1m_1n_1})-(u^y_{(l_1+1)(m_1-1)n_1}-u^y_{l_1m_1n_1})\big]
\end{aligned}
\tag{7}
$$

类似对于 Zn 原子受力分析

$$
\begin{aligned}
M\ddot{u}^x_{l_2m_2n_2} = &-\frac{C}{3}(u^x_{l_2m_2n_2}+u^y_{l_2m_2n_2}+u^z_{l_2m_2n_2}-u^x_{l_1m_1n_1}-u^y_{l_1m_1n_1}-u^x_{l_1m_1n_1})\\
&-\frac{C}{3}(u^x_{l_2m_2n_2}-u^x_{l_1(m_1+1)n_1}+u^y_{l_2m_2n_2}-u^y_{l_1(m_1+1)n_2}-u^z_{l_2m_2n_2}+u^z_{l_1(m_1+1)n_1})\\
&-\frac{C}{3}(u^x_{l_2m_2n_2}-u^x_{l_1m_1(n_1+1)}-u^y_{l_2m_2n_2}+u^y_{l_1m_1(n_1+1)}-u^z_{l_2m_2n_2}+u^z_{l_1m_1(n_1+1)})\\
&-\frac{C}{3}(u^x_{l_2m_2n_2}-u^x_{(l_1+1)m_1n_1}-u^y_{l_2m_2n_2}+u^y_{(l_1+1)m_1n_1}+u^z_{l_2m_2n_2}-u^z_{(l_1+1)m_1n_1})\\
&+\frac{B}{2}\big[(u^x_{(l_2+1)m_2n_2}-u^x_{l_2m_2n_2})+(u^x_{(l_2-1)m_2n_2}-u^x_{l_2m_2n_2})+(u^x_{l_2(m_2+1)n_2}-u^x_{l_2m_2n_2})+(u^x_{l_2(m_2-1)n_2}-u^x_{l_2m_2n_2})\\
&+(u^x_{(l_2+1)m_2(n_2-1)}-u^x_{l_2m_2n_2})+(u^x_{(l_2-1)m_2(n_2+1)}-u^x_{l_2m_2n_2})+(u^x_{l_2(m_2+1)(n_2-1)}-u^x_{l_2m_2n_2})+(u^x_{l_2(m_2-1)(n_2+1)}-u^x_{l_2m_2n_2})\\
&+(u^y_{l_2(m_2+1)n_2}-u^y_{l_2m_2n_2})+(u^y_{l_2(m_2-1)n_2}-u^y_{l_2m_2n_2})-(u^y_{(l_2+1)m_2(n_2-1)}-u^y_{l_2m_2n_2})-(u^y_{(l_2-1)m_2(n_2+1)}-u^y_{l_2m_2n_2})\\
&+(u^z_{(l_2+1)m_2n_2}-u^z_{l_2m_2n_2})+(u^z_{(l_2-1)m_2n_2}-u^z_{l_2m_2n_2})-(u^z_{l_2(m_2+1)(n_2-1)}-u^z_{l_2m_2n_2})-(u^z_{l_2(m_2-1)(n_2+1)}-u^z_{l_2m_2n_2})\big]
\end{aligned}
\tag{8}
$$

$$\begin{aligned}
M\ddot{u}^y_{l_2,m_2,n_2} = &-\frac{C}{3}(u^x_{l_2m_2n_2}+u^y_{l_2m_2n_2}+u^z_{l_2m_2n_2}-u^x_{l_1m_1n_1}-u^y_{l_1m_1n_1}-u^x_{l_1m_1n_1})\\
&-\frac{C}{3}(u^x_{l_2m_2n_2}-u^x_{l_1(m_1+1)n_1}+u^y_{l_2m_2n_2}-u^y_{l_1(m_1+1)n_2}-u^z_{l_2m_2n_2}+u^z_{l_1(m_1+1)n_1})\\
&+\frac{C}{3}(u^x_{l_2m_2n_2}-u^x_{l_1m_1(n_1+1)}-u^y_{l_2m_2n_2}+u^y_{l_1m_1(n_1+1)}-u^z_{l_2m_2n_2}+u^z_{l_1m_1(n_1+1)})\\
&+\frac{C}{3}(u^x_{l_2m_2n_2}-u^x_{(l_1+1)m_1n_1}-u^y_{l_2m_2n_2}+u^y_{(l_1+1)m_1n_1}+u^z_{l_2m_2n_2}-u^z_{(l_1+1)m_1n_1})\\
&+\frac{B}{2}\big[(u^y_{l_2m_2(n_2+1)}-u^y_{l_2m_2n_2})+(u^y_{l_2m_2(n_2-1)}-u^y_{l_2m_2n_2})+(u^y_{l_2(m_2+1)n_2}-u^y_{l_2m_2n_2})+(u^y_{l_2(m_2-1)n_2}-u^y_{l_2m_2n_2})\\
&+(u^y_{(l_2+1)m_2(n_2-1)}-u^y_{l_2m_2n_2})+(u^y_{(l_2-1)m_2(n_2+1)}-u^y_{l_2m_2n_2})+(u^y_{(l_2-1)(m_2+1)n_2}-u^y_{l_2m_2n_2})+(u^y_{(l_2+1)(m_2-1)n_2}-u^y_{l_2m_2n_2})\\
&+(u^x_{l_2(m_2+1)n_2}-u^x_{l_2m_2n_2})+(u^x_{l_2(m_2-1)n_2}-u^x_{l_2m_2n_2})-(u^x_{(l_2+1)m_2(n_2-1)}-u^x_{l_2m_2n_2})-(u^x_{(l_2-1)m_2(n_2+1)}-u^x_{l_2m_2n_2})\\
&+(u^z_{l_2m_2(n_2+1)}-u^z_{l_2m_2n_2})+(u^z_{l_2m_2(n_2-1)}-u^z_{l_2m_2n_2})-(u^z_{(l_2-1)(m_2+1)n_2}-u^z_{l_2m_2n_2})-(u^z_{(l_2+1)(m_2-1)n_2}-u^z_{l_2m_2n_2})\big]
\end{aligned} \tag{9}$$

$$\begin{aligned}
M\ddot{u}^z_{l_2,m_2,n_2} = &-\frac{C}{3}(u^x_{l_2m_2n_2}+u^y_{l_2m_2n_2}+u^z_{l_2m_2n_2}-u^x_{l_1m_1n_1}-u^y_{l_1m_1n_1}-u^x_{l_1m_1n_1})\\
&+\frac{C}{3}(u^x_{l_2m_2n_2}-u^x_{l_1(m_1+1)n_1}+u^y_{l_2m_2n_2}-u^y_{l_1(m_1+1)n_2}-u^z_{l_2m_2n_2}+u^z_{l_1(m_1+1)n_1})\\
&+\frac{C}{3}(u^x_{l_2m_2n_2}-u^x_{l_1m_1(n_1+1)}-u^y_{l_2m_2n_2}+u^y_{l_1m_1(n_1+1)}-u^z_{l_2m_2n_2}+u^z_{l_1m_1(n_1+1)})\\
&-\frac{C}{3}(u^x_{l_2m_2n_2}-u^x_{(l_1+1)m_1n_1}-u^y_{l_2m_2n_2}+u^y_{(l_1+1)m_1n_1}+u^z_{l_2m_2n_2}-u^z_{(l_1+1)m_1n_1})\\
&+\frac{B}{2}\big[(u^z_{l_2m_2(n_2+1)}-u^z_{l_2m_2n_2})+(u^z_{l_2m_2(n_2-1)}-u^z_{l_2m_2n_2})+(u^z_{(l_2+1)m_2n_2}-u^z_{l_2m_2n_2})+(u^z_{(l_2-1)m_2n_2}-u^y_{l_2m_2n_2})\\
&+(u^z_{l_2(m_2+1)(n_2-1)}-u^z_{l_2m_2n_2})+(u^z_{l_2(m_2-1)(n_2+1)}-u^z_{l_2m_2n_2})+(u^z_{(l_2-1)(m_2+1)n_2}-u^z_{l_2m_2n_2})+(u^z_{(l_2+1)(m_2-1)n_2}-u^z_{l_2m_2n_2})\\
&+(u^x_{(l_2+1)m_2n_2}-u^x_{l_2m_2n_2})+(u^x_{(l_2-1)m_2n_2}-u^x_{l_2m_2n_2})-(u^x_{l_2(m_2-1)(n_2+1)}-u^x_{l_2m_2n_2})-(u^x_{l_2(m_2+1)(n_2-1)}-u^x_{l_2m_2n_2})\\
&+(u^y_{l_2m_2(n_2+1)}-u^y_{l_2m_2n_2})+(u^y_{l_2m_2(n_2-1)}-u^y_{l_2m_2n_2})-(u^y_{(l_2-1)(m_2+1)n_2}-u^y_{l_2m_2n_2})-(u^y_{(l_2+1)(m_2-1)n_2}-u^y_{l_2m_2n_2})\big]
\end{aligned} \tag{10}$$

可以得到方程解的形式

$$\boldsymbol{u}_{l_1m_1n_1}=\vec{S}\exp\big[i(\omega t-k_xa\frac{l_1+m_1}{2}-k_ya\frac{m_1+n_1}{2}-k_za\frac{l_1+n_1}{2})\big] \tag{11}$$

$$\boldsymbol{u}_{l_2m_2n_2}=\vec{Z}\exp\big[i(\omega t-k_xa\frac{l_2+m_2}{2}-k_ya\frac{m_2+n_2}{2}-k_za\frac{l_2+n_2}{2})\big] \tag{12}$$

根据 S 原子和 Zn 原子位置关系，$(l_2,m_2,n_2)=(l_1+\frac{1}{4},m_1+\frac{1}{4},n_1+\frac{1}{4})$

$$\boldsymbol{u}_{l_2m_2n_2}=\vec{Z}\exp\big[i(\omega t-k_xa\frac{l_1+m_1+\frac{1}{2}}{2}-k_ya\frac{m_1+n_1+\frac{1}{2}}{2}-k_za\frac{l_1+n_1+\frac{1}{2}}{2})\big] \tag{13}$$

将解反带回方程 (5)-(10)，为便于计算，这里取 $\boldsymbol{k}=(k,0,0)$ 即波矢沿 x 方向，可以得到以下线性方程组

$$\big\{m\omega^2-\frac{4}{3}C+A[4\cos(\frac{k}{2}a)-4]\big\}S_x+\frac{4}{3}C\cos(\frac{k}{4}a)Z_x=0 \tag{14}$$

$$\big\{m\omega^2-\frac{4}{3}C+A[2\cos(\frac{k}{2}a)-2]\big\}S_y+\frac{4}{3}C\cos(\frac{k}{4}a)Z_y-i\frac{4}{3}C\sin(\frac{k}{4}a)Z_z=0 \tag{15}$$

$$\big\{m\omega^2-\frac{4}{3}C+A[2\cos(\frac{k}{2}a)-2]\big\}S_z+\frac{4}{3}C\cos(\frac{k}{4}a)Z_z-i\frac{4}{3}C\sin(\frac{k}{4}a)Z_y=0 \tag{16}$$

$$\left\{M\omega^2-\frac{4}{3}C+B[4\cos(\frac{k}{2}a)-4]\right\}Z_x+\frac{4}{3}C\cos(\frac{k}{4}a)S_x=0 \tag{17}$$

$$\left\{M\omega^2-\frac{4}{3}C+B[2\cos(\frac{k}{2}a)-2]\right\}Z_y+\frac{4}{3}C\cos(\frac{k}{4}a)S_y+i\frac{4}{3}C\sin(\frac{k}{4}a)S_z=0 \tag{18}$$

$$\left\{M\omega^2-\frac{4}{3}C+B[2\cos(\frac{k}{2}a)-2]\right\}Z_z+\frac{4}{3}C\cos(\frac{k}{4}a)S_z+i\frac{4}{3}C\sin(\frac{k}{4}a)S_y=0 \tag{19}$$

带入 Mathematica 进行求解行列式得到色散关系，根据有解条件, 得到符合物理实际的 6 个正根 其中 f[k],t[k] 对

f[k] =

$$\sqrt{\left(\frac{A}{m}+\frac{2c}{3m}+\frac{B}{M}+\frac{2c}{3M}-\frac{A\,\mathrm{Cos}[\frac{ak}{2}]}{m}-\frac{B\,\mathrm{Cos}[\frac{ak}{2}]}{M}-\frac{1}{6mM}\left(\sqrt{\left(\left(-6Bm-4cm-6AM-4cM+6Bm\,\mathrm{Cos}[\frac{ak}{2}]+6AM\,\mathrm{Cos}[\frac{ak}{2}]\right)^2-12mM\left(18AB+8Ac+8Bc-24AB\,\mathrm{Cos}[\frac{ak}{2}]-8Ac\,\mathrm{Cos}[\frac{ak}{2}]-8Bc\,\mathrm{Cos}[\frac{ak}{2}]+6AB\,\mathrm{Cos}[ak]\right)\right)}\right)\right)}$$

g[k] =

$$\sqrt{\left(\frac{A}{m}+\frac{2c}{3m}+\frac{B}{M}+\frac{2c}{3M}-\frac{A\,\mathrm{Cos}[\frac{ak}{2}]}{m}-\frac{B\,\mathrm{Cos}[\frac{ak}{2}]}{M}+\frac{1}{6mM}\left(\sqrt{\left(\left(-6Bm-4cm-6AM-4cM+6Bm\,\mathrm{Cos}[\frac{ak}{2}]+6AM\,\mathrm{Cos}[\frac{ak}{2}]\right)^2-12mM\left(18AB+8Ac+8Bc-24AB\,\mathrm{Cos}[\frac{ak}{2}]-8Ac\,\mathrm{Cos}[\frac{ak}{2}]-8Bc\,\mathrm{Cos}[\frac{ak}{2}]+6AB\,\mathrm{Cos}[ak]\right)\right)}\right)\right)}$$

t[k] =

$$\sqrt{\left(\frac{2A}{m}+\frac{2c}{3m}+\frac{2B}{M}+\frac{2c}{3M}-\frac{2A\,\mathrm{Cos}[\frac{ak}{2}]}{m}-\frac{2B\,\mathrm{Cos}[\frac{ak}{2}]}{M}-\frac{1}{18mM}\left(\sqrt{\left(\left(-36Bm-12cm-36AM-12cM+36Bm\,\mathrm{Cos}[\frac{ak}{2}]+36AM\,\mathrm{Cos}[\frac{ak}{2}]\right)^2-36mM\left(216AB+48Ac+48Bc+8c^2-288AB\,\mathrm{Cos}[\frac{ak}{2}]-48Ac\,\mathrm{Cos}[\frac{ak}{2}]-48Bc\,\mathrm{Cos}[\frac{ak}{2}]-8c^2\,\mathrm{Cos}[\frac{ak}{2}]+72AB\,\mathrm{Cos}[ak]\right)\right)}\right)\right)}$$

n[k] =

$$\sqrt{\left(\frac{2A}{m}+\frac{2c}{3m}+\frac{2B}{M}+\frac{2c}{3M}-\frac{2A\,\mathrm{Cos}[\frac{ak}{2}]}{m}-\frac{2B\,\mathrm{Cos}[\frac{ak}{2}]}{M}+\frac{1}{18mM}\left(\sqrt{\left(\left(-36Bm-12cm-36AM-12cM+36Bm\,\mathrm{Cos}[\frac{ak}{2}]+36AM\,\mathrm{Cos}[\frac{ak}{2}]\right)^2-36mM\left(216AB+48Ac+48Bc+8c^2-288AB\,\mathrm{Cos}[\frac{ak}{2}]-48Ac\,\mathrm{Cos}[\frac{ak}{2}]-48Bc\,\mathrm{Cos}[\frac{ak}{2}]-8c^2\,\mathrm{Cos}[\frac{ak}{2}]+72AB\,\mathrm{Cos}[ak]\right)\right)}\right)\right)}$$

应声学支,$k\to 0$ 时 $\omega\to 0$;g[k],n[k] 对应光学支，$k\to 0$ 时 $\omega\to\sqrt{\frac{4C}{3}(\frac{1}{m}+\frac{1}{M})}$;f[k],g[k] 均为二重根,t[k],n[k] 为单根

带入 $\frac{M}{m}=\frac{65}{32}$, 并假设 $A=B=C$, 可得如图6色散关系

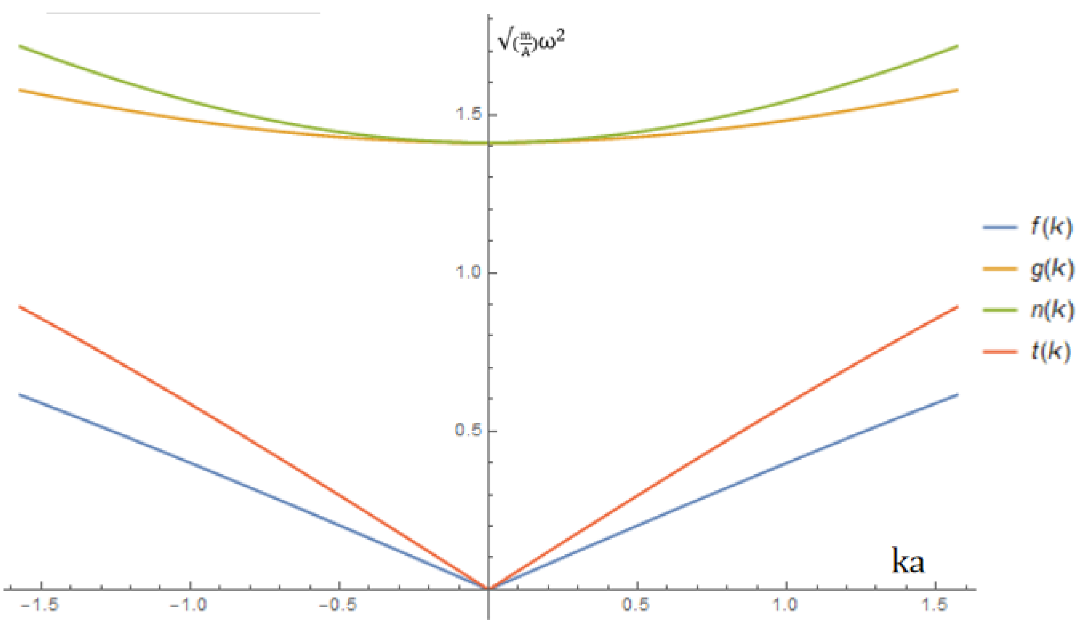


图 6: ZnS **晶体色散关系**

4 晶体能带

4.1 近自由电子近似

根据图4, 可见由于能隙是 Bloch 波入射与反射波的干涉结果，根据式 (3) 得到的几何结构因子，可知在第一布里渊区的 $(\pm1,0,0),(0,\pm1,0),(0,0,\pm1)$ 的三个方向上 $F_{HKL}=0$，界面上的能隙为 0 。因此得到简约布里渊区能带如图7, 可得第 1、2 布里渊区边界不存在禁带。

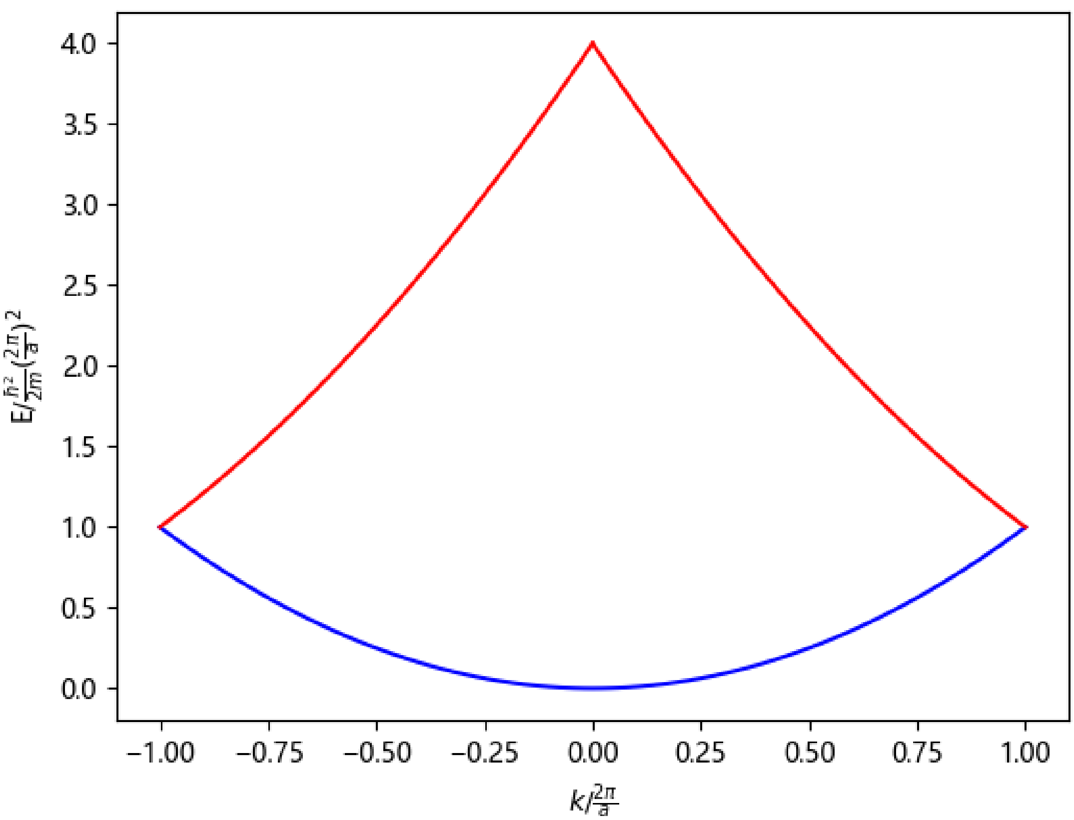


图 7: 近自由电子近似下 ZnS 简约能带

4.2 紧束缚近似

考虑 ZnS 结构的 S 带，得到方程为

$$\alpha\big[(\epsilon_A-E)-\sum_{\vec{R}_l}J_A(\vec{R}_S)\exp(-i\vec{k}\cdot\vec{R}_S)\big]-\beta\sum_{\vec{R}_l}J_{AB}(\vec{R}_S)\exp(i\vec{k}\cdot(\vec{R}_l+\vec{r}_A-\vec{r}_B))=0 \tag{20}$$

$$\alpha\sum_{\vec{R}_l}J_{BA}(\vec{R}_S)\exp(i\vec{k}\cdot(\vec{R}_l-\vec{r}_A+\vec{r}_B))-\beta\big[(\epsilon_B-E)-\sum_{\vec{R}_l}J_B(\vec{R}_S)\exp(-i\vec{k}\cdot\vec{R}_S)\big]=0 \tag{21}$$

其中 A 对应 Zn 原子，B 对应 S 原子，其中

$$J_A = -\int \phi_A^*(\vec{\xi}-\vec{R}_S-\vec{r}_A)\big[V(\vec{\xi})-U_A(\vec{\xi}-\vec{r}_A)\big]\phi_A(\vec{\xi}-\vec{r}_A)d\vec{\xi} \tag{22}$$

$$J_B = -\int \phi_B^*(\vec{\xi}-\vec{R}_S-\vec{r}_B)\big[V(\vec{\xi})-U_B(\vec{\xi}-\vec{r}_B)\big]\phi_B(\vec{\xi}-\vec{r}_B)d\vec{\xi} \tag{23}$$

$$J_{AB} = -\int \phi_A^*(\vec{\xi}-\vec{R}_S-\vec{r}_A)\big[V(\vec{\xi})-U_B(\vec{\xi}-\vec{r}_B)\big]\phi_B(\vec{\xi}-\vec{r}_B)d\vec{\xi} \tag{24}$$

$$J_{BA} = -\int \phi_B^*(\vec{\xi}-\vec{R}_S-\vec{r}_B)\big[V(\vec{\xi})-U_A(\vec{\xi}-\vec{r}_A)\big]\phi_A(\vec{\xi}-\vec{r}_A)d\vec{\xi} \tag{25}$$

带入只考虑最邻近原子

$$\begin{vmatrix} \epsilon_A - E - J_A & -2J_{AB}\big[\exp(i\frac{k_z a}{4})\cos(\frac{k_x-k_y}{4}a)+\exp(-i\frac{k_z a}{4})\cos(\frac{k_x+k_y}{4}a)\big] \\ -2J_{BA}\big[\exp(i\frac{k_z a}{4})\cos(\frac{k_x+k_y}{4}a)+\exp(-i\frac{k_z a}{4})\cos(\frac{k_x-k_y}{4}a)\big] & \epsilon_B - E - J_B \end{vmatrix} = 0 \tag{26}$$

假设 $J_{AB}=J_{BA}$，得到结果

$$E_\pm(\vec{k}) = \frac{\epsilon_A+\epsilon_B-J_A-J_B}{2} \pm \sqrt{(\frac{\epsilon_A-\epsilon_B-J_A+J_B}{2})^2 + 16J_{AB}^2(\cos^2\frac{k_x a}{4}\cos^2\frac{k_y a}{4}\cos^2\frac{k_z a}{4}+\sin^2\frac{k_x a}{4}\sin^2\frac{k_y a}{4}\sin^2\frac{k_z a}{4})} \tag{27}$$

4.3 空格子模型

取波矢 k 沿 [010] 方向，根据面心立方结构，取 k 单位 $\frac{2\pi}{a}$，E 单位 $\frac{\hbar^2}{2m}(\frac{2\pi}{a})^2$，可得一下各情况

(1)$(n_x n_y n_z)$=(000)

$$E_1 = (k_y)^2 \tag{28}$$

能量范围 $0 \to 1 \times \frac{\hbar^2}{2m}(\frac{2\pi}{a})^2$，非简并。

(2)$(n_x n_y n_z)$=$(1\bar{1}1)$, $(1\bar{1}\bar{1})$, $(\bar{1}\bar{1}1)$, $(\bar{1}\bar{1}\bar{1})$

$$E_2 = \big[1+(k_y-1)^2+1\big] \tag{29}$$

能量范围 $3 \to 2 \times \frac{\hbar^2}{2m}(\frac{2\pi}{a})^2$，4 重简并。

(3)$(n_x n_y n_z)$=(111), $(11\bar{1})$, $(\bar{1}11)$, $(\bar{1}1\bar{1})$

$$E_3 = \big[1+(k_y+1)^2+1\big] \tag{30}$$

能量范围 $3 \to 6 \times \frac{\hbar^2}{2m}(\frac{2\pi}{a})^2$，4 重简并。

(4)$(n_x n_y n_z)$=$(0\bar{2}0)$

$$E_4 = (k_y-2)^2 \tag{31}$$

能量范围 $4 \to 1 \times \frac{\hbar^2}{2m}(\frac{2\pi}{a})^2$，非简并。

(5)$(n_x n_y n_z)$=(200), $(\bar{2}00)$, $(00\bar{2})$, (002)

$$E_5 = \big[(k_y+1)^2+4\big] \tag{32}$$

能量范围 $4 \to 5 \times \frac{\hbar^2}{2m}(\frac{2\pi}{a})^2$，4 重简并。

(6)$(n_x n_y n_z)$=(020)

$$E_6 = (k_y + 2)^2 \tag{33}$$

能量范围 $4 \to 9 \times \frac{\hbar^2}{2m}(\frac{2\pi}{a})^2$，非简并。

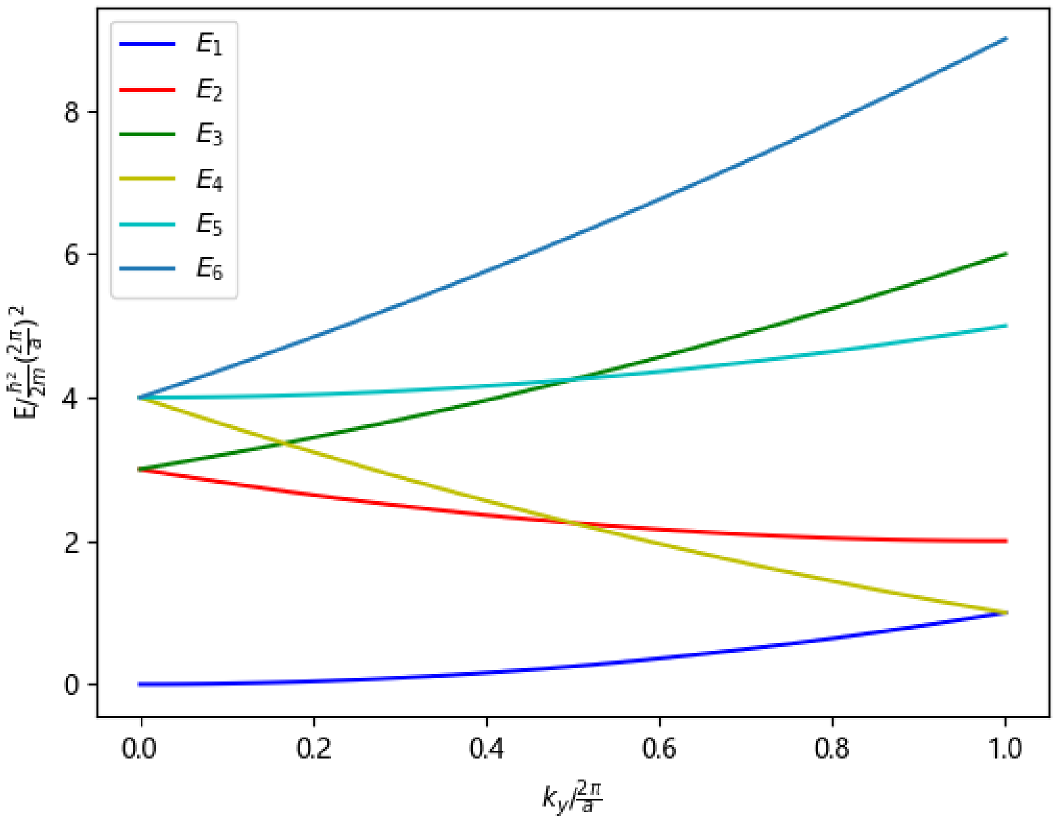


图 8：空格子模型能带

4.4 能态密度

将紧束缚近似结果带入能态密度为

$$
\begin{aligned}
N(E) &= \frac{1}{4\pi^3}\oiint_{E=Const}\frac{dS}{|\nabla_k E(k)|} \\
&= \frac{\sqrt{(\frac{\epsilon_A-\epsilon_B-J_A+J_B}{2})^2+16J_{AB}^2(\cos^2\frac{k_xa}{4}\cos^2\frac{k_ya}{4}\cos^2\frac{k_za}{4}+\sin^2\frac{k_xa}{4}\sin^2\frac{k_ya}{4}\sin^2\frac{k_za}{4})}}{8\pi^3 aJ_{AB}^2} \\
&\oiint_{E=Const}\frac{dS}{\sqrt{\sin^2\frac{k_xa}{2}\cos^2\frac{k_y+k_z}{4}a\cos^2\frac{k_y-k_z}{4}a+\sin^2\frac{k_ya}{2}\cos^2\frac{k_x+k_z}{4}a\cos^2\frac{k_x-k_z}{4}a+\sin^2\frac{k_za}{2}\cos^2\frac{k_y+k_x}{4}a\cos^2\frac{k_y-k_x}{4}a}}
\end{aligned}
\tag{34}
$$

存在 Van Hove 奇点 $\boldsymbol{k}=\frac{2\pi}{a}(0,0,0)$，$\frac{2\pi}{a}(1,0,0)$，$\frac{2\pi}{a}(1,1,0)$，$\frac{2\pi}{a}(1,1,1)$，$\frac{2\pi}{a}(\frac{1}{2},\frac{1}{2},\frac{1}{2})$

5 晶体电子运动

利用紧束缚近似结果，ZnS 晶体中电子运动的速度

$$
\begin{aligned}
\boldsymbol{v} &= \frac{1}{\hbar}\nabla_k E \\
&= \frac{2aJ_{AB}^2(\hat{x}\sin\frac{k_x a}{2}\cos\frac{k_y+k_z}{4}a\cos\frac{k_y-k_z}{4}a+\hat{y}\sin\frac{k_y a}{2}\cos\frac{k_x+k_z}{4}a\cos\frac{k_x-k_z}{4}a+\hat{z}\sin\frac{k_z a}{2}\cos\frac{k_y+k_x}{4}a\cos\frac{k_y-k_x}{4}a)}{\hbar\sqrt{(\frac{\epsilon_A-\epsilon_B-J_A+J_B}{2})^2+16J_{AB}^2(\cos^2\frac{k_x a}{4}\cos^2\frac{k_y a}{4}\cos^2\frac{k_z a}{4}+\sin^2\frac{k_x a}{4}\sin^2\frac{k_y a}{4}\sin^2\frac{k_z a}{4})}}
\end{aligned}
\tag{35}
$$

取 k 沿 x 方向，观察速度规律，可得速度也沿 x 方向，变化规律如图9，速度在能带底和顶均为 0，在中间处存在极大值。

$$
\boldsymbol{v} = \frac{2aJ_{AB}^2\sin\frac{k_x a}{2}}{\hbar\sqrt{(\frac{\epsilon_A-\epsilon_B-J_A+J_B}{2})^2+16J_{AB}^2\cos^2\frac{k_x a}{4}}}\hat{x} \tag{36}
$$

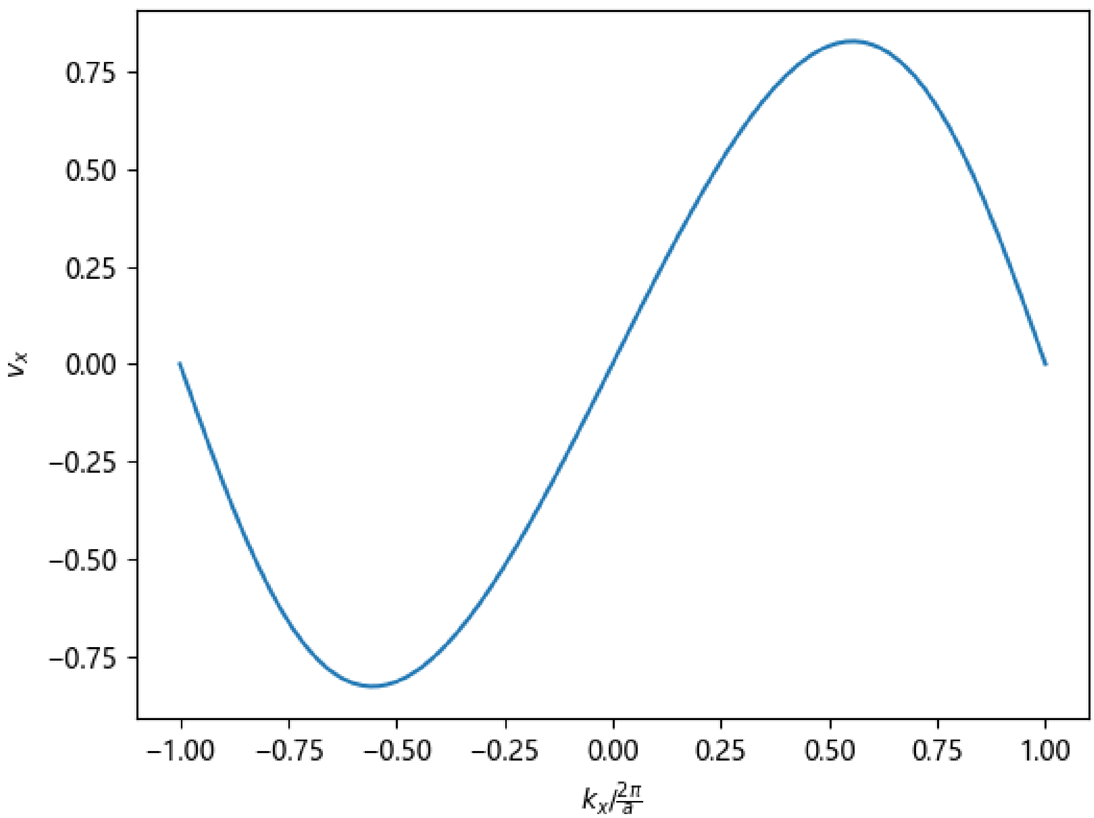


图 9: 电子运动速度规律

进一步可以得到电子的有效质量矩阵

$$
[\frac{1}{m^*}] = \frac{1}{\hbar^2}\begin{bmatrix} E_{xx} & E_{xy} & E_{xz} \\ E_{yx} & E_{yy} & E_{yz} \\ E_{zx} & E_{zy} & E_{zz} \end{bmatrix} \tag{37}
$$

其中各矩阵元为 其中 $A=(\frac{\epsilon_A-\epsilon_B-J_A+J_B}{2})^2$, $B=16J_{AB}^2$，x,y,z 分别代表 k_x,k_y,k_y

$$\begin{aligned}
&E_{xx} = \\
&\quad 2*a*J_{AB}{}^2* \\
&\quad \Big(\Big(a\underset{\text{余弦}}{\cos}\Big[\frac{1}{4}\,a\,(y-z)\Big]\,\underset{\text{余弦}}{\cos}\Big[\frac{1}{4}\,a\,(y+z)\Big] \\
&\qquad \Big(B\Big(\underset{\text{余弦}}{\cos}\Big[\frac{a\,y}{2}\Big]+\underset{\text{余弦}}{\cos}\Big[\frac{a\,z}{2}\Big]\Big)\sin\Big[\frac{a\,x}{2}\Big]^2+8\,\underset{\text{余弦}}{\cos}\Big[\frac{a\,x}{2}\Big]\Big(A+B\cos\Big[\frac{a\,x}{4}\Big]^2\cos\Big[\frac{a\,y}{4}\Big]^2\cos\Big[\frac{a\,z}{4}\Big]^2+B\sin\Big[\frac{a\,x}{4}\Big]^2\sin\Big[\frac{a\,y}{4}\Big]^2\sin\Big[\frac{a\,z}{4}\Big]^2\Big)\Big)\Big)\Big/ \\
&\quad \Big(16\Big(A+B\cos\Big[\frac{a\,x}{4}\Big]^2\cos\Big[\frac{a\,y}{4}\Big]^2\cos\Big[\frac{a\,z}{4}\Big]^2+B\sin\Big[\frac{a\,x}{4}\Big]^2\sin\Big[\frac{a\,y}{4}\Big]^2\sin\Big[\frac{a\,z}{4}\Big]^2\Big)^{3/2}\Big)\Big)
\end{aligned}$$

$$\begin{aligned}
&E_{xy} = \\
&\quad E_{yx} = \\
&\quad -2*a*J_{AB}{}^2* \\
&\quad \Big(\Big(a\underset{\text{正弦}}{\sin}\Big[\frac{a\,x}{2}\Big] \\
&\qquad \Big(\underset{\text{余弦}}{\cos}\Big[\frac{1}{4}\,a\,(y+z)\Big]\Big(B\underset{\text{余弦}}{\cos}\Big[\frac{1}{4}\,a\,(y-z)\Big]\sin\Big[\frac{a\,x}{4}\Big]^2\underset{\text{正弦}}{\sin}\Big[\frac{a\,y}{2}\Big]\sin\Big[\frac{a\,z}{4}\Big]^2+ \\
&\qquad\quad 2\underset{\text{正弦}}{\sin}\Big[\frac{1}{4}\,a\,(y-z)\Big]\Big(A+B\cos\Big[\frac{a\,x}{4}\Big]^2\cos\Big[\frac{a\,y}{4}\Big]^2\cos\Big[\frac{a\,z}{4}\Big]^2+B\sin\Big[\frac{a\,x}{4}\Big]^2\sin\Big[\frac{a\,y}{4}\Big]^2\sin\Big[\frac{a\,z}{4}\Big]^2\Big)\Big)+ \\
&\qquad 2\underset{\text{余弦}}{\cos}\Big[\frac{1}{4}\,a\,(y-z)\Big]\Big(B\cos\Big[\frac{a\,x}{4}\Big]^2\underset{\text{余弦}}{\cos}\Big[\frac{a\,y}{4}\Big]\cos\Big[\frac{a\,z}{4}\Big]^2\underset{\text{正弦}}{\sin}\Big[\frac{a\,z}{4}\Big]+\Big(A+B\sin\Big[\frac{a\,x}{4}\Big]^2\sin\Big[\frac{a\,y}{4}\Big]^2\sin\Big[\frac{a\,z}{4}\Big]^2\Big)\underset{\text{正弦}}{\sin}\Big[\frac{1}{4}\,a\,(y+z)\Big]\Big)\Big)\Big)\Big/ \\
&\quad \Big(8\Big(A+B\cos\Big[\frac{a\,x}{4}\Big]^2\cos\Big[\frac{a\,y}{4}\Big]^2\cos\Big[\frac{a\,z}{4}\Big]^2+B\sin\Big[\frac{a\,x}{4}\Big]^2\sin\Big[\frac{a\,y}{4}\Big]^2\sin\Big[\frac{a\,z}{4}\Big]^2\Big)^{3/2}\Big)\Big)
\end{aligned}$$

$$\begin{aligned}
&E_{xz} = \\
&\quad E_{zx} = \\
&\quad 2*a*J_{AB}{}^2* \\
&\quad \Big(a\underset{\text{正弦}}{\sin}\Big[\frac{a\,x}{2}\Big] \\
&\qquad \Big(\underset{\text{余弦}}{\cos}\Big[\frac{1}{4}\,a\,(y+z)\Big]\Big(4\underset{\text{正弦}}{\sin}\Big[\frac{1}{4}\,a\,(y-z)\Big]\Big(A+B\cos\Big[\frac{a\,x}{4}\Big]^2\cos\Big[\frac{a\,y}{4}\Big]^2\cos\Big[\frac{a\,z}{4}\Big]^2+B\sin\Big[\frac{a\,x}{4}\Big]^2\sin\Big[\frac{a\,y}{4}\Big]^2\sin\Big[\frac{a\,z}{4}\Big]^2\Big)+ \\
&\qquad\quad B\Big(\underset{\text{余弦}}{\cos}\Big[\frac{a\,x}{2}\Big]+\underset{\text{余弦}}{\cos}\Big[\frac{a\,y}{2}\Big]\Big)\underset{\text{余弦}}{\cos}\Big[\frac{1}{4}\,a\,(y-z)\Big]\underset{\text{正弦}}{\sin}\Big[\frac{a\,z}{2}\Big]\Big)- \\
&\qquad 4\underset{\text{余弦}}{\cos}\Big[\frac{1}{4}\,a\,(y-z)\Big]\Big(A+B\cos\Big[\frac{a\,x}{4}\Big]^2\cos\Big[\frac{a\,y}{4}\Big]^2\cos\Big[\frac{a\,z}{4}\Big]^2+B\sin\Big[\frac{a\,x}{4}\Big]^2\sin\Big[\frac{a\,y}{4}\Big]^2\sin\Big[\frac{a\,z}{4}\Big]^2\Big)\underset{\text{正弦}}{\sin}\Big[\frac{1}{4}\,a\,(y+z)\Big]\Big)\Big)\Big/ \\
&\quad \Big(16\Big(A+B\cos\Big[\frac{a\,x}{4}\Big]^2\cos\Big[\frac{a\,y}{4}\Big]^2\cos\Big[\frac{a\,z}{4}\Big]^2+B\sin\Big[\frac{a\,x}{4}\Big]^2\sin\Big[\frac{a\,y}{4}\Big]^2\sin\Big[\frac{a\,z}{4}\Big]^2\Big)^{3/2}\Big)
\end{aligned}$$

$$\begin{aligned}
&E_{yy} = \\
&\quad 2*a*J_{AB}{}^2* \\
&\quad \Big(\Big(a\underset{\text{余弦}}{\cos}\Big[\frac{1}{4}\,a\,(x-z)\Big]\,\underset{\text{余弦}}{\cos}\Big[\frac{1}{4}\,a\,(x+z)\Big] \\
&\qquad \Big(B\Big(\underset{\text{余弦}}{\cos}\Big[\frac{a\,x}{2}\Big]+\underset{\text{余弦}}{\cos}\Big[\frac{a\,z}{2}\Big]\Big)\sin\Big[\frac{a\,y}{2}\Big]^2+8\,\underset{\text{余弦}}{\cos}\Big[\frac{a\,y}{2}\Big]\Big(A+B\cos\Big[\frac{a\,x}{4}\Big]^2\cos\Big[\frac{a\,y}{4}\Big]^2\cos\Big[\frac{a\,z}{4}\Big]^2+B\sin\Big[\frac{a\,x}{4}\Big]^2\sin\Big[\frac{a\,y}{4}\Big]^2\sin\Big[\frac{a\,z}{4}\Big]^2\Big)\Big)\Big)\Big/ \\
&\quad \Big(16\Big(A+B\cos\Big[\frac{a\,x}{4}\Big]^2\cos\Big[\frac{a\,y}{4}\Big]^2\cos\Big[\frac{a\,z}{4}\Big]^2+B\sin\Big[\frac{a\,x}{4}\Big]^2\sin\Big[\frac{a\,y}{4}\Big]^2\sin\Big[\frac{a\,z}{4}\Big]^2\Big)^{3/2}\Big)\Big)
\end{aligned}$$

```
Eyz =
 Ezy =
  2*a*JAB^2*
   (a Sin[a y/2]
      (Cos[1/4 a (x + z)] (4 Sin[1/4 a (x - z)] (A + B Cos[a x/4]^2 Cos[a y/4]^2 Cos[a z/4]^2 + B Sin[a x/4]^2 Sin[a y/4]^2 Sin[a z/4]^2) +
           B (Cos[a x/2] + Cos[a y/2]) Cos[1/4 a (x - z)] Sin[a z/2]) -
        4 Cos[1/4 a (x - z)] (A + B Cos[a x/4]^2 Cos[a y/4]^2 Cos[a z/4]^2 + B Sin[a x/4]^2 Sin[a y/4]^2 Sin[a z/4]^2) Sin[1/4 a (x + z)]))/
   (16 (A + B Cos[a x/4]^2 Cos[a y/4]^2 Cos[a z/4]^2 + B Sin[a x/4]^2 Sin[a y/4]^2 Sin[a z/4]^2)^(3/2))
Ezz =
 2*a*JAB^2*
  ((a Cos[1/4 a (x - y)] Cos[1/4 a (x + y)]
      (8 Cos[a z/2] (A + B Cos[a x/4]^2 Cos[a y/4]^2 Cos[a z/4]^2 + B Sin[a x/4]^2 Sin[a y/4]^2 Sin[a z/4]^2) + B (Cos[a x/2] + Cos[a y/2]) Sin[a z/2]^2))/
    (16 (A + B Cos[a x/4]^2 Cos[a y/4]^2 Cos[a z/4]^2 + B Sin[a x/4]^2 Sin[a y/4]^2 Sin[a z/4]^2)^(3/2)))
```

对于在加了外磁场的晶格中运动的电子，假设磁场沿 z 方向。分析在 $k_z=0$ 的平面运动的电子，垂直于磁场方向的速度

$$|v_\perp| = \frac{2aJ_{AB}^2\sqrt{\sin^2\frac{k_xa}{2}\cos^4\frac{k_ya}{4}+\sin^2\frac{k_ya}{2}\cos^4\frac{k_xa}{4}}}{\hbar\sqrt{(\frac{\epsilon_A-\epsilon_B-J_A+J_B}{2})^2+16J_{AB}^2\cos^2\frac{k_xa}{4}\cos^2\frac{k_ya}{4}}} \tag{38}$$

可得电子回旋运动的周期

$$T=\frac{\hbar^2}{2aJ_{AB}^2eB}\oint_{E=Const}\frac{\sqrt{(\frac{\epsilon_A-\epsilon_B-J_A+J_B}{2})^2+16J_{AB}^2\cos^2\frac{k_xa}{4}\cos^2\frac{k_ya}{4}}}{\sqrt{\sin^2\frac{k_xa}{2}\cos^4\frac{k_ya}{4}+\sin^2\frac{k_ya}{2}\cos^4\frac{k_xa}{4}}}d\vec{k} \tag{39}$$

在磁场中加入沿磁场的交变电场，发生回旋共振时，考虑处于能带底的电子 $\boldsymbol{k}=(000)$，此时有效质量退化为标量

$$m^*=\hbar^2\frac{\sqrt{(\frac{\epsilon_A-\epsilon_B-J_A+J_B}{2})^2+16J_{AB}^2}}{a^2J_{AB}^2} \tag{40}$$

可得共振频率

$$\omega_c=\frac{eBa^2J_{AB}^2}{\hbar^2\sqrt{(\frac{\epsilon_A-\epsilon_B-J_A+J_B}{2})^2+16J_{AB}^2}} \tag{41}$$

也可取能带顶 $k=(\frac{\pi}{a},\frac{\pi}{a},\frac{\pi}{a})$，对角化可得主轴有效质量

$$\begin{cases} m_1=m_2=\frac{\hbar^2\sqrt{4(\frac{\epsilon_A-\epsilon_B-J_A+J_B}{2})^2+16J_{AB}^2}}{a^2J_{AB}^2} \\ m_3=-2\frac{\hbar^2\sqrt{4(\frac{\epsilon_A-\epsilon_B-J_A+J_B}{2})^2+16J_{AB}^2}}{a^2J_{AB}^2} \end{cases} \tag{42}$$

取 θ 为磁场方向与主轴 3 的夹角

$$m_c^*=(\frac{\sin^2\theta}{m_1m_3}+\frac{\cos^2\theta}{m_1^2})^{-\frac{1}{2}}=\frac{\hbar^2\sqrt{4(\frac{\epsilon_A-\epsilon_B-J_A+J_B}{2})^2+16J_{AB}^2}}{a^2J_{AB}^2}(\frac{1+\cos^2\theta}{2})^{-\frac{1}{2}} \tag{43}$$

该点共振频率

$$\omega_c=\frac{eBa^2J_{AB}^2}{\hbar^2\sqrt{4(\frac{\epsilon_A-\epsilon_B-J_A+J_B}{2})^2+16J_{AB}^2}}(\frac{1+\cos^2\theta}{2})^{\frac{1}{2}} \tag{44}$$

根据三维自由电子气模型，在磁场中能量随磁场变化周期

$$\Delta(\frac{1}{B})=\frac{2\pi e}{\hbar A_F}=\frac{2e}{\hbar(3\pi^2n)^{\frac{2}{3}}} \tag{45}$$