Influence of ferromagnetic ordering on Raman scattering in CoS$_2$

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The effects of phonon anharmonicity, phonon-magnon and electron-phonon interactions on the temperature dependence of Raman optical phonon modes are theoretically investigated. Besides the Klemens result for the phonon width due to anharmonicity, the corresponding lineshift is derived. We argue that the phonon decay into two magnons has very low intensity in ferromagnets with low Curie temperatures. Therefore, the electron interband transitions accompanied with the ferromagnetic ordering are included in considerations to get a good quantitative agreement with experiments.

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I. INTRODUCTION

Thermal broadening of phonon lines in the Raman scattering is usually described in terms of three-phonon anharmonicity, i.e. by the decay of an optical phonon with a frequency $\omega$ in two phonons.

The simplest case when the final state has two acoustic phonon from one branch was theoretically studied by Klemens, who obtained the temperature dependence of the Raman linewidth. The corresponding lineshift was considered in Refs. 1,2.

This theory was compared in works 3,4 with experimental data for Si, Ge, C, $\alpha$-Sn. A model was also considered with the phonons in the final state from different branches. It was found that anharmonic interactions of the forth order should also be included in order to describe precisely the Raman line behavior at high temperatures $T > 300$ K.

The interaction of phonons with magnons in antiferromagnets was discussed also in the analysis of the thermal conductivity, the spin Seebeck effect, high-temperature superconductivity, and optical spectra.

The magnon-phonon interaction result in the magnon damping, however, no effect for phonons was shown. Damping of the optical phonons was found to become large in the rear-earth Gd and Tb below the Curie temperature achieving a value of 15 cm$^{-1}$, which is much greater than the three-phonon interaction effect.

Temperature variation of the electronic structure of half-metallic CoS$_2$ was investigated by means of reflectivity measurements. Recently, the Raman scattering in CoS$_2$ was studied at temperatures nearby the ferromagnetic transition at $T_c = 122$ K. The shift and width of the $\omega = 400$ cm$^{-1}$ line are observed as functions of temperature. It is seen that an additional mechanism of the lineshift is incorporated around the Curie temperature.

In this theoretical paper, we consider the different interactions of the optical phonons in order to explain their temperature dependences observed. First, we obtain both the width and shift of the Raman line due to anharmonic interactions of the third order. Then, the interaction of phonons with magnons below the Curie temperature is considered. At last, the effect of the ferromagnetic ordering on the phonon-electron interaction is studied.

II. SHIFT AND WIDTH OF THE OPTICAL PHONON DUE TO ANHARMONIC INTERACTIONS OF THE THIRD ORDER

Here we calculate the Raman phonon self-energy due to three-phonon anharmonicity represented by the loop in Fig. 1. Two lines of the loop correspond with two phonons in the final state, and the shaded circle shows the interaction vertex of these two phonons with the initial optical phonon. At given frequency $\omega$ and momentum $k$ of the optical phonon, we have to summarize over the momenta $k_1$ and $k_2$ of phonons in the final state and to perform the Matsubara summation over the frequencies $\omega_n = 2\pi n T$. One summation over the momentum of the final phonon can be done using the conservation law $k_1 + k_2 = k$.

Then we meet the sum

$$S_{ph-ph}(\omega, k) = -T \sum_{n, k_1} \frac{2\omega_{k_1}}{\omega_{k_1}^2 + \omega_n^2} \frac{2\omega_{k-k_1}}{\omega_{k-k_1}^2 + (\omega - \omega_n)^2},$$

where each of the two factors is the Green function of the phonon in the final state

$$D_{ph}(k_1, \omega_n) = \frac{-2\omega_{k_1}}{\omega_{k_1}^2 + \omega_n^2}.$$

We perform the summation over $n$ considering the integral over the large circle in the complex $z$-plane of the integrand $f(i\omega_n = z) n_B(z)/2\pi i$, where $f(i\omega_n)$ is the function under the sum-sign in Eq. (1) and $n_B(z) = [\exp(z/T) - 1]^{-1}$. If the circle radius goes to the infinity, then the integral tends obviously to zero. It means that the sum of all the residues inside the circle equals zero. Then the residues of the function $n_B(z)$ at the poles give the sum in Eq. (1), which is thus equal to the sum with
the opposite sign of four residues at the poles $\pm \omega_{k_1}$ and $\pm \omega_{k-k_1}$. For definiteness, we assume that the frequencies $\omega_{k_1}$ and $\omega_{k-k_1}$ are positive. At $z = \omega_{k_1}$, the function $n_B(z)$ coincides with the number of phonons $N(\omega_{k_1})$ and it gives $-[N(\omega_{k_1}) + 1]$ at $z = -\omega_{k_1}$.

Finally, the analytical continuation on the real frequency $\omega$ is performed by the substitution $\omega \rightarrow \omega - \delta$ with the infinitesimal positive $\delta$. The following four terms appear:

$$
\frac{2\omega_{k-k_1}N(\omega_{k_1})}{\omega_{k-k_1}^2 - (\omega_{k_1} + \omega + i\delta)^2} + \frac{2\omega_{k-k_1}[N(\omega_{k_1}) + 1]}{\omega_{k-k_1}^2 - (\omega_{k_1} - \omega - i\delta)^2}
+ \frac{2\omega_{k_1}N(\omega_{k-k_1})}{\omega_{k_1}^2 - (\omega_{k-k_1} + \omega + i\delta)^2} + \frac{2\omega_{k_1}[N(\omega_{k-k_1}) + 1]}{\omega_{k_1}^2 - (\omega_{k-k_1} - \omega - i\delta)^2}.
$$

We are interested in the Raman phonon with $k = 0$, and the phonon dispersion satisfies the condition $\omega(k_1) = \omega(-k_1)$. Therefore, we can combine the terms in Eq. (2) to get

$$
\frac{4\omega_{k_1}[1 + 2N(\omega_{k_1})]}{4\omega_{k_1}^2 - (\omega + i\delta)^2}.
$$

To obtain the phonon self-energy, the Eq. (3) should be integrated over $k_1$ with the three-phonon anharmonic vertex squared. This vertex appears at the three-phonon Hamiltonian is expressed in terms of the phonon operators giving a factor $(\omega_{k_1}^2)^{-1/2}$.

The phonon self-energy writes

$$
\Sigma_{ph-ph}(\omega, T) = \frac{1}{2\pi^3\omega} \int \frac{d^3k_1}{\omega_{k_1}[4\omega_{k_1}^2 - (\omega + i\delta)^2]} [1 + 2N(\omega_{k_1})]d^3k_1
$$

with real and imaginary parts.

The imaginary part of Eq. (4) integrated over $k_1$ or over $\omega_{k_1} = k_1/s$, where $s$ is the sound velocity, yields the Klemens formula

$$
\Gamma_{ph-ph}(\omega, T) = \Gamma_{ph-ph}(\omega, 0)[1 + 2N(\omega/2)]
$$

with the linewidth at zero temperature

$$
\Gamma_{ph-ph}(\omega, 0) = \frac{g_{ph-ph}^2\omega}{24\pi s^5},
$$

where the averaging with respect to angles is denoted by the overline.

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**FIG. 1**: (Color online) Phonon self-energy; two lines of the loop represent two phonons in the case of three-phonon interactions or two magnons for the phonon-magnon interactions.

**FIG. 2**: (Color online) Calculated width and shift of the Raman line $\omega = 400$ cm$^{-1}$ due to the anharmonic interaction of the third order as functions of temperature.

The Raman lineshift due to the phonon anharmonicity is given by the real part of Eq. (4), i.e. by the principal integral value

$$
\delta\omega_{ph-ph}(\omega, T) = \frac{1}{2\pi^3\omega} \int \frac{g_{ph-ph}^2\omega_{k_1}^3\delta\omega_{k_1}d\Omega}{s^3(4\omega_{k_1}^2 - \omega^2)}[1 + 2N(\omega_{k_1})].
$$

Here, the temperature dependent part appears because of the phonon distribution function $N(\omega_{k_1})$. At low temperatures, $T \ll \omega/2$, we can omit $4\omega_{k_1}^2$, and the lineshift becomes

$$
\delta\omega_{ph-ph}(\omega, T) = -\frac{1}{\pi^3\omega^2} \int_0^{\omega_D/T} \frac{x^3dx}{e^x - 1} \int \frac{g_{ph-ph}^2d\Omega}{s^3}.
$$

We express the lineshift in Eq. (8) in terms of the linewidth at zero temperature, Eq. (9),

$$
\delta\omega_{ph-ph}(T) = -\Gamma_{ph-ph}(\omega, 0) \frac{g_{ph-ph}^2}{\pi} \left(\frac{T}{\omega}\right)^4 \int_0^{\omega_D/T} \frac{x^3dx}{e^x - 1}.
$$

The shift and width are shown in Fig. 2 for the Raman line 400 cm$^{-1}$ and the Debye temperature $T_D = 500$ K estimated for CoS$_2$. Menéndez and Cardona noted that the discrepancy between the calculated phonon linewidth
and experimental results may be of the order of ten, "mainly from the poor description of the phonon dispersion curves". Therefore, Eq. (10) should be used in fitting with caution.

Let us emphasize, that the calculated Raman linewidth due to three-phonon anharmonicity corresponds to the estimation

$$\Gamma_{ph-ph}(\omega, 0) \approx H_{ph-ph}^2 / \omega \sim (m/M)^{1/4} \omega \sim 5 \text{ cm}^{-1},$$

where \( m \) is the free electron mass, \( M \) is the lattice cell mass, and the anharmonic interaction has the order

$$H_{ph-ph} \approx \varepsilon_0 (u/a_0)^3$$

with \( \varepsilon_0 \sim \omega(M/m)^{1/2} \sim 3 \text{ eV} \) of the order of the atom energy. The ratio of the phonon displacement \( u \) to the lattice constant \( a_0 \) is of \((m/M)^{1/4}\).

III. EFFECT OF THE PHONON-MAGNON INTERACTION ON THE OPTICAL PHONON

As seen from experimental data, besides the phonon anharmonicity, the ferromagnetic ordering in CoS\(_2\) affects the Raman line form. The influence of antiferromagnetic ordering is considered in Ref.\(^\text{15}\), however, the line shift was only calculated.

Here, we analyse the Raman shift and width due to the phonon-magnon interaction at ferromagnetic ordering. The problem can be solved in the same manner as in the previous section considering the magnons instead of the acoustic phonons and taking into account that the magnons exist only below the Curie temperature. In the Matsubara technique, the magnon Green function has the form

$$G(\omega_n, k) = \frac{1}{-i\omega_n - \varepsilon_k},$$

where the magnon dispersion law writes as \( \varepsilon_k = A(a_0 k)^2 \) for temperatures in the range \( 1 \text{ K} \ll T < T_c \) with a constant \( A \) of the order of the Curie temperature. The summation should be carried out over frequencies \( \omega_n = 2\pi T n \) in the product of two magnon Green functions:

$$S_{ph-m}(\omega, k) = \sum_n \frac{-T}{-i\omega_n - \varepsilon_k} \frac{-T}{-i(\omega - \omega_n) - \varepsilon_k - \varepsilon_{k1}}.$$

Similarly to the previous section, the summation and continuation to the real frequency give

$$S_{ph-m}(\omega, k) = \frac{1}{-\varepsilon_k} \frac{1 + N(\varepsilon_k) + N(\varepsilon_{k-k1})}{-\varepsilon_{k-k1} + \omega + i\delta}.$$

The Raman phonon self-energy is obtained integrating Eq. (13) with \( k = 0 \) over \( k_1 \)

$$\Sigma_{ph-m} = \frac{1}{8\pi^2} \int \frac{w_{ph-m}(k_1) d^3k_1}{2\varepsilon_{k_1} - \omega - i\delta} [1 + 2N(\varepsilon_{k_1})],$$

where \( w_{ph-m}(k_1) = g_{ph-m} a_0 k_1 \) is the phonon-magnon interaction vertex with \( g_{ph-m} \sim T_c / \sqrt{\omega_M a_0^2} \sim T_c (m/M)^{1/4} \).

The imaginary part of Eq. (14) vanishes for the phonon frequency \( \omega \sim 600 \text{ K} \) in CoS\(_2\), because it is higher than the maximal value of \( 2\varepsilon_{k_1} \sim 2T_c \sim 250 \text{ K} \). So, the real decay of the considered optical phonon into two magnons is forbidden.

However, if the phonon frequency is lower, the decay becomes possible producing the width

$$\Gamma_{ph-m} = \frac{g_{ph-m}^2 \omega^3}{4\pi(2A)^{3/2}} \left[ 1 + \frac{2}{\exp(\omega/2T) - 1} \right].$$

The temperature dependence of the real part of Eq. (14) giving the Raman lineshift can be easily extracted as

$$\delta\omega_{ph-m}(\omega, T) = -\frac{g_{ph-m}^2}{2\pi^2 \omega} \frac{\Gamma_{ph-m}}{A} (\frac{T}{A})^{5/2} \int_0^\infty \frac{x^{3/2} dx}{\exp(x) - 1},$$

where we omit the magnon energy compared with the phonon frequency, \( \omega \gg 2\varepsilon_{k_1}, \sim 2T_c \).

In Fig. 3 the phonon shift, Eq. (16) as a result of the phonon-magnon interaction is shown in the solid line assuming that the magnon dispersion is given with the constant \( A \) for all temperatures below the Curie temperature. We see a sharp jump just at the Curie temperature. Such a behavior is not observed in experiments. Collecting the values of the vertexes, we can estimate the result of the phonon-magnon interactions as

$$\delta\omega_{ph-m} / \omega \sim (T_c / \omega)^2 (m/M)^{1/2} \sim 0.3 \text{ cm}^{-1},$$

FIG. 3: (Color online) Temperature dependence of the Raman lineshift as a result of phonon-magnon interactions.
IV. ELECTRON-PHONON INTERACTIONS AT THE FERROMAGNETIC ORDERING

We assume that the electron bands in CoS$_2$ have a form shown in Fig. 4. The lower band is filled and the upper band is empty. At low temperatures, below the Curie temperature, the Raman frequency $\omega$ is less than the total gap, which consists of the usual band gap $\Delta$ joined with the magnetic splitting $\mu H_e$ in the effective Weiss field $H_e$, where $\mu$ is the total electron magneton for the considered bands. In this case, the interband electron transitions are forbidden, and the phonon width is determined only by the anharmonicity. While the temperature increases, the magnetization, determined in the mean field approximation as

$$M = M_0 \sqrt{1 - (T/T_c)^2},$$

becomes lower. Then the frequency $\omega$ can exceed the total gap $\Delta + \mu H_e$, and the interband transitions are possible. According to experimental data, this occurs in CoS$_2$ approximately at $T = 100$ K. The proposed scheme differs from the conventional electron-phonon interaction only in the combination of the interband electronic transition with the ferromagnetic ordering.

The phonon self-energy resulted from the interband electron transition has the form

$$\Sigma_{el-ph} = g^2 \sum_{n \neq m} \int d^3p \frac{f(\epsilon_{pm}) - f(\epsilon_{pn})}{(2\pi)^3} \frac{\epsilon_{pn} - \epsilon_{pm} - \omega - i\delta},$$

(18)

where the contribution of the electron transitions between the different $n, m$ bands is included, because we are interested in the phonon frequency $\omega \sim 400$ cm$^{-1}$, which is large compared with the electron energy in half-metals. The electron-phonon interaction vertex $g$ is taken off the integrand, since it has no singularities in the electron energy interval considered. An estimation gives the vertex $g \sim \epsilon_0 (m/M)^{1/4}$, where $m$ and $M$ are the electron and ion masses, and $\epsilon_0 \sim 3$ eV is the typical electron energy. The interval of values given in literature is $g = 0.04 \pm 0.1$ eV.

The imaginary and real parts of the integral (18) determine the variation of the phonon linewidth $\Gamma$ and lineshift $\delta \omega$, correspondingly. Results look simply when the chemical potential is situated in the gap and the temperature is much less than the gap, which value should be about the Raman phonon frequency 400 K. Then, the distribution function of the lower band is $f(\epsilon_{pm}) = 1$ and for the upper band $f(\epsilon_{pn}) = 0$. If the chemical potential belongs to any electron band, we have to add its value to the value of the gap. An additional simplification arises when the phonon frequency $\omega$ is close to the value of the gap $\Delta$. Then we can use the quadratic expansion

$$\epsilon_{pm} - \epsilon_{pn} = \Delta + \mu H_e + p^2/2m,$$

with the reduced mass $m$ of two bands.

Extracting the imaginary part and integrating $\delta$-function in Eq. (18), we find the width

$$\Gamma_{el-ph} = g^2 m/2\pi \sqrt{a}, \quad \text{for} \quad a > 0,$$

(19)

where $a = 2\bar{m}(\omega - \Delta - \mu H_e)$. This contribution to the linewidth vanishes, for $a < 0$.

Taking the estimation of the vertex $g$ into account, we get the order of the width $\Gamma_{el-ph}/\omega \sim (m/M)^{1/4}/\pi \sim 3 \times 10^{-2}$, which corresponds with experimental data.

The temperature dependence of the width is shown in Fig. 5 with the parameters $g^2 \bar{m}^{3/2} \sqrt{\omega_0}/2\pi = 8$ cm$^{-1}$, $\mu H_e(T = 0) = 0.5 \omega_0$, $\Delta = 0.95 \omega_0$, $\omega = 400$ cm$^{-1}$. This value of $\Delta$ is in agreement with the gap $\sim 0.1$ eV calculated in Ref. at the $\Sigma$ direction in the Brillouin zone.
V. SUMMARY

The Klemens formula describes quantitatively the optical phonon width due to three-phonon anharmonic interactions. The corresponding lineshift matches with the width. However, the phonon-magnon interactions should be taken into account in order to interpret the effect of ferromagnetic ordering on the Raman line. In such ferromagnets as CoS$_2$ with the low Curie temperature, these interactions are found to be too weak to describe quantitatively the experimental data. Therefore, we propose the mechanism of the electron-phonon interaction attended with the effect of the ferromagnetic ordering on the electron bands. The corresponding Raman line width and shift are calculated in agreement with experiments.

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