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EFFECT OF ELECTRON–PHONON INTERACTIONS ON RAMAN LINE AT FERROMAGNETIC ORDERING

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The theory of Raman scattering in half-metals by optical phonons interacting with conduction electrons is developed. We evaluate the effect of electron–phonon interactions at ferromagnetic ordering in terms of the Boltzmann equation for carriers. The chemical potential is found to decrease as the temperature decreases. Both the linewidth and frequency shift exhibit a dependence on temperature.

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1. INTRODUCTION

Recently, the Raman scattering in the half-metallic CoS_2 was studied [1] in a wide temperature region. The $\omega = 400\ \mathrm{cm}^{-1}$ Raman line, observed previously at room temperature in Refs. [2, 3], demonstrates a particular behavior near the ferromagnetic transition at $T_c = 122$ K. The unusual large Raman linewidth and shift of the order of $10\ \mathrm{cm}^{-1}$ were observed. The reflectivity singularities of CoS_2 were explained in Ref. [4] by the temperature variation of the electronic structure. Another example of electron–phonon interactions is adduced in Ref. [5] in order to explain the phonon singularity at the Γ point in graphene. The electron–phonon interactions should also be considered in interpreting the observed Raman scattering around the Curie temperature.

Thermal broadening of phonon lines in Raman scattering is usually described in terms of the three-phonon anharmonicity, i. e., by the decay of an optical phonon with a frequency ω into two phonons. The simplest case where the final state has two acoustic phonons from one branch (the Klemens channel) was theoretically studied by Klemens [6], who obtained the temperature dependence of the Raman linewidth. The corresponding line shift was considered in Refs. [7, 8]. This theory was compared in Refs. [7–9] with experimental data for Si, Ge, C, and α-Sn. A model was also considered with the final-state phonons from different branches. It was found that anharmonic interactions of the forth order should be taken at high temperatures $T > 300$ K into account.

The situation is more complicated in substances with magnetic ordering. The interaction of phonons with magnons in antiferromagnets was discussed in review article [10] and more recently in the analysis of thermal conductivity [11], the spin Seebeck effect [12, 13], high-temperature superconductivity [14], and optical spectra [15]. The magnon–phonon interaction results in the magnon damping [16], but no effect for phonons was observed. The influence of antiferromagnetic ordering is considered in Ref. [17], where only the line shift was calculated. Damping of the optical phonons was found [18] to become large in the rare-earth Gd and Tb below the Curie temperature, achieving a value of $15\ \mathrm{cm}^{-1}$, which is much greater than the three-phonon interaction effect.

A contradiction is known to exist in the Migdal theory [19] of electron–phonon interaction. On one hand, Migdal showed that the vertex corrections for acoustic phonons are small by the adiabatic parameter $\sqrt{m/M}$, where m and M are the respective electron and ion masses (the "Migdal theorem"). The theory correctly described the electron lifetime and renormalization of the Fermi velocity v_F. But on the other hand, the theory resulted in a strong renormalization of the sound velocity $\tilde{s} = s(1 - 2\lambda)^{1/2}$, where λ is the dimensionless

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coupling constant. For a sufficiently large electron–phonon coupling constant $\lambda \to 1/2$, the phonon frequency approaches zero, marking an instability point of the system. Instead, one would intuitively expect the phonon renormalization to be weak along with the adiabatic parameter.

This discrepancy was resolved by Brovman and Kagan [20] almost a decade later (see also [21]). They found that there are two terms in the second-order perturbation theory that compensate each other and produce a result small by the adiabatic parameter. Namely, in calculating the phonon self-energy function $\Pi(\omega, k)$ with the help of the diagram technique, one should eliminate an adiabatic contribution of the Fröhlich model by subtracting $\Pi(\omega, k) - \Pi(0, k)$.

The interaction of electrons with optical phonons was considered first. A splitting of the optical phonon into two branches at finite wavenumbers k was predicted by Engelsberg and Schrieffer [22] within Migdal's many-body approach for dispersionless phonons. Later, Ipatova and Subashiev [23] calculated the optical phonon attenuation in the collisionless limit and pointed out that the Brovman–Kagan renormalization should be carried out for optical phonons in order to obtain the correct phonon renormalization. In Ref. [24], Alexandrov and Schrieffer corrected the calculational error in Ref. [22] and argued that no splitting was in fact found. Instead, they predicted an extremely strong dispersion of optical phonons, $\omega_k = \omega_0 + \lambda v_F^2 k^2/3\omega_0$, due to the coupling to electrons. The large phonon dispersion is a typical result of Migdal's theory [25] using the Frölich Hamiltonian. No such dispersion has ever been observed experimentally. The usual dispersion of optical phonons in metals has the order of the sound velocity. Reizer [26] stressed the importance of taking screening effects into account. Papers [24, 26] are limited to the case where both electron and phonon systems are collisionless. Moreover, only the phonon renormalization was considered, with no results available for the attenuation of optical phonons.

A semiclassical approach, which is different from the many-body technique and is based on the Boltzmann equation and the elasticity theory equations was developed by Akhiezer, Silin, Gurevich, Kontorovich, and many others (we refer the reader to review [27]). This approach was compared with various experiments, such as attenuation of sound waves, the effects of strong magnetic fields, crystal anisotropy, and sample surfaces on sound attenuation, and so on. It can be applied to the problem of the electron–optical-phonon interaction [28] as well.

In the previous paper [29], we developed a quantum theory for the optical-phonon attenuation and shift induced by the interband electron transitions and tuned with a temperature variation. Here, we consider the optical phonon renormalization as a result of the electron–phonon interaction taking ferromagnetic ordering into account. We argue that the reasonable phonon damping and shift can be obtained using the semiclassical Boltzmann equation for electrons and the equation of motion for phonons coupled by the deformation potential.

2. ELECTRON–PHONON INTERACTIONS AT FERROMAGNETIC ORDERING

We assume that the electron bands in CoS_2 have the shape shown in Fig. 1. The ferromagnetic ordering results in a spin splitting $\mu_B H_e$ of the unfilled half-metallic band,

$$\varepsilon_\uparrow(\mathbf{p}) = \frac{p^2}{2m^*} - \mu_B H_e, \quad \varepsilon_\downarrow(\mathbf{p}) = \frac{p^2}{2m^*} + \mu_B H_e \qquad (1)$$

in the effective Weiss field H_e. As the temperature decreases, the magnetization, determined in the mean-field approximation as

$$m = m_0\sqrt{1 - (T/T_c)^2}\,, \qquad (2)$$

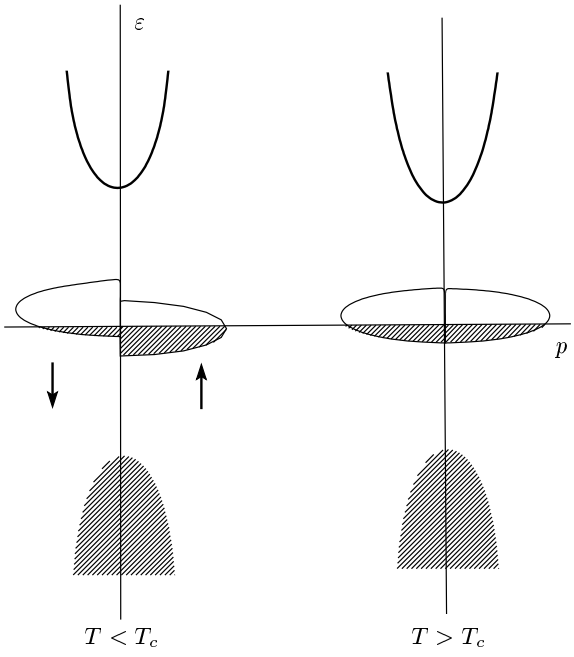

Fig. 1. Proposed band scheme for two-electron spin projections

appears according to experimental data in CoS_2 at approximately $T_c = 122$ K, and the spin splitting is proportional to the magnetization.

We write the interaction of electrons with the optical phonon u_i as the deformation potential

$$H_{int} = \frac{u_i}{N} \sum_s \int \frac{d^3p}{(2\pi\hbar)^3} \zeta_i(\mathbf{p}) f(\mathbf{p}), \qquad (3)$$

where $N \sim 1/a^3$ is the number of cells in unit volume and a is the interatomic distance. For the acoustic phonon–electron interaction, we should substitute the strain tensor u_{ij} instead of the displacement u_i in order to satisfy the translation symmetry of the lattice.

The Boltzmann equation for the nonequilibrium part of the distribution function $f(\mathbf{p})$ has the form

$$[-i(\omega - \mathbf{k}\cdot\mathbf{v}) + \tau^{-1}] f(\mathbf{p}) = \\ = -\frac{\partial f_0}{\partial \varepsilon} [e\mathbf{v}\cdot\mathbf{E} - i\omega u_i \zeta_i(\mathbf{p})], \qquad (4)$$

where f_0 is the equilibrium distribution function. In Boltzmann equation (4), we omit the spin index s that determines all the electron parameters. The electron collision frequency τ^{-1} takes the collisions with impurities and phonons into account. The collision frequency is calculated for CoS_2 in the Debye model with the temperature $T_D = 500$ K [30]. It follows from Eq. (4) that the condition

$$\langle \zeta_i \rangle = 0$$

must be satisfied for the current continuity equation to hold; here, the brackets denote averaging over the Fermi surface for temperatures $T \ll \varepsilon_F$.

In the ferromagnetic phase, as the temperature changes, the carriers overflow from one spin state to another, but the total number of carriers

$$N = \sum_s \int \frac{d^3p}{(2\pi\hbar)^3} f_0(\varepsilon_s) \qquad (5)$$

remains constant. This condition determines the chemical potential and the concentration of carries with spin up and spin down, shown in Fig. 2. All figures correspond here and in what follows to the carrier concentration $N = 10^{21}$ cm^{-3} in the considered band with the chemical potential $\mu = 0.36$ eV above the Curie temperature.

We write the equation of motion for the phonon mode in the form

$$(\omega_0^2 - \omega^2) u_i = \frac{QE_i}{M} - \frac{1}{M} \frac{\partial H_{int}}{\partial u_i}, \qquad (6)$$

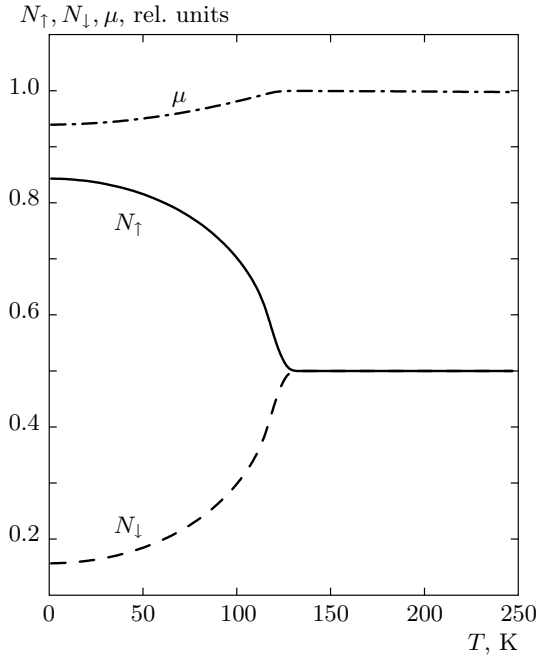

Fig. 2. Calculated temperature dependence of the carrier concentration for spin up $N_\uparrow$ and spin down $N_\downarrow$ (relative to the total concentration at temperatures above the ferromagnetic ordering temperature), and the dependence of the chemical potential μ

where M is the reduced ion mass of the cell, Q is the charge corresponding to the optical vibration, and ω_0 is the frequency of the considered mode. Here, the last term represents the electron–phonon interaction. Using Boltzmann equation (4), we rewrite this term as

$$-\frac{1}{M}\frac{\partial H_{int}}{\partial u_i} = -\frac{u_i}{MN} \times \\ \times \sum_s \int \frac{\omega\tau\zeta_i^2(\mathbf{p})}{\omega\tau + i} \left(-\frac{\partial f_0}{\partial \varepsilon}\right) \frac{d^3p}{(2\pi\hbar)^3}. \qquad (7)$$

The term with the electric field in the Boltzmann equation disappears in integrating over $\mathbf{p}$ due to the velocity inversion $\mathbf{v} \to -\mathbf{v}$. The term with the wave vector $\mathbf{k}$ has to be omitted for a Raman phonon, because the vector $\mathbf{k}$ is determined in this case by the laser frequency ω_i and the optical-phonon frequency satisfies the condition $\omega \gg \omega_i v/c$.

The electric field is not excited in TO vibrations. Therefore, setting $E = 0$ and integrating over the energy ε instead of p, we use Eqs. (6) and (7) to find the line shift $\delta\omega$ and linewidth $\delta\Gamma$ determined by the electron–phonon interaction as

$$\delta\omega_{TO} - i\delta\Gamma_{TO} = \\ = \frac{1}{2MN}\sum_s \int \frac{\tau(\omega\tau - i)\zeta^2(\mathbf{p})\, dS}{(\omega^2\tau^2+1)v(2\pi\hbar)^3}\bigg|_{\varepsilon=\varepsilon_F}, \quad (8)$$

where dS is an element of the Fermi surface and v is the Fermi velocity. Estimating $S = 4\pi p_F^2$, $\zeta(\mathbf{p}) \sim \varepsilon_0/a$, and $\varepsilon_0^2 \sim \omega^2 M/m_e$, where $\varepsilon_0 \sim 3$ eV is the typical electron energy in metals, we obtain

$$\delta\omega_{TO} - i\delta\Gamma_{TO} \sim \frac{ap_F\tau\omega_{TO}^2}{2\pi^2\hbar(\tau\omega_{TO}+i)}.$$

To find the LO mode frequency, we should evaluate the dielectric function $\varepsilon(\omega)$. Equations (6) and (7) allow us to express the phonon displacement u in terms of the electric field E and to calculate the phonon contribution uNQ to the polarization. We find the total dielectric permittivity by adding the contributions ε_∞ of the filled bands:

$$\varepsilon(\omega) = \varepsilon_\infty - \frac{4\pi e^2}{3\omega}\sum_s \int \frac{\tau v dS}{(\omega\tau+i)(2\pi\hbar)^3} + \frac{4\pi NQ^2}{M} \times \\ \times \left[\omega_0^2 - \omega^2 + \frac{\omega\tau}{MN}\sum_s \int \frac{\zeta^2(\mathbf{p})\, dS}{(\omega\tau+i)v(2\pi\hbar)^3}\right]^{-1}. \quad (9)$$

The frequency of the longitudinal phonon mode is determined by the condition $\varepsilon(\omega) = 0$. In the absence of free carriers, we find the frequency of the LO mode as

$$\omega_{LO}^2 = \omega_0^2 + \omega_{pi}^2,$$

where $\omega_{pi}^2 = 4\pi NQ^2/M\varepsilon_\infty$ is the ion plasma frequency squared.

Using Eq. (9), we find the LO frequency in the presence of carriers as

$$\omega_{LO}^2 - \omega_0^2 = \frac{\omega}{(2\pi\hbar)^3 MN} \times \\ \times \sum_s \int \frac{\tau\zeta^2(\mathbf{p})\, dS}{(\omega\tau+i)v} - \frac{\omega_{pi}^2}{\omega_{pe}^2}\omega(\omega + i\tau^{-1}), \quad (10)$$

where the electron plasma frequencies squared

$$\omega_{pe}^2 = \frac{4\pi e^2}{3\varepsilon_\infty}\sum_s \int \frac{v\, dS}{(2\pi\hbar)^3} \quad (11)$$

is assumed to be large in comparison with ω_{pi}^2. We can also set $\omega = \omega_{LO}$ in the right-hand side of Eq. (10). Here, the last term takes the screening of the electric field by free carriers into account. For the typical carrier concentrations in conductors, the main role is played by the first term, which coincides with the result for the TO mode, Eq. (8), shown in Figs. 3 and 4

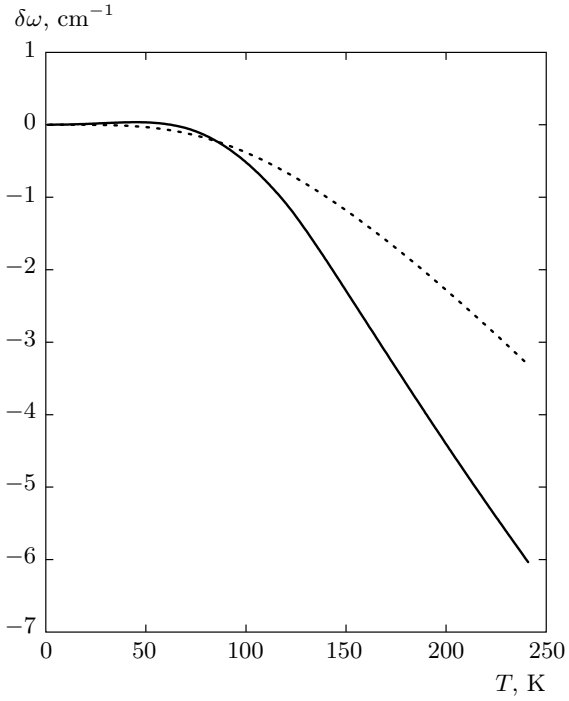

Fig. 3. Calculated shift of the Raman line $\omega = 400$ cm^{-1} due to the electron–phonon interaction and anharmonicity (solid line), and the line shift in the Klemens channel (dashed line)

(the results for the Klemens channel are taken from Ref. [29]).

We emphasize that the temperature dependence of the linewidth and shift, Eq. (8), is determined mainly by the electron collision rate τ^{-1} , for instance, also involved in the dc conductivity. For a cubic crystal, the dc conductivity (i. e., the conductivity at $\omega = k = 0$) is given by

$$\sigma = \sum_s \frac{e^2}{3(2\pi\hbar)^3}\int \tau v\, dS.$$

The details of the electron density of states and of the deformation potential are responsible for peculiarities of the Raman line temperature dependence.

3. SUMMARY

The Klemens formula describes the optical phonon width due to three-phonon anharmonic interactions. The corresponding line shift matches the linewidth. In ferromagnets with a low Curie temperature, such as CoS_2, these interactions are found to be too weak to describe the experimental data quantitatively

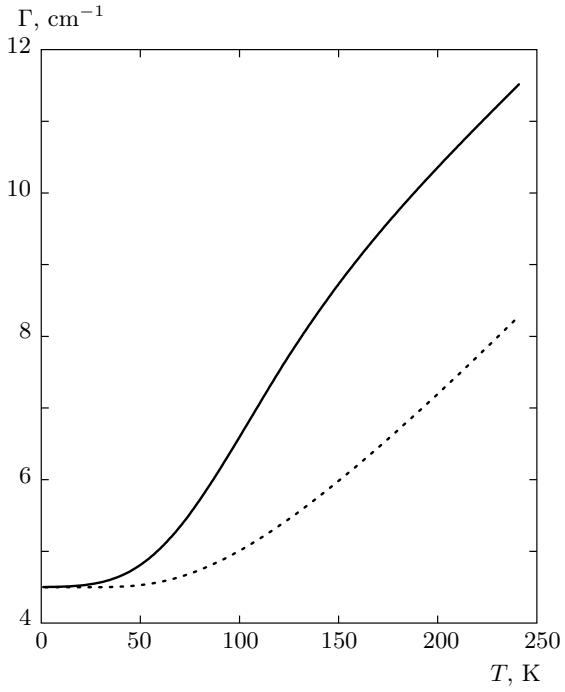

Fig. 4. Calculated temperature dependence of the width for the Raman line $\omega = 400$ cm^{-1} at the ferromagnetic ordering (solid line), and the linewidth in the Klemens channel (dashed line)

and to explain the very large Raman linewidth and shift. Therefore, we propose the mechanism of electron–phonon interaction attended with the effect of ferromagnetic ordering on the electron bands. The deformation potential couples the Boltzmann equation for electrons and the equation of motion for phonons, producing a renormalization of the phonon frequency. The corresponding Raman line width and shift are in agreement with experiments in Ref. [1].

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