Nacl 晶体原子振荡

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2023 年 1 月 15 日

1 NaCl 晶体原子力学分析

NaCl 晶体的结构如图1所示

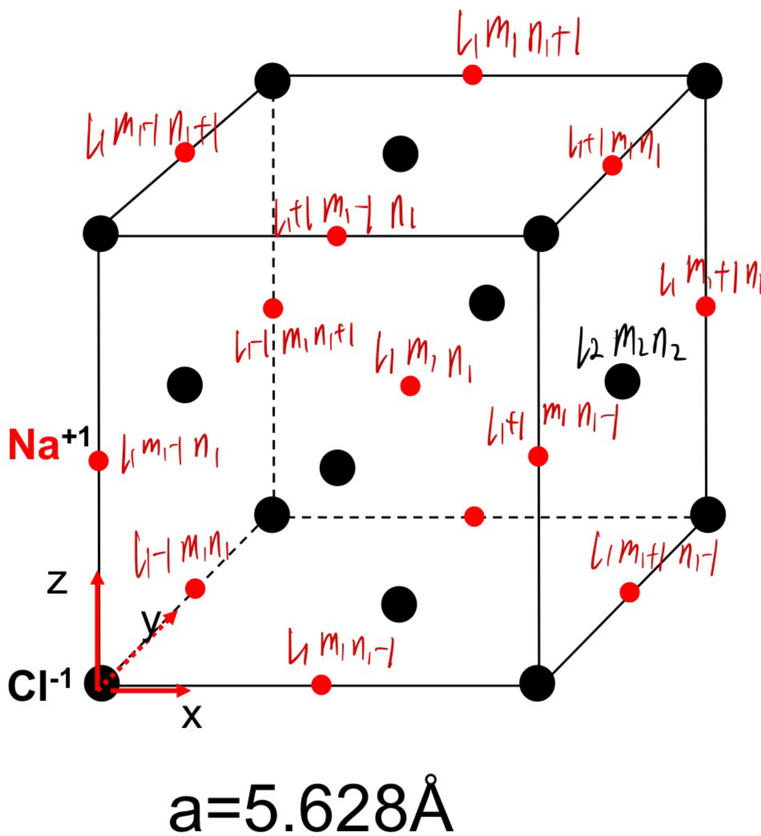

图 1: NaCl **晶体结构**

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 Na 原子与临近 x 轴正方向的一个 Cl 原子为原胞，Na 原子位于 1 位置，Cl 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 Na 与 Cl 原子间相互作用力系数为 β，Na 与 Na 原子之间相互作用系数为 β_1,Cl 与 Cl 之间的力相互作用系数为 β_2。Na 原子质量 m，Cl 原子质量为 M。现在对第 (l_1, m_1, n_1) 与 (l_2, m_2, n_2) 的 Na 原子和 Cl 原子作为原胞进行受力分析。

首先是 Na 原子:

$$
\begin{aligned}
m\ddot{u}^x_{l_1,m_1,n_1} &= -\beta(2u^x_{l_1,m_1,n_1} - u^x_{l_2,m_2,n_2} - u^x_{l_2-1,m_2-1,n_2+1}) \\
&+ \frac{\beta_1}{2}\big[(u^x_{(l_1+1)m_1n_1} - u^x_{l_1m_1n_1}) + (u^x_{(l_1-1)m_1n_1} - u^x_{l_1m_1n_1}) + (u^x_{l_1(m_1+1)n_1} - u^x_{l_1m_1n_1}) + (u^x_{l_1(m_1-1)n_1} - u^x_{l_1m_1n_1}) \\
&+ (u^x_{(l_1+1)m_1(n_1-1)} - u^x_{l_1m_1n_1}) + (u^x_{(l_1-1)m_1(n_1+1)} - u^x_{l_1m_1n_1}) + (u^x_{l_1(m_1+1)(n_1-1)} - u^x_{l_1m_1n_1}) + (u^x_{l_1(m_1-1)(n_1+1)} - u^x_{l_1m_1n_1}) \\
&+ (u^y_{l_1(m_1+1)n_1} - u^y_{l_1m_1n_1}) + (u^y_{l_1(m_1-1)n_1} - u^y_{l_1m_1n_1}) - (u^y_{(l_1+1)m_1(n_1-1)} - u^y_{l_1m_1n_1}) - (u^y_{(l_1-1)m_1(n_1+1)} - u^y_{l_1m_1n_1}) \\
&+ (u^z_{(l_1+1)m_1n_1} - u^z_{l_1m_1n_1}) + (u^z_{(l_1-1)m_1n_1} - u^z_{l_1m_1n_1}) - (u^z_{l_1(m_1+1)(n_1-1)} - u^z_{l_1m_1n_1}) - (u^z_{l_1(m_1-1)(n_1+1)} - u^z_{l_1m_1n_1})\big]
\end{aligned} \tag{1}
$$

$$
\begin{aligned}
m\ddot{u}^y_{l_1,m_1,n_1} &= -\beta(2u^y_{l_1,m_1,n_1} - u^y_{l_2-1,m_2,n_2+1} - u^y_{l_2,m_2-1,n_2}) \\
&+ \frac{\beta_1}{2}\big[(u^y_{l_1m_1(n_1+1)} - u^y_{l_1m_1n_1}) + (u^y_{l_1m_1(n_1-1)} - u^y_{l_1m_1n_1}) + (u^y_{l_1(m_1+1)n_1} - u^y_{l_1m_1n_1}) + (u^y_{l_1(m_1-1)n_1} - u^y_{l_1m_1n_1}) \\
&+ (u^y_{(l_1+1)m_1(n_1-1)} - u^y_{l_1m_1n_1}) + (u^y_{(l_1-1)m_1(n_1+1)} - u^y_{l_1m_1n_1}) + (u^y_{(l_1-1)(m_1+1)n_1} - u^y_{l_1m_1n_1}) + (u^y_{(l_1+1)(m_1-1)n_1} - u^y_{l_1m_1n_1}) \\
&+ (u^x_{l_1(m_1+1)n_1} - u^x_{l_1m_1n_1}) + (u^x_{l_1(m_1-1)n_1} - u^x_{l_1m_1n_1}) - (u^x_{(l_1+1)m_1(n_1-1)} - u^x_{l_1m_1n_1}) - (u^x_{(l_1-1)m_1(n_1+1)} - u^x_{l_1m_1n_1}) \\
&+ (u^z_{l_1m_1(n_1+1)} - u^z_{l_1m_1n_1}) + (u^z_{l_1m_1(n_1-1)} - u^z_{l_1m_1n_1}) - (u^z_{(l_1-1)(m_1+1)n_1} - u^z_{l_1m_1n_1}) - (u^z_{(l_1+1)(m_1-1)n_1} - u^z_{l_1m_1n_1})\big]
\end{aligned} \tag{2}
$$

$$
\begin{aligned}
m\ddot{u}^z_{l_1,m_1,n_1} &= -\beta(2u^z_{l_1,m_1,n_1} - u^z_{l_2,m_2-1,n_2+1} - u^z_{l_2-1,m_2,n_2}) \\
&+ \frac{\beta_1}{2}\big[(u^z_{l_1m_1(n_1+1)} - u^z_{l_1m_1n_1}) + (u^z_{l_1m_1(n_1-1)} - u^z_{l_1m_1n_1}) + (u^z_{(l_1+1)m_1n_1} - u^z_{l_1m_1n_1}) + (u^z_{(l_1-1)m_1n_1} - u^y_{l_1m_1n_1}) \\
&+ (u^z_{l_1(m_1+1)(n_1-1)} - u^z_{l_1m_1n_1}) + (u^z_{l_1(m_1-1)(n_1+1)} - u^z_{l_1m_1n_1}) + (u^z_{(l_1-1)(m_1+1)n_1} - u^z_{l_1m_1n_1}) + (u^z_{(l_1+1)(m_1-1)n_1} - u^z_{l_1m_1n_1}) \\
&+ (u^x_{(l_1+1)m_1n_1} - u^x_{l_1m_1n_1}) + (u^x_{(l_1-1)m_1n_1} - u^x_{l_1m_1n_1}) - (u^x_{l_1(m_1-1)(n_1+1)} - u^x_{l_1m_1n_1}) - (u^x_{l_1(m_1+1)(n_1-1)} - u^x_{l_1m_1n_1}) \\
&+ (u^y_{l_1m_1(n_1+1)} - u^y_{l_1m_1n_1}) + (u^y_{l_1m_1(n_1-1)} - u^y_{l_1m_1n_1}) - (u^y_{(l_1-1)(m_1+1)n_1} - u^y_{l_1m_1n_1}) - (u^y_{(l_1+1)(m_1-1)n_1} - u^y_{l_1m_1n_1})\big]
\end{aligned} \tag{3}
$$

类似对于 Cl 原子

$$
\begin{aligned}
M\ddot{u}^x_{l_2,m_2,n_2} &= -\beta(2u^x_{l_2,m_2,n_2} - u^x_{l_1,m_1,n_1} - u^x_{l_1+1,m_1+1,n_1-1}) \\
&+ \frac{\beta_2}{2}\big[(u^x_{(l_2+1)m_2n_2} - u^x_{l_2m_2n_2}) + (u^x_{(l_2-1)m_2n_2} - u^x_{l_2m_2n_2}) + (u^x_{l_2(m_2+1)n_2} - u^x_{l_2m_2n_2}) + (u^x_{l_2(m_2-1)n_2} - u^x_{l_2m_2n_2}) \\
&+ (u^x_{(l_2+1)m_2(n_2-1)} - u^x_{l_2m_2n_2}) + (u^x_{(l_2-1)m_2(n_2+1)} - u^x_{l_2m_2n_2}) + (u^x_{l_2(m_2+1)(n_2-1)} - u^x_{l_2m_2n_2}) + (u^x_{l_2(m_2-1)(n_2+1)} - u^x_{l_2m_2n_2}) \\
&+ (u^y_{l_2(m_2+1)n_2} - u^y_{l_2m_2n_2}) + (u^y_{l_2(m_2-1)n_2} - u^y_{l_2m_2n_2}) - (u^y_{(l_2+1)m_2(n_2-1)} - u^y_{l_2m_2n_2}) - (u^y_{(l_2-1)m_2(n_2+1)} - u^y_{l_2m_2n_2}) \\
&+ (u^z_{(l_2+1)m_2n_2} - u^z_{l_2m_2n_2}) + (u^z_{(l_2-1)m_2n_2} - u^z_{l_2m_2n_2}) - (u^z_{l_2(m_2+1)(n_2-1)} - u^z_{l_2m_2n_2}) - (u^z_{l_2(m_2-1)(n_2+1)} - u^z_{l_2m_2n_2})\big]
\end{aligned} \tag{4}
$$

$$
\begin{aligned}
M\ddot{u}^y_{l_2,m_2,n_2} &= -\beta(2u^y_{l_2,m_2,n_2} - u^y_{l_1,m_1+1,n_1} - u^y_{l_1+1,m_1,n_1-1}) \\
&+ \frac{\beta_2}{2}\big[(u^y_{l_2m_2(n_2+1)} - u^y_{l_2m_2n_2}) + (u^y_{l_2m_2(n_2-1)} - u^y_{l_2m_2n_2}) + (u^y_{l_2(m_2+1)n_2} - u^y_{l_2m_2n_2}) + (u^y_{l_2(m_2-1)n_2} - u^y_{l_2m_2n_2}) \\
&+ (u^y_{(l_2+1)m_2(n_2-1)} - u^y_{l_2m_2n_2}) + (u^y_{(l_2-1)m_2(n_2+1)} - u^y_{l_2m_2n_2}) + (u^y_{(l_2-1)(m_2+1)n_2} - u^y_{l_2m_2n_2}) + (u^y_{(l_2+1)(m_2-1)n_2} - u^y_{l_2m_2n_2}) \\
&+ (u^x_{l_2(m_2+1)n_2} - u^x_{l_2m_2n_2}) + (u^x_{l_2(m_2-1)n_2} - u^x_{l_2m_2n_2}) - (u^x_{(l_2+1)m_2(n_2-1)} - u^x_{l_2m_2n_2}) - (u^x_{(l_2-1)m_2(n_2+1)} - u^x_{l_2m_2n_2}) \\
&+ (u^z_{l_2m_2(n_2+1)} - u^z_{l_2m_2n_2}) + (u^z_{l_2m_2(n_2-1)} - u^z_{l_2m_2n_2}) - (u^z_{(l_2-1)(m_2+1)n_2} - u^z_{l_2m_2n_2}) - (u^z_{(l_2+1)(m_2-1)n_2} - u^z_{l_2m_2n_2})\big]
\end{aligned} \tag{5}
$$

$$
\begin{aligned}
M\ddot{u}^z_{l_2,m_2,n_2} &= -\beta(2u^z_{l_2,m_2,n_2} - u^z_{l_1+1,m_1,n_1} - u^z_{l_1,m_1+1,n_1-1}) \\
&+ \frac{\beta_2}{2}\big[(u^z_{l_2m_2(n_2+1)} - u^z_{l_2m_2n_2}) + (u^z_{l_2m_2(n_2-1)} - u^z_{l_2m_2n_2}) + (u^z_{(l_2+1)m_2n_2} - u^z_{l_2m_2n_2}) + (u^z_{(l_2-1)m_2n_2} - u^y_{l_2m_2n_2}) \\
&+ (u^z_{l_2(m_2+1)(n_2-1)} - u^z_{l_2m_2n_2}) + (u^z_{l_2(m_2-1)(n_2+1)} - u^z_{l_2m_2n_2}) + (u^z_{(l_2-1)(m_2+1)n_2} - u^z_{l_2m_2n_2}) + (u^z_{(l_2+1)(m_2-1)n_2} - u^z_{l_2m_2n_2}) \\
&+ (u^x_{(l_2+1)m_2n_2} - u^x_{l_2m_2n_2}) + (u^x_{(l_2-1)m_2n_2} - u^x_{l_2m_2n_2}) - (u^x_{l_2(m_2-1)(n_2+1)} - u^x_{l_2m_2n_2}) - (u^x_{l_2(m_2+1)(n_2-1)} - u^x_{l_2m_2n_2}) \\
&+ (u^y_{l_2m_2(n_2+1)} - u^y_{l_2m_2n_2}) + (u^y_{l_2m_2(n_2-1)} - u^y_{l_2m_2n_2}) - (u^y_{(l_2-1)(m_2+1)n_2} - u^y_{l_2m_2n_2}) - (u^y_{(l_2+1)(m_2-1)n_2} - u^y_{l_2m_2n_2})\big]
\end{aligned} \tag{6}
$$

可以得到方程解的形式为

$$\vec{u}_{l_1m_1n_1} = \vec{A}\exp i[wt - \vec{k}\cdot\vec{a}_1 l_1 - \vec{k}\cdot\vec{a}_2 m_1 - \vec{k}\cdot\vec{a}_3 n_1] \tag{7}$$

$$\vec{u}_{l_2m_2n_2} = \vec{B}\exp i[wt - \vec{k}\cdot\vec{a}_1 l_2 - \vec{k}\cdot\vec{a}_2 m_2 - \vec{k}\cdot\vec{a}_3 n_2] \tag{8}$$

根据 Na 原子与 Cl 原子位置关系可得 $(l_2, m_2, n_2) = (l_1 + \frac{1}{2}, m_1 + \frac{1}{2}, n_1 - \frac{1}{2})$。

$$\vec{u}_{l_1m_1n_1} = \vec{A}\exp i[wt - k_x a\frac{l_1+m_1}{2} - k_y a\frac{m_1+n_1}{2} - k_z a\frac{l_1+n_1}{2}] \tag{9}$$

$$\vec{u}_{l_2m_2n_2} = \vec{B}\exp i[wt - k_x a\frac{l_1+m_1+1}{2} - k_y a\frac{m_1+n_1}{2} - k_z a\frac{l_1+n_1}{2}] \tag{10}$$

将解反代回方程 (9)(10) 可以得

$$
\begin{aligned}
0 &= \{\beta_1[4 - \cos\frac{a}{2}(k_x+k_z) - \cos\frac{a}{2}(k_x-k_z) - \cos\frac{a}{2}(k_x+k_y) - \cos\frac{a}{2}(k_x-k_y)] + 2\beta - mw^2\}A_x \\
&+ \beta_1[\cos\frac{a}{2}(k_x-k_y) - \cos\frac{a}{2}(k_x+k_y)]A_y + \beta_1[\cos\frac{a}{2}(k_x-k_z) - \cos\frac{a}{2}(k_x+k_z)]A_z - 2\beta\cos(\frac{a}{2}k_x)B_x
\end{aligned} \tag{11}
$$

$$
\begin{aligned}
0 &= \{\beta_1[4 - \cos\frac{a}{2}(k_y+k_z) - \cos\frac{a}{2}(k_y-k_z) - \cos\frac{a}{2}(k_x+k_y) - \cos\frac{a}{2}(k_x-k_y)] + 2\beta - mw^2\}A_y \\
&+ \beta_1[\cos\frac{a}{2}(k_x-k_y) - \cos\frac{a}{2}(k_x+k_y)]A_x + \beta_1[\cos\frac{a}{2}(k_y-k_z) - \cos\frac{a}{2}(k_y+k_z)]A_z - 2\beta\cos(\frac{a}{2}k_y)B_y
\end{aligned} \tag{12}
$$

$$
\begin{aligned}
0 &= \{\beta_1[4 - \cos\frac{a}{2}(k_x+k_z) - \cos\frac{a}{2}(k_x-k_z) - \cos\frac{a}{2}(k_z+k_y) - \cos\frac{a}{2}(k_z-k_y)] + 2\beta - mw^2\}A_z \\
&+ \beta_1[\cos\frac{a}{2}(k_x-k_z) - \cos\frac{a}{2}(k_x+k_z)]A_x + \beta_1[\cos\frac{a}{2}(k_y-k_z) - \cos\frac{a}{2}(k_y+k_z)]A_y - 2\beta\cos(\frac{a}{2}k_z)B_z
\end{aligned} \tag{13}
$$

$$
\begin{aligned}
0 &= \{\beta_2[4 - \cos\frac{a}{2}(k_x+k_z) - \cos\frac{a}{2}(k_x-k_z) - \cos\frac{a}{2}(k_x+k_y) - \cos\frac{a}{2}(k_x-k_y)] + 2\beta - Mw^2\}B_x \\
&+ \beta_2[\cos\frac{a}{2}(k_x-k_y) - \cos\frac{a}{2}(k_x+k_y)]B_y + \beta_2[\cos\frac{a}{2}(k_x-k_z) - \cos\frac{a}{2}(k_x+k_z)]B_z - 2\beta\cos(\frac{a}{2}k_x)A_x
\end{aligned} \tag{14}
$$

$$
\begin{aligned}
0 &= \{\beta_2[4 - \cos\frac{a}{2}(k_y+k_z) - \cos\frac{a}{2}(k_y-k_z) - \cos\frac{a}{2}(k_x+k_y) - \cos\frac{a}{2}(k_x-k_y)] + 2\beta - Mw^2\}B_y \\
&+ \beta_2[\cos\frac{a}{2}(k_x-k_y) - \cos\frac{a}{2}(k_x+k_y)]B_x + \beta_2[\cos\frac{a}{2}(k_y-k_z) - \cos\frac{a}{2}(k_y+k_z)]B_z - 2\beta\cos(\frac{a}{2}k_y)A_y
\end{aligned} \tag{15}
$$

$$
\begin{aligned}
0 &= \{\beta_2[4 - \cos\frac{a}{2}(k_x+k_z) - \cos\frac{a}{2}(k_x-k_z) - \cos\frac{a}{2}(k_z+k_y) - \cos\frac{a}{2}(k_z-k_y)] + 2\beta - Mw^2\}B_z \\
&+ \beta_2[\cos\frac{a}{2}(k_z-k_y) - \cos\frac{a}{2}(k_z+k_y)]B_y + \beta_2[\cos\frac{a}{2}(k_x-k_z) - \cos\frac{a}{2}(k_x+k_z)]B_x - 2\beta\cos(\frac{a}{2}k_z)A_z
\end{aligned} \tag{16}
$$

计算矩阵行列式得到 w 的 12 次方程，为了简化计算，我们取波沿 x 方向传播，即 $k_x = k, k_y = k_z = 0$，可以得到

w 的 2 个 3 重正根如下

$$
\begin{aligned}
w_1(k)=w_2(k)=w_3(k)=&\Bigg(\frac{\beta}{m}+\frac{\beta}{M}+\frac{\beta_1}{m}-\frac{\cos(\frac{ak}{2})\beta_1}{m}+\frac{\beta_2}{M}-\frac{\cos(\frac{ak}{2})\beta_2}{M}\\
&-\frac{1}{2mM}\big((-2m\beta-2M\beta-2M\beta_1+2M\cos(\frac{ak}{2})\beta_1-2m\beta_2+2m\cos(\frac{ak}{2})\beta_2)^2\\
&-4mM(4\beta\beta_1-4\beta\cos(\frac{ak}{2})\beta_1+4\beta\beta_2-4\beta\cos(\frac{ak}{2})\beta_2+6\beta_1\beta_2-8\cos(\frac{ak}{2})\beta_1\beta_2+2\cos(ak)\beta_1\beta_2)\big)^{\frac{1}{2}}\Bigg)^{\frac{1}{2}}
\end{aligned} \tag{17}
$$

$$
\begin{aligned}
&w_4(k)=w_5(k)=w_6(k)=\Bigg(\frac{\beta}{m}+\frac{\beta}{M}+\frac{2\beta_1}{m}-\frac{2\cos(\frac{ak}{2})\beta_1}{m}+\frac{2\beta_2}{M}-\frac{2\cos(\frac{ak}{2})\beta_2}{M}\\
&-\frac{1}{2mM}\big((-2m\beta-2M\beta-4M\beta_1+4M\cos(\frac{ak}{2})\beta_1-4m\beta_2+4m\cos(\frac{ak}{2})\beta_2)^2\\
&-4mM(2\beta^2-2\beta^2\cos(ak)+8\beta\beta_1-8\beta\cos(\frac{ak}{2})\beta_1+8\beta\beta_2-8\beta\cos(\frac{ak}{2})\beta_2+24\beta_1\beta_2-32\cos(\frac{ak}{2})\beta_1\beta_2+8\cos(ak)\beta_1\beta_2)\big)^{\frac{1}{2}}\Bigg)^{\frac{1}{2}}
\end{aligned} \tag{18}
$$

计算当 $k\to 0$ 可得 $w_1,w_2,w_3\to 0$ 为声学支，$w_4,w_5,w_6\to\sqrt{\frac{2\beta}{M}+\frac{2\beta}{m}}$ 为光学支。由于我们主要关心曲线的趋势，可将相关的参数取为 $\beta=\beta_1=\beta_2, M=35.5/23*m$, 作图如图2 其中横坐标为 ak, 纵坐标为 $\sqrt{\frac{m}{\beta}}w$

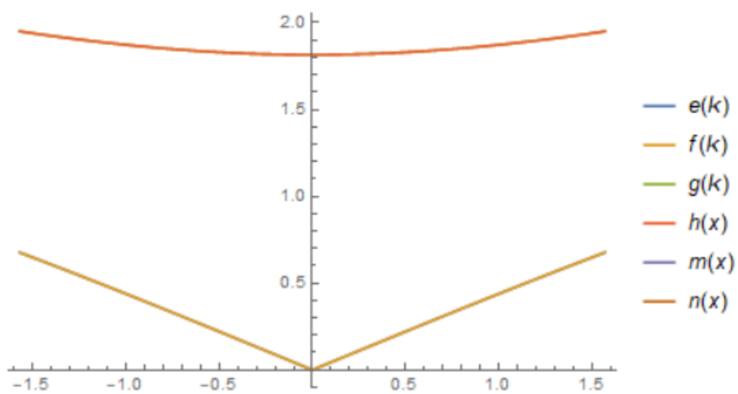

图 2: NaCl 晶体色散关系

这里另解了 $k_x=k_y=k_z=\frac{k}{\sqrt{3}}$ 的情况，如图3, 存在 3 个相同的声学支，3 个光学支中 1 个 2 重根与 1 个单根。

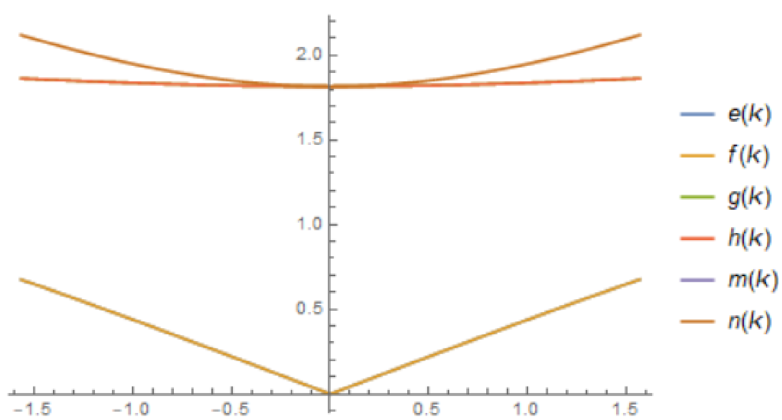

图 3: NaCl 晶体色散关系

2 结果讨论

由此可见确实都有 3 个声学支。本次计算中由于取了特殊沿对称轴方向的波矢，导致根存在一定的简并，如果选取更多的较为一般的波矢方向，则可得到更多分立的解。