Pressure-induced effect on electronic excitations in osmium

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Abstract. Electronic Raman scattering has been studied in single crystals of 5d transition metal osmium under pressures up to 60 GPa in the temperature range of 10 – 300K. With the use of green and blue excitation wavelengths we observe an appearance of well-defined electronic peaks at \( \sim 580 \) cm\(^{-1} \) for wave vector direction \( q || [0001] \) and at \( \sim 350 \) cm\(^{-1} \) for \( q || [10\overline{1}0] \) in the pressure range of 20 – 30 GPa. It was shown in our combined experimental and theoretical investigation that a consideration of both a renormalization of the electron self-energies near the Fermi level and a change in the Fermi surface under pressure and temperature variation is needed to describe the observed spectra.

In a clean metal with anisotropic Fermi surface (FS) intraband electronic scattering may be observed in the wide frequency range of \( \omega < v_F / \delta \) (\( v_F \) – electron Fermi velocity, \( \delta \) is the penetration depth) under an assumption of \( \omega > \Gamma \), where \( \Gamma \) is the relaxation frequency of the conduction electrons [1, 2]. In the region of the maximum scattering intensity at \( \omega \sim v_F / \delta \) the scattering cross section is determined by a contribution from all the electrons at the FS and its magnitude may be rather large. The study of its frequency dependence may give supplementary information both on the FS topology and a renormalization of the electron self-energies by any relaxation process such as an electron–phonon (e–ph) and/or electron–electron (e–e) scattering [3, 4, 5, 6].

Recently the wave vector dependence of the electronic light scattering (ELS) in the normal state has been observed in hcp transition metal osmium [7]. A tuning of the momenta \( q \) by the changing incident laser energy allowed studying the dispersion of the phonon and electronic excitations. Abrupt and anisotropic optical phonon frequency softening (2-3\%) has been found in the range of \( q \sim 10^6 \) cm\(^{-1} \) at low temperatures. Anomalous dispersion and maximal widths together with clear Fano shapes of the phonon lines have been observed in the momenta range corresponding to crossing of the electron and phonon excitation’s energies indicating strong e–ph interaction. The observed \( q \)--dependences of the self–energies of the optical phonons in osmium are in qualitative agreement with the theoretical predictions [8, 9] confirming the existence of nonadiabatic effects in the e–ph interaction in transition metals.

The application of pressure may modify both the electronic band structure near the Fermi level and internal scattering processes, which result in the Raman spectra. This gives an additional tool to study the electronic excitations responsible for anomalous dispersion effects. Anomalous temperature–induced phonon hardening in osmium has been found at pressures \( \geq \)
15 GPa at nonhydrostatic conditions [10]. Recently anomaly in the c/a ratio of osmium has been observed at pressures of 20–25 GPa [11] which was attributed to a possible change in the FS topology.

The goal of this work was to study the changes in the fine details of the electronic structure near the Fermi level in the pressure range where the abovementioned anomalies have been found. Here we present an evolution of the electronic Raman response of osmium at pressures up to 60 GPa in the temperature range 10–300 K for different q values and directions. First-principle calculations of the frequency dependences of the electronic scattering cross section have also been performed for comparison with the measured Raman spectra.

Plates of osmium single crystals with (0001) and (10\bar{1}0) orientation thinned to 5–10 \( \mu m \) by mechanical and electropolishing were loaded into a diamond anvil cell and placed in an optical cryostat. The high purity of the crystals was confirmed by their low residual resistivity ratio (\( \geq 1000 \)). The pressure-transmitting medium was argon. Calibration was done by the ruby luminescence method. Four laser lines \( \lambda_i \) (488, 514, 633, and 740 nm) of an Ar ion, He-Ne and Ti:sapphire lasers with powers up to 150 mW were used for spectra excitation. Spectra were collected in quasibackscattering geometry (\( \sim 145^\circ \)) [12], the laser spot diameter was about 20 \( \mu m \). The spectra were analyzed using a HR-460 spectrograph equipped with notch filters and a CCD detector.

Raman spectra (divided by the Bose factor \( 1 - \exp(-\hbar \omega / kT) \)) measured from the basal plane (0001) (wave vector \( q \) is perpendicular to the sample plane) with the excitation energy \( E_i=2.41 \) eV.

**Figure 1.** Raman spectra at different pressures (numbers, GPa), measured from (0001) plane at T=10K\( -\)\( (a) \) and 300K\( -\)\( (b) \), \( E_i=2.41 \) eV. Calculated at 50 GPa ELS spectrum-red line. Inset— the ELS intensity vs pressure at T=10K.

**Figure 2.** Raman spectra at different pressures (numbers, GPa), measured from (10\bar{1}0) plane at T=10K\( -\)\( (a) \) and 300K\( -\)\( (b) \), \( E_i=2.41 \) eV. Calculated at 50 GPa ELS spectrum-red line Inset— the ELS intensity vs pressure at T=10K.
eV (514 nm) are shown in Fig.1. A structure—less background with the superimposed $E_{2g}$ phonon line near 165 cm$^{-1}$ was observed in the low—pressure spectra taken at all temperatures. Here we report a strong intensity increase by more than one order of magnitude with an appearance of well-defined peak near 580 cm$^{-1}$ at 10K at pressures higher than 20 GPa. A broad continuum near 620 cm$^{-1}$ was also observed in the spectra measured with the 488 nm excitation.

The spectra obtained from the (10\overline{1}0) plane are presented in Fig.2. Here the structure—less background was also observed up to pressures ~ 20 GPa at all temperatures. In this geometry a pronounced electronic peak at 350 cm$^{-1}$ appears at T=10K under further pressure increase. The insets in Fig.1a and 2a show that peak intensities grow sharply in the pressure range 20–30 GPa. When temperature increases the electronic spectra smear out and become structure—less.

For the $q \parallel [0001]$ the decrease in intensity at high temperature by a factor about 2.5 was also found while intensity for $q \parallel (10\overline{1}0)$ was even higher at T=300K in comparison to T=10K. At the same time, the spectra measured with red and infrared excitation show only moderate evolution: the well—defined zero-pressure peaks soften under pressure by ~ 10% without apparent changes in the linewidth. The spectra also show much lower $q$ anisotropy (~ 10%) and their intensity increases by no more than factor of 2 (Fig.3).

Besides the one-phonon scattering the two-phonon scattering at 200÷500 cm$^{-1}$ is seen in the spectra shown in Fig 1 and 2. For the $q \parallel [10\overline{1}0]$ its intensity increases by order of magnitude at 300K and this sharp growth starts in the 20–30 GPa pressure range as in the case of electronic scattering. At low temperatures the intensity of the two-phonon scattering essentially decreases in contrast to the electronic peak intensity behavior.

The presented results provide the evidence for the existence of an abnormal pressure behavior of the ELS spectra. First, an anomalous intensity growth occurs with blue and green excitation accompanied by the transformation of the structure—less background into the well-defined electronic continuum peaks in the 20-30 GPa pressure range. Second, we observe the large decrease in the electronic peak positions and their anisotropy upon decrease of the excitation energy. Third, we observe a different temperature behavior of the ELS intensity for two probed $q$ directions.

In order to understand the reasons of the observed anomalies the calculations of the frequency dependence of the ELS by noninteracting electron-hole pairs were performed. The intensity of the intraband ELS is determined by computing the integral over the whole FS from imaginary time. Third, we observe a different temperature behavior of the ELS intensity for two probed $q$ directions.

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suggesting resonance enhancement for the whole FS. Moreover, the observed resonance has rather large width $\sim 0.5$ eV and doesn’t distort the continua lineshapes. Thus, in this calculation we used a constant $\gamma(p, q, \omega)$ to simulate the resonant conditions which suggests the interband matrix elements of the momentum operator are constant in the $p$ space.

The band structure calculations were performed using linearized muffin-tin method (LMTO) [16] in the local density approximation (LDA). In the course of the self-consistency the mesh of 1728 k-points in the irreducible part of the Brillouin-zone was used. The integration over the FS surface was performed with the fine mesh of 125 000 $p$-points in the full Brillouin-zone. The calculation of the Fermi velocity was done in the OpenDX package. The obtained FS is in agreement with that calculated before [17, 18, 19, 20]. It consists out of main 4 sheets: electronic ones $\Gamma 9e$ and $\Gamma 10e$, small hole sheets $U7h$ in the $LM$ direction and a complicated “monster” surface $KMh8$. Our calculations were perfomed for the volumes corresponding to 0 and 50 GPa[11]. As in Refs [19, 20] in this pressure region no new sheets of the FS were found. Note however, that our calculation scheme does not include the spin−orbit interaction for the Os 5d states.

Fig.1 and 2 show rather close correspondence of the measured and calculated high-pressure Raman spectra for both $q$ directions with the $E_i = 2.41$ eV excitation. This implies that the observed in the resonant conditions ELS spectra have an intraband origin. Our simulations show a substantial broadening of the calculated spectra compared to the measured ones. The measured spectra for another excitation energies are also narrower than the calculated ones. That may be due to a difference of the real FS topology or the velocity distribution at the FS

![Figure 3](image-url)  

**Figure 3.** The measured (points) and calculated (dashed lines−0 GPa, solid lines−50 GPa) ELS peak positions vs $E_i$ for $q || [10\overline{1}0]$−(a) and $q || [0001]$−(b), $T=10K$. Inset shows the wave vector distribution $|U(q)|^2$ for different $E_i$ (numbers in eV).

from the one obtained in this calculation. A comparison of the calculated and measured continua frequencies for the different excitation energies and pressures in Fig.3 also supports such a suggestion. The calculated spectra become harder and broader under pressure by $\sim 10\%$ for $q || [0001]$ and by $\sim 20\%$ for $q || [10\overline{1}0]$ at all excitation energies and their intensities decrease at the same ratio. This contradicts the observed strong intensity growth, the electronic peak position softening and narrowing when using the excitation in the blue-green range compared to only a negligible frequency softening with the red excitation. At the excitation energies $E_i \leq 2.2$ e V the calculated frequencies substantially exceed (up to 2 times) the measured ones. For the excitation energies of $E_i \geq 2.2$ e V, the calculations predict at all pressures well-defined electronic peaks at the frequencies which are smaller than those corresponding to the observed almost structure-less electronic continua (Fig.1, 2). The appearance of pronounced peaks in the spectra measured at pressures $P \geq 20$ GPa improves the agreement to the calculation in this excitation energy range. The $q$− anisotropy of the electronic peak frequencies calculated with a constant $\gamma(q, \omega)$ doesn’t depend on $E_i$ in
contrast to the observed decrease with the red and near infrared excitations.

The discrepancy between the experimental and calculated data implies an importance of the electron scattering mechanisms going beyond the LDA. A substantial increase of the calculated frequencies in comparison to the measured ones occurs in the range of 200–500 cm\(^{-1}\), i.e. in the energy region of the two-phonon states of osmium. Strong temperature effects at all pressures suggest also an important role of the inelastic e–ph scattering [4, 5, 6] which may lead to the electron dispersion renormalization at small \(q\) (low-energy excitation-inset in Fig.3a). The observation of the structure–less electronic background at low pressures with \(E_i \geq 2.2\) eV provides the evidence for the increase of the damping of the electronic states for large wave vectors \(q\), essential part of which is probed by the high-energy excitation (inset in Fig. 3a). This implies the existence of additional scattering mechanisms for electronic states lying away from the Fermi energy by 500–100 cm\(^{-1}\). The Fermi surface topology having large nearly parallel sections of the FS with wave vectors \(Q\) in the basal plane favors the enhancement of the e–e scattering. An anomalous growth of the two–phonon cross section under pressure for \(q || [10\bar{T}0]\) at T=300K supports this suggestion. It was shown theoretically [21] that such an enhancement of the two–phonon Raman spectra in transition metals may be due to successive phonon \(\omega +Q\) and \(\omega -Q\) emission between electronic states close to the Fermi level when the conditions for double-photon resonance are fulfilled. If \(\omega +Q + \omega -Q \approx v_F \mathbf{q}\), the same resonance mechanism may provide an anomalous ELS intensity growth under pressure due to an extended region of phase space for the scattering events. This is possible if the leading resonance term is determined by the scattering processes near the Fermi level having energy denominators with a little damping. A correlation of the peak narrowing with the ELS intensity increase under pressure supports this possibility. Both final state consisting of one phonon plus an electron-hole pair and two-pair final state will provide an electronic background which could interfere with two-phonon Raman scattering [21]. In turn, the decrease of the electronic damping at high-energy excitation (probing larger \(q\)-magnitudes) may be due both to the electron and phonon spectra change and to the interplay of the e-ph and e–e scattering contributions which determine the \(q\)- and \(\omega\)- dependence of the effective e–ph coupling [22].

A decrease of the electronic peak position anisotropy for the studied \(q\)-directions with the red excitation may be explained by a change of the \(p\)-dependence of the electron-photon matrix element for nonresonant scattering. In our simple calculation, the constant matrix element was used for the resonant case. This implies that the whole FS is in resonance which is possible for a small FS sheet but is difficult to imagine for the main osmium FS sheets. In any case the detailed band structure calculations of the resonant behavior are necessary. They are important for understanding of the ELS cross section increase at high–energy excitation and they are needed to explain why the frequency’s anisotropy for the studied \(q\)-orientations varies strongly upon the excitation energy change. The unusual temperature behavior of the ELS intensity for the different \(q\)-directions remains unclear so far. It is natural to expect a similar temperature behavior if the large FS sheets determine the observed electronic scattering. Another possibility may arise if this scattering originates from the electronic states near the L point which are strongly coupled to the phonons and vary under the pressure and temperature.

In summary, an anomalous increase of the ELS cross section under pressure was found in Raman spectra of osmium excited with the blue and green excitation. In the pressure range of 20–30 GPa, the low-temperature structure-less background transformed to pronounced and strongly temperature dependent peaks at \(\sim 580\) cm\(^{-1}\) for \(q || [0001]\) and at \(\sim 350\) cm\(^{-1}\) for \(q || [10\bar{T}0]\) showing a strong temperature dependences. The comparision of the measured and calculated within LDA ELS spectra implies the electron self-energy renormalization in the energy range \(\sim 1000\) cm\(^{-1}\) from the Fermi level due to the e–ph and e–e scattering. The detailed calculations of the resonance effects which take into account the phonon renormalization of the electron band structure are needed to understand found anomalies.
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