On the Lattice Dynamics of AgGaS$_2$.

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Summary. — The vibrational spectrum and one-phonon density of states of a chalcopyrite crystal AgGaS$_2$ are calculated in an extended Keating’s model with two–bond-stretching and one–bond-bending force constants. Three charges of ions and three force constants are determined by a least-square fitting to experimental frequencies of long-wave phonons taken from Raman-scattering experiments. The calculated constant-volume specific heat, Debye temperature and elastic constants, of AgGaS$_2$ are in agreement with the experimental data of other authors.

PACS 63.20 - Phonons and vibrations in crystal lattices.

The ternary semiconducting compound AgGaS$_2$ attracts much attention as a perspective nonlinear optic material in the infra-red region[1]. Lattice dynamical properties of AgGaS$_2$ were investigated extensively in recent years. Raman scattering was measured by several authors[2-4], infra-red reflectivity is reported in ref.[4], elastic properties were studied in ref.[5,8]. The measurements of specific heat and Debye temperatures are reported by Abrahams and Hsu[6].

Theoretical calculations of the phonon spectrum in AgGaS$_2$ were performed by Koshel and Bettini[3] with Keating’s model of interatomic forces and by Lauwers and Herman[7] with Urey-Bradly’s model. These calculations are restricted to the long-wave limit.

In this paper we report a calculation of the phonon spectrum of AgGaS$_2$ with Keating’s model over the whole Brillouin zone together with the one-phonon density of states and the constant-volume specific heat in the harmonic approximation.

AgGaS$_2$ crystallizes in the chalcopyrite lattice[1] (space group is $D_{4d}$. It has eight atoms in the unit cell and therefore the phonon spectrum consists of 24 phonon branches. A group-theoretical classification of the vibrational spectrum is reported in a number of works ([9] for example).

In our work the force constant matrices were taken in Keating’s model[10,3]. They consist of three terms:

$$
\vec{\phi} = \vec{\phi}_{\text{Coul}} + \vec{\phi}_{\text{Keat}} + \vec{\phi}_{\text{R}}.
$$
Here $\tilde{\varphi}_{\text{Coul}}$ is the Coulomb contribution in the rigid-ion approximation and it is calculated by Evald’s method[11]. The three ionic charges $Z_{Ag}$, $Z_{Ga}$, $Z_S$ are parameters of the theory. Only two of them are independent because of the charge neutrality condition. $\tilde{\varphi}_{\text{Keating}}$ is Keating’s short-range force constant matrix[10] with two–bond-stretching constants $\alpha(AgS)$, $\alpha(GaS)$ and one–angle-bending constant $\beta$.

It appears that the Coulomb contribution breaks down the symmetry of elastic properties in the chalcopyrite crystal. An additional term $\tilde{\varphi}_R$ is necessary to restore the proper permutational symmetry of Cartesian indexes in the elastic constants. The choice of $\tilde{\varphi}_R$ is not unique. We have adopted here the simplest diagonal form:

$$\begin{align*}
\tilde{\varphi}_{R xx}(AgS) &= \tilde{\varphi}_{R yy}(AgS) = -\tilde{\varphi}_{R zz}(GaS) = -\tilde{\varphi}_{R yy}(GaS) = \frac{\lambda}{2}, \\
\tilde{\varphi}_{R xx}(AgS) &= \frac{\lambda}{2} + \frac{\mu - 2\delta}\sqrt{2(2 - \delta^2)}, \\
\tilde{\varphi}_{R z z}(GaS) &= -\frac{\lambda}{2} + \frac{\mu - 2\delta}\sqrt{2(2 - \delta^2)}, \\
\varepsilon &= 4x_f - 1.
\end{align*}$$

(2)

The constants $\lambda$ and $\mu$ can be expressed through the first and second derivatives of the dynamical matrix with respect to the wave vector. They are structure and charge dependent and can be calculated by Evald’s method[11]

$$\begin{align*}
\lambda &= 4\gamma Q e Q e / V_a, \\
\mu &= 2(\mu_{QQ} Q^2 + \mu_{Qe} Q e + \mu_{ee} e^2) / (\pi V_a).
\end{align*}$$

(3)

Here $Q(Z_{Ag} + Z_{Ga})/2 = -Z_S$, $e = (Z_{Ag} - Z_{Ga})/2$, $V_a = a^2 c$ is the unit cell volume. With the lattice parameters of AgGaS$_2$: $a = 5.75$ Å, $2c = 10.29$ Å, $x_f = 0.304$[12], our calculation gives $\lambda_{Qe} = 4.02$, $\mu_{QQ} = 5.02$, $\mu_{Qe} = 7.93$, $\mu_{ee} = 7.71$. One must note that $\lambda$ and $\mu$ do not vanish even for the ideal chalcopyrite structure with lattice constants $c = a$ and the anion shift parameter $x_f = 0.25$.

The five model parameters $\alpha(AgS)$, $\alpha(GaS)$, $\beta$, $Q$, $e$ were obtained then by a least-square fitting to the experimental Raman-scattering data[12] and are: $\alpha(AgS) = 22.6$, $\alpha(GaS) = 59.5$, $\beta = 1.88$ (in $10^8$ dyn/cm), $Z_{Ag} = 0.902$, $Z_{Ga} = 0.839$ (a.u.).

Koshel and Bettini have shown[3] that Keating’s model is unable to reproduce the optical frequencies of chalcopyrites which are folded back from X- and W-points of the binary zinc-blende analogs. So we did not make any attempts to adjust the low-lying modes to frequencies less than 100 cm$^{-1}$.

Table I shows a comparison of the calculated and measured long-wave phonon frequencies. Figure 1 displays the calculated phonon spectrum in two high-symmetry directions of the Brillouin zone. The central panel [$\Gamma$-$\Gamma$] exhibits the directional dependence of polar phonons in the vicinity of $\Gamma$. $\theta$ is the angle between the phonon wave vector and the tetragonal axis. Phonons of symmetry $\Gamma_3$ are doubly degenerated at $\theta = 0$ and they are LO-TO splitted at $\theta = \pi/2$. Phonons $\Gamma_4$ are nondegenerate and they are of LO character at $\theta = 0$ and of TO character at $\theta = \pi/2$. Phonons $\Gamma_1$, $\Gamma_2$, $\Gamma_3$ have no angle dispersion. Low-lying $\Gamma_4$ and $\Gamma_3$ phonons are dispersionless too, because of a vanishing electric-dipole moment at the chosen set of model parameters.