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SURFACE PHONON-POLARITONS IN *GeSe*

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A theoretical study of the surface phonon-polaritons spectra in *GeSe* has been made for the most conventional geometry of experiment when the normal $\boldsymbol{n}$ to the surface is perpendicular to the cleavage plane, and the wavevector $\boldsymbol{k}$ is oriented along either $\hat{a}$ or $\hat{b}$ axes which both lie in the cleavage plane. It has been concluded that in the case of $\boldsymbol{k}\|\hat{b}$, there are two branches of the surface phonon-polariton dispersion curve, and each branch has either virtual or real excitation character in dependence on different frequency regions. In the case when $\boldsymbol{k}\|\hat{a}$ there are two real excitation branches, one virtual excitation branch, and one mixed branch which has either virtual or real excitation character in dependence on frequency.

1. Introduction

Germanium selenide, like the IV-VI semiconductors *GeS, SnS* and *SnSe*, belongs to the group of layered crystals. Vibrational spectra of these crystals were studied in a number of publications [1-4]. In particular, it has been established that infrared spectra have one active phonon mode for polarization $\boldsymbol{E}\|\hat{b}$ and three phonon modes for each of polarizations $\boldsymbol{E}\|\hat{a}$ and $\boldsymbol{E}\|\hat{c}$ which is in agreement with the selection rules and symmetry of these crystals (here both the axes $\hat{a}$ and $\hat{b}$ lie in the cleavage plane perpendicular to axis $\hat{c}$). Unfortunately, there are no experimental investigations on the surface phonons in the IV-VI layered semiconductors. Such investigations would be interested because the non-trivial peculiarities can be expected as a result of large anisotropy and the richness of phonon spectra in these crystals.

In the present paper the calculation of the surface phonon-polariton spectra for *GeSe* has been made in order to stimulate the experimental investigations. The calculation has been done on the basis of theory developed in the references [5-8]. The study has been made for the most conventional geometry of experiment when the normal $\boldsymbol{n}$ to the surface is perpendicular to the cleavage plane, and the wavevector $\boldsymbol{k}$ is oriented along either $\hat{a}$ or $\hat{b}$ axes. It has been concluded that in the case of $\boldsymbol{k}\|\hat{b}$, there are two branches of the surface phonon-polariton dispersion curve, and each branch has either virtual or real excitation character in dependence on different frequency regions. In the case when $k \| \hat{a}$ there are two real excitations branches, one virtual excitation branch, and one mixed branch which has either virtual or real excitation character.

2. Basic Formulae.

We study the surface phonon-polaritons in the half infinite *GeSe* crystal placed in vacuum. Let the wavevector k and the surface normal $\boldsymbol{n}$ be oriented along the principal axes of the dielectric tensor ε. For simplificity, we ignore the dielectric loss. As it is known, the basic features of the surface polaritons are revealed even if damping is not taken into consideration. In this case the dielectric tensor has diagonal form and its components are real functions of frequency only.The dispersion relation for the surface waves propagating along the crystal-vacuum interface and exponentially attenuating in the direction perpendicular to the interface, is given by [5-8]

$$k^2(\omega) = (\omega/c)^2\, \varepsilon_n(\omega) \frac{\varepsilon_k(\omega) - 1}{\varepsilon_n(\omega)\varepsilon_k(\omega) - 1} \tag{1}$$

Here ω is the frequency of surface phonon-polariton, c is light velocity, ε_n and ε_k are the components of dielectric tensor for electric vector $\boldsymbol{E}$ polarized along $\boldsymbol{n}$ and k, respectively.

We shall consider only non-radiative modes, i.e. the case when $\omega < kc$. A necessary condition of the existence of surface polaritons is $\varepsilon_k < 0$. Under this condition the dispersion equation (1) yields two types of surface polaritons. The first type occurs when $\varepsilon_n < 0$. This type is known as 'real excitation' or 'type I' surface polariton. The second type occurs when ε_n is positive and reduced wave number $\ae = kc/\omega$ is less than $\sqrt{\varepsilon_n}$. This type is known as 'virtual excitation', or 'type II' surface polariton. At the point $\ae = \sqrt{\varepsilon_n}$ (so-called 'endpoint') the dispersion curve of the virtual excitation surface polariton coincides with that of the bulk polariton. As it follows from equation (1), at this point the component ε_k equals to zero.

According to ref. 9, the component of the dielectric tensor may be expressed in the terms of the transverse optical phonon frequency ω_{TO} and the longitudinal optical phonon frequency ω_{LO}

$$\varepsilon_{\boldsymbol{E}}(\omega) = \varepsilon_\infty^{\boldsymbol{E}} \prod_i f_i^{\boldsymbol{E}}(\omega) \tag{2}$$

where ε_∞ is high frequency dielectric constant, $\prod$ is the product sign, i is the number of phonon modes, and

$$f_i^{E}(\omega) = \frac{(\omega_{LO}^{E})_i^2 - \omega^2}{(\omega_{TO}^{E})_i^2 - \omega^2} \tag{3}$$

It follows from (2) and (3) that the component ε_E has poles at $\omega = (\omega_{TO}^{E})_i$ and zeroes at $\omega = (\omega_{LO}^{E})_i$. In the frequency range $(\omega_{TO}^{E})_i < \omega < (\omega_{LO}^{E})_i$ the component ε_E is negative.

3. Results and Discussion.

The *GeSe* crystals cleave very easily in the plane perpendicular to the $\hat{c}$ axis, thus suggesting a weak inter-layer bonding. On the basis of the dispersion relation (1), and formulae (2) and (3), we have theoretically studied the surface phonon-polaritons on *GeSe* for the most conventional geometry of experiment when the normal to the surface is perpendicular to the cleavage plane (i.e. $n \parallel \hat{c}$), and the wave vector k is oriented along either $\hat{a}$ or $\hat{b}$ axes which lie in the cleavage plane. We have used the values of the *LO* and *TO* phonon frequencies and the high frequency dielectric constant of *GeSe* given in table 1. As it is seen from table 1, there are three phonon modes ($i = 1 \ldots 3$) for each of the polarizations $E \parallel \hat{a}$ and $E \parallel \hat{c}$, and only one phonon mode ($i = 1$) for the polarization $E \parallel \hat{b}$.

Table 1.

The *LO* and *TO* phonon frequencies and dielectric constant of *GeSe*. All phonon frequencies are given in units of cm^{-1} . Data taken from ref. 1.

	$E \parallel \hat{a}$	$E \parallel \hat{b}$	$E \parallel \hat{c}$
$(\omega_{TO})_1$	88.0	150.0	83.0
$(\omega_{LO})_1$	91.5	210.5	86.0
$(\omega_{TO})_2$	175.0		172.0
$(\omega_{LO})_2$	178.0		194.0
$(\omega_{TO})_3$	186.0		198.0
$(\omega_{LO})_3$	224.0		221.5
ε_∞	18.7	21.9	14.4

3.1. The Case of $\mathbf{k} \| \hat{b}$.

From fig. 1, it is seen that in the case when $k \| \hat{b}$ the surface phonon-polariton dispersion curve has two branches. Fig. 2 makes it possible to establish the nature of these branches. In fig. 2 we have plotted the dielectric tensor components and the squared wave number as function of frequency. As one can seen from fig. 2, in the range from $(\omega_{TO}^{k})_1=150$ cm^{-1} to $(\omega_{LO}^{k})_1=210$ cm^{-1} the component ε_k is negative. The component $\varepsilon_n < 0$ in the frequency ranges $(\omega_{TO}^{n})_2=172$ cm^{-1} to $(\omega_{LO}^{n})_2=194$ cm^{-1}, and $(\omega_{TO}^{n})_3=198$ cm^{-1} to $(\omega_{LO}^{n})_3=221.5$ cm^{-1}. In the frequency ranges $\omega < (\omega_{TO}^{n})_2$ and $194.2 < \omega < (\omega_{TO}^{n})_3$, the component ε_n is positive and greater than $æ^2$. The wave number extends to infinity at the frequency values $\omega=194$ cm^{-1} and $\omega=210.1$ cm^{-1} (where $\varepsilon_n \varepsilon_k = 1$).

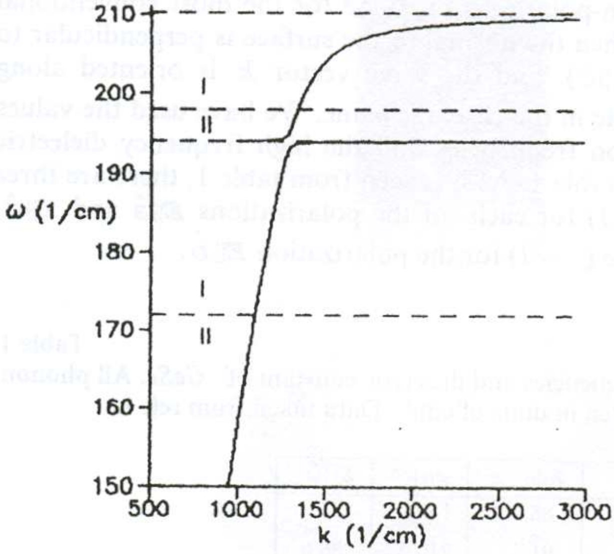

Fig. 1. The surface phonon-polariton dispersion curve for *GeSe* in the case when $\mathbf{n} \| \hat{c}$ and $\mathbf{k} \| \hat{b}$. Roman numerals stand for the frequency regions where (I) the real excitation and (II) the virtual excitation surface phonon-polaritons occur.

Therefore each of the surface phonon-polariton branches has either virtual or real excitation character in different frequency regions. The lower branch is virtual excitation surface phonon-polariton in the range $(\omega_{TO}^{k})_1 < \omega < (\omega_{TO}^{n})_2$ where $\varepsilon_n > æ^2$, and is a real excitation surface

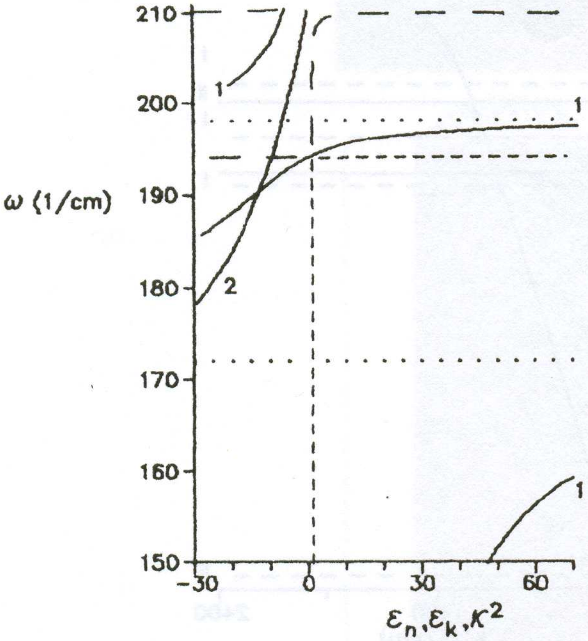

Fig. 2. The frequency dependences of the dielectric tensor components ε_n (curve 1) and ε_k (curve 2), and squared wave number $æ^2$ (dashed curves) in the case when $n \| \hat{c}$ and $k \| \hat{b}$. The wave number has poles at ω=193.979 cm^{-1} and ω=210.127 cm^{-1} (where $\varepsilon_n \ \varepsilon_k = 1$).The dotted lines correspond to the poles of ε_n at ω=172 cm^{-1} and ω=198 cm^{-1}.

phonon-polariton in the range $(\omega^n_{TO})_2 < \omega < (\omega^n_{LO})_2$ where $\varepsilon_n < 0$. The upper branch has virtual character in the frequency range $194.2 cm^{-1} < \omega < (\omega^n_{TO})_3$ and real character in the range $(\omega^n_{TO})_3 < \omega < 210.1$ cm^{-1}.

3.2. The Case of $k \| \hat{a}$.

Fig. 3 shows the dispersion curve in the case of $k \| \hat{a}$. The curve has four branches. The lowermost branch is the virtual excitation surface phonon-polariton because in the frequency range $(\omega^k_{TO})_1$=88 cm^{-1} to $(\omega^k_{LO})_1$=91.5 cm^{-1} the component ε_k is negative and $\varepsilon_n > æ^2$. The frequency $(\omega^k_{LO})_1$ corresponds to so-called 'endpoint' where ε_k=0, $\varepsilon_n = æ^2$ and k is limited to the value k_e = 2388 cm^{-1}. In the frequency ranges $(\omega^k_{LO})_1$ to

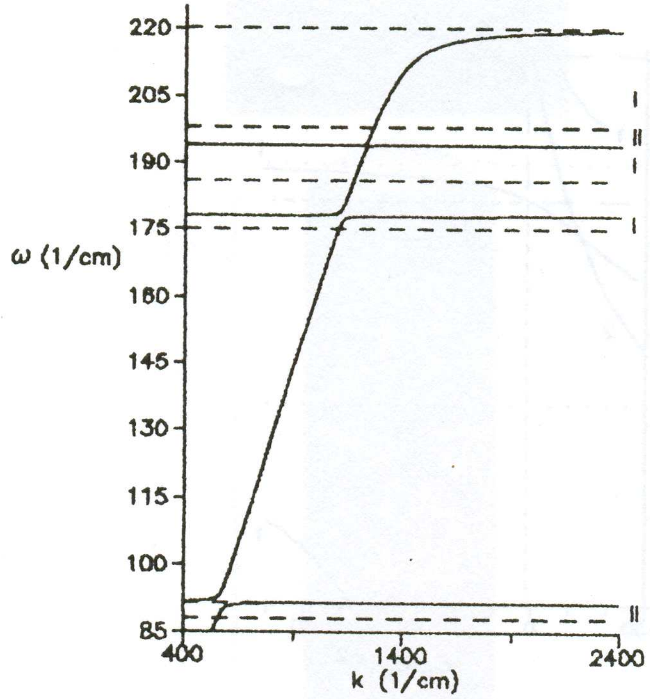

Fig.3. The dispersion curve for *GeSe* in the case $\mathbf{n}\|\hat{c}$ and $\mathbf{k}\|\hat{a}$. Roman numerals stand for the frequency regions where (I) the real excitation and (II) the virtual excitation surface phonon-polaritons occur.

$(\omega^k_{TO})_2 = 175$ cm^{-1} and $(\omega^k_{LO})_2 = 178$ cm^{-1} to $(\omega^k_{TO})_3 = 186$ cm^{-1}, the component ε_k is positive and there are no surface phonon-polaritons. The real excitation surface phonon-polariton occurs in the ranges $(\omega^k_{TO})_2 < \omega < (\omega^k_{LO})_2$ and $(\omega^k_{TO})_3 < \omega < (\omega^k_{LO})_3$ where $\varepsilon_k < 0$ and $\varepsilon_n < 0$. In fig. 3 the uppermost branch is the virtual excitation surface phonon-polariton in the range $194.2 cm^{-1} < \omega < (\omega^n_{TO})_3$, and is the real excitation surface phonon-polariton in the range $(\omega^n_{TO})_3 < \omega < 220.2\ cm^{-1}$. The wave number extends to infinity at the frequencies 178, 194 and 220.2 cm^{-1}.

References

1. *Chandrasekhar H.R. and Zwick U.*Solid State Commun.1976,v.18.p.1509.

2. *Chandrasekhar H.R., Humphreys R.G., Zwick U. and Cardona M.* Phys. Rev. B, 1977, v. 15, p. 2177.

3. *Wiley J.D., Buckel W.J. and Schmidt R.L.* Phys. Rev.B,1976, v.13, p. 2489.

4. *Siapkas D.I., Kyriakos D.S. and Economou N.A.* Solid State Commun. 1976, v. 19, p. 765.

5. *Hartstein A., Burstein E., Brion J.J. and Wallis R.F.* Solid State Commun. 1973, v. 2, p. 1083.

6. *Hartstein A., Burstein E.,Brion J.J. and Wallis R.F.* Surface Sci. 1973, v. 34, p. 81.

7. *Falge H.J. and Otto A.* Phys. Status Solidi (b) 1973, v. 56, p. 523.

8. *Agranovich V.M. and Mills D.L. (editors),*Surface Polaritons,v.1 of Modern Problems of the Condensed Matter Science, Moskow: Nauka and Amsterdam: North-Holland, 1985.

9. *Kurosawa T.* J. Phys. Soc. Japan 1961, v. 16, p. 1298.

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*GeSe*KRISTALLARINDA SƏTH FONON-POLYARITONLARI

Maqalədə *GeSe* kristallarında səth fonon-polyaritonları tədqiq edilir. Nəzəri hesablamalar təcrübədə asanlıqla əldə olunan hal üçün aparılır: kristalın səthi onun parçalanma müstəvisinə, dalğa vektoru isə bu müstəvi üzərində yerləşən $\hat{a}$ və $\hat{b}$ oxlarından birinə təsadüf edir. Dalga vektoru $\hat{b}$ oxuna paralel olduqda dispersiya asılılığı iki qarışıqtəbiətli əyridən ibarətdır. Bu əyilər müxtəlif tezlik diapazonlarında həqiqi, ya da ki virtual səth fonon-polyaritonlarına məxsusdur. Dalğa vektoru $\hat{a}$ oxuna paralel olduqda dispersiya asılılığı iki həqiqi, bir virtual və bir qarışıqtəbiətli əyridən ibarətdir.

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ПОВЕРХНОСТНЫЕ ПОЛЯРИТОНЫ В *GeSe*

Теоретически исследован спектр поверхностных фонон-поляритонов в *GeSe* для наиболее приемлимой с экспериментальной точки зрения геометрии, когда нормаль к поверхности перпендикулярна плоскости скола (т.е. $\mathbf{n} \| \hat{c}$), а волновой вектор $\boldsymbol{k}$ ориентирован или вдоль оси $\hat{a}$, или вдоль оси $\hat{b}$, лежащих в этой плоскости. Установлено, что в случае $\boldsymbol{k} \| \hat{b}$ дисперсионная кривая поверхностных фонон-поляритонов состоит их двух ветвей, каждая из которых в различных областях частот имеет или виртуальный, или же реальный характер. В случае $\boldsymbol{k} \| \hat{a}$ дисперсионная кривая состоит из двух реальных, одной виртуальной и одной смешанной ветви, соответствующей, в зависимости от частоты, или виртуальному, или же реальному фонон-поляритону.