Resonant second-order Raman scattering and electron-photon interaction in rhenium

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The two-phonon Raman scattering spectra in a metal with a hexagonal close packed structure are measured for the first time. The completely symmetric A_{1g} component predominates in the spectra. According to a group-theoretical analysis, this component contains contributions only from overtone transitions. The specific features of the observed spectra can be assessed by comparing the essential data with those of neutron spectroscopy with allowance for the selection rules. The discrepancy between the spectra and the phonon density of state distribution can be attributed to the strong interaction between phonons with anomalous dispersion and electron states in the vicinity of the Fermi level. The unusual temperature behavior of the intensity and the anisotropy of the scattering tensor in a plane containing the crystal axis suggest that the same states may play an essential role in light scattering processes.

A number of transition metals and their compounds reveal a correlation between the anomalies in the phonon distribution curves and an increase in the temperature of the superconducting transition T_c. Among metals with hcp lattices, a deep valley exists near the center of the Brillouin zone for the optical branches, with atom displacements along the crystallographic axes for technetium and rhenium,[2] which have the highest values of T_c, 7.8 and 1.7 K, respectively.

A significant negative contribution of the *d*-electrons to the dynamical matrix, to which the phonon anomalies in the transition metal are attributed,[3] occurs also for transverse optical branches in Tc and Re, in contrast to their neighbors in the periodic system with lower T_c. Evidence for this is found from a comparison of the frequencies of the *TO* phonons with $\mathbf{k} = 0$, obtained in optical and neutron experiments[1,2,4–6] for Tc ($130\ \mathrm{cm}^{-1}$) and Ru ($192\ \mathrm{cm}^{-1}$) and also for Re ($121\ \mathrm{cm}^{-1}$) Os ($165\ \mathrm{cm}^{-1}$). The appearance of electron-phonon interactions (EPI) in hcp metals is indicated also by the analous temperature dependence of the damping E_{2g} of the optical phonons.[5,6] A detailed interpretation of the observed anomalies requires careful investigation of the phonon spectrum and of the electronic structure close to the Fermi level.

In addition to the data on inelastic neutron scattering, the second-order Raman-scattering spectra can give information on the distribution of the density of phonon states. In the general case, the Raman light scattering is indicative of the two-phonon density of states, which includes both overtone and combination transitions. However, in the completely symmetric A_{1g}-component of the spectrum, the principal contribution is made by the (always allowed by the selection rules[7]) overtone transitions with participation of phonons having equals and opposite directions of the wave vectors, belonging to one and the same branch of the vibration spectrum. The measured spectra of second-order Raman scattering of vanadium, niobium, and tantalum, for example, take excellent account of the energy distribution of the density of phonon states.[8] Naturally, the density of states is represented in the intensity of the two-phonon Raman scattering with a weight determined both by the matrix elements of the momentum for the optical transitions and resonance denominators and by the matrix elements of the EPI.

For transition metals, the high density of electron states in the region of the Fermi level makes it possible for the principal term in the matrix element of the two-phonon Raman scattering to be approximately proportional to the electron contribution to the self-energy of the phonon; this leads to the selective amplification of phonons with anomalous dispersion.[9] Consequently, the softening can be accompanied by an increase of the intensity at the frequencies of these phonons relative to the level determined by the density of phonon states.

One of the candidates in the search for similar effects is rhenium. Data on its phonon dispersion are limited to a single direction of the Brillouin zone; moreover, information is lacking on the temperature behavior of the anomaly in the phonon spectrum. In order to investigate the phonon spectrum and its temperature dependence we have measured the polarization dependences of the spectra of Raman light scattering of second order in rhenium. On the basis of a group-theoretical analysis we carried out an identification of the observed features and a comparison of the spectra of Raman light scattering with neutron and microcontact spectra. The contribution of the intermediate electron states in the vicinity of the Fermi level to the scattering cross section (in connection with the unusual temperature dependences and the anisotropy of the spectra) are discussed.

1. EXPERIMENT

Measurements were carried out on the electropolished (1010) and (0001) planes of a single crystal of Re[4,6] in the geometry of the quasi-inverse scattering. The spectra were excited by the lines of an LGN-503 argon laser and were obtained at 120, 330, and 450 K. For separation of the components of the scattering tensor, measurements were made in the geometries $X(YY)\bar{X}$, $X(YZ)\bar{X}$ abd $X(ZZ)\bar{X}$ on the (1010) plane and also in the geometries $Z(YY)\bar{Z}$ and $Z(YY)\bar{Z}$ on the (0001) plane. The axes *X*, *Y*, *Z* in these designations refer respectively to the directions $[10\bar{1}0]$, $[1\bar{1}20]$ and [0001]. The resoltuion in the experiments amounted to $6\ \mathrm{cm}^{-1}$.

2. GROUP-THEORETICAL ANALYSIS OF THE SECOND-ORDER SPECTRUM IN HCP METALS

The crystalline structure of rhenium, which as an hcp lattice with two atoms per cell, is described by the space

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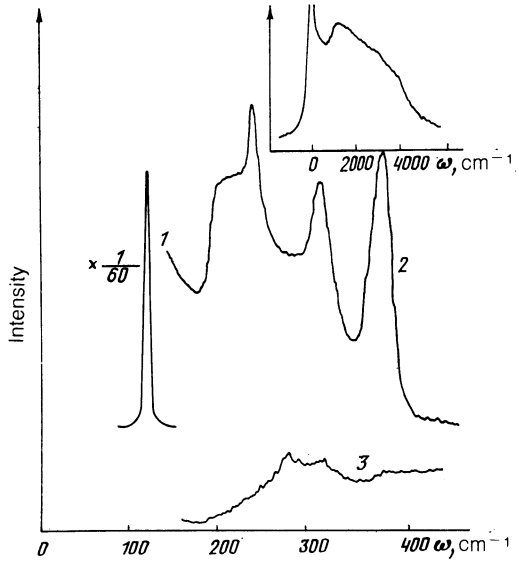

FIG. 1. Spectra of Raman light scattering of first and second orders of a single crystal of rhenium, obtained with a 4880 Å exciting line (2.54 eV) at room temperature: 1—scattering geometry YY (E_{2g}), 2—YY ($A_{1g} + E_{2g}$), 3—YZ (E_{1g}). The two-phonon spectrum in the geometry YX (E_{2g}) was not obtained because of the weakness of the signal. Inset—spectrum of rhenium in the region of electron scattering.

group D^4_{6h}. The symmetry and degeneracy multiplicity of the phonon branches are given in Ref. 10. The analysis performed showed that the points Γ, M, K, and H are symmetry critical points for the given structure. The selection rules for the activity of the critical irreducible representations corresponding to these points are given in the Table. It follows from these results that the completely symmetric component of the two-phonon spectrum of Raman light scattering is determined only by overtone transitions and, consequently, the A_{1g} spectrum for hcp metals should give the density of phonon states at twice the frequency. By the use of the projection operator it can be shown that all the vibrational overtones make a contribution to the different components of the scattering tensor.

3. RESULTS AND DISCUSSION

Figure 1 shows the spectra of first and second order in Re for the components of the scattering tensor associated with the representations A_{1g}, E_{1g} and E_{2g} that are active in Raman light scattering. The ratio of the intensities of the one-phonon and two-phonon A_{1g} scattering is of the order of 60. In the two-phonon spectrum the A_{1g} component dominates. This component, in accordance with the selection rules, is determined by the overtone transitions and can be comparable with the density of phonon states from other experiments. In order to carry out such a comparison, the data must be divided by the frequency-dependent factor $[n(\omega/2) + 1]^2/\omega^2$ in the scattering cross section, where $N(\omega/2)$ is the Bose–Einstein factor and ω is the frequency of the two-phonon spectrum. Since this correction leads to a significant redistribution of the intensities in the spectra, Fig. 2 gives the uncorrected data for the YY and ZZ components of the tensor A_{1g}, together with the results of neutron measurements of the density of states $F(\omega/2)$ (Ref. 11) and the microcontact spectra $\alpha_{P_c} F(\omega/2)$ (Ref. 12), where α_{P_c} is the matrix element of the EPI in microcontact spectroscopy.

TABLE I. Activity of overtone and combination transitions in Raman light scattering spectra for different irreducible representations of the scattering tensor (hcp structure D^4_{6h}).

Point	Combination or overtone	$\Gamma_1^+(A_{1g})$	$\Gamma_6^+(E_{1g})$	$\Gamma_5^+(E_{2g})$
Γ	$[\Gamma_2^-]^2$	+		
	$[\Gamma_3^+]^2$	+		
	$[\Gamma_6^-]^2$	+		+
	$[\Gamma_5^+]^2$	+		+
	$[\Gamma_2^- \times \Gamma_6^-]$		+	
	$[\Gamma_3^+ \times \Gamma_5^+]$		+	
M	$[M_1^+]^2$	+		+
	$[M_2^-]^2$	+		+
	$[M_4^+]^2$	+		+
	$[M_3^-]^2$	+		+
	$[M_3^+]^2$	+		+
	$[M_4^-]^2$	+		+
	$[M_1^+ \times M_4^+]$			+
	$[M_1^+ \times M_3^+]$		+	
	$[M_3^+ \times M_4^+]$		+	
	$[M_2^- \times M_3^-]$		+	
	$[M_2^- \times M_4^-]$		+	
	$[M_3^- \times M_4^-]$			+
H	$[H_3]^2$	+		+
K	$[K_1]^2$	+		
	$[K_3]^2$	+		

The reason for the increase in the intensity of high-frequency region of the spectrum when account is taken of the factor just mentioned will be discussed below. The character of the energy dependence and of the frequency of the basic features are similar in all spectra; however, the two phonon spectra of Raman light scattering show a finer structure and a different ratio of the intensities of these features. A similar structure appears also in the anisotropic microcontact spectra of single crystals of Re, but all the anomalies in these spectra have higher frequencies, by ~ 10 cm^{-1} ($\omega/2$) on the average. This can be connected with the fact that the micrcontact spectra were measured at helium temperature, although the rather small increase in the frequency of the peaks in the spectra of the Raman light scattering upon decrease in the temperature to 120 K (~ 2–3 cm^{-1} at $\omega/2$) should be noted.

It follows unambiguously from the first-order spectrum and the neutron data on the dispersion (see Fig. 4 below) that the peaks at 242 cm^{-1} in the YY spectrum, and at 245 cm^{-1} in the ZZ spectrum, are overtones of the TO (E_{2g}) and LO (B_{1g}) oscillations in the center of the Brillouin zone. Although complete data for rhenium are lacking, the just noted similarity of the anomalies in the phonon spectra allow us, in the case of further identification, to make use of the well-studied dispersion curves of technetium.[13] Thus, for T_c, only two lower levels are located at the point M below the level Γ_5^+ (E_{2g}). Therefore, the anomaly at 205 cm^{-1} in the ZZ spectrum and the broad shoulder in this same region of the YY spectrum can be attributed to overtones of the acoustic oscillations at this critical point. The high-frequency peak at 386 cm^{-1}, which appears only in the YY component of the A_{1g} spectrum, can be identified as the sum of overtones of the upper levels in M and K, due essentially to oscillations with displacement of the atoms in the basal plane. One should note the anisotropy of the two-phonon spectrum at this frequency ($\alpha_{yy} \gg \alpha_{zz}$), which is not the consequence of the group theoretical limitations.

A special circumstance exists with regard to the peak of the intensity of the two-phonon scattering in the region of 317 cm^{-1}, which is not revealed in practice in the $F(\omega/2)$

spectrum by neutron data, and in the microcontact spectrum the similar singularity arises only at a particular orientation of the microcontact axis (along [1$\bar{1}$20]). It is essential that this peak is located in the energy region of the anomalous phonons of the *LO*-branch (120–180 cm^{-1}). Thus, there is reason for assuming that this singularity is due to strong EPI which leads to selective amplification of the Raman light scattering on oscillations with displacements of the atoms along the crystal axis. The specific position of the singularity produced in the Raman light scattering spectrum is probably determined by the effect of factors associated with the density of anomalous phonons and their "amplification coefficient."

The mechanism of amplification of the anomalous phonons is connected with the dominant contribution to the scattering cross section of three-band processes with participation of small gaps in the region of the Fermi level.[9] There are such gaps of spin-orbital origin in the electron spectrum of rhenium in the AHL plane and its vicinity.[14] A similar resonance in the region ≈ 2.5 eV occurs in the second-order *YY* spectrum. The resonance curve for the *ZZ* spectrum is shifted into the region of higher energies.

The anomalous temperature dependences, with correction by the factor $[n(\omega/2)+1]^2$ in the intensities of the second-order spectra, also testifies to the significant role of the three-band contribution (Fig. 3). As a whole, the temperature dependences of the *YY* and *ZZ* spectra (with the exception of the 245 cm^{-1} line in the *ZZ* spectrum) duplicate the temperature dependence of the damping and scattering cross section of the E_{2g} phonon under resonance conditions of excitation.[15] In the case of the three-band scattering of light, with participation of the small gap

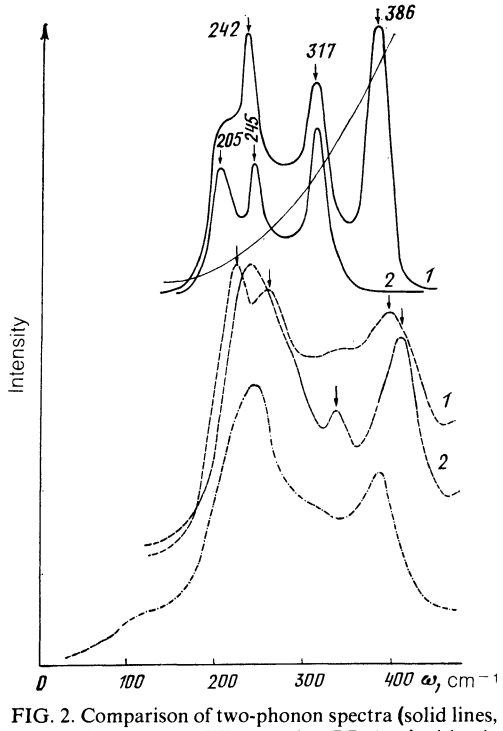

FIG. 2. Comparison of two-phonon spectra (solid lines, background subtracted: 1—geometry $YY(A_{1g})$, 2—$ZZ(A_{1g})$) with microcontact spectra $\alpha_{P_c}{}^2 F(\omega/2)$ (dashed lines: 1—orientation of contact [0001], 2—[1$\bar{1}$20] (Ref. 12)) in the density of phonon states $F(\omega/2)$ (Ref. 11) (dot-dash curve). The thin continuous line represents the factor $\omega^2/[n(\omega/2)+1]^2$, which must be multiplied by the experimental intensity for comparison with the density of states.

formed by the levels *a* and *b*, the temperature dependence of the intensity will be determined by the difference in the Fermi distributions

$$f(E_a)-f(E_b)=\mathrm{sh}\,(E/kT)/[\mathrm{ch}\,(\Delta/kT)+\mathrm{ch}\,(E/kT)],$$

where $E=E_a-E_b$ is the size of the gap and $\Delta=(1/2)(E_a-E_b)$ is the location of the center of gravity of the gap relative to the Fermi level. At $|\Delta|<E/2$ (levels *a* and *b* are located on opposite sides of the Fermi level) the difference $f(E_a)-f(E_b)$ decreases monotonically with increase in the temperature, in particular, according the law $E/4kT$ at $kT\gg E$, which is also observed for the data shown in Fig. 3.

Another type of dependence is also possible, in which the levels *a* and *b* are on the same side of the Fermi level. In this case, a maximum will be observed in the temperature dependence. Qualitatively, such a behavior is characteristic for the singularity at 245 cm^{-1} in the *ZZ* spectrum, the intensity of which can decrease upon cooling below room temperature, almost vanishing at 120 K (Fig. 4). Such an exceptional behavior can indicate a connection between this line and the anomalous Γ_3^+ (B_{1g})-phonon. As is known, similar anomalies and further softening upon decrease in temperature are observed for these oscillations in a number of hcp metals and are well described within the framework of the charge-fluctuation model.[13] It is not excluded that perturbation of the electron structure near the Fermi surface by these oscillations is reflected in the observed temperature dependence. Moreover, the decrease in the intensity upon cooling can be connected with a decrease in the density of states in the region of the Γ_3^+ overtones, if a significant softening of these phonons takes place.

The difference in the temperature behavior of the intensities of the lines 242 cm^{-1} in the *YY* spectrum and 245 cm^{-1} in the *ZZ* spectrum, and also the strong anisotropy of the line 386 cm^{-1}, due to the overtones of oscillations with displacements of the atoms in the basal plane, leads to an intuitive conclusion on the preferential appearance of oscillations with polarization vectors along the crystal axis in the *ZZ* spectrum and polarized in the basic place in the *YY* spectrum. In this connection, we note that in the given case the resonance terms describing the three-band contribution are determined by the change in the matrix elements of the momentum for the optical transition in the band near the Fermi level. Consequently, the modulation, for example, of the

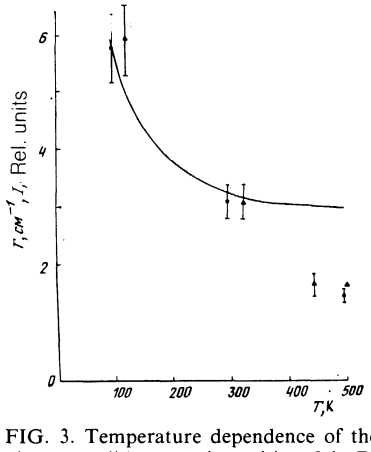

FIG. 3. Temperature dependence of the width of the E_{2g} line of the phonon (solid curve), intensities of the Raman light scattering spectra of first (●)[15] and second (▲) orders in a single crystal of rhenium.

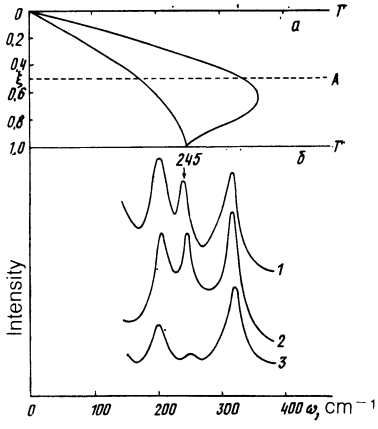

FIG. 4. a—Dispersion of phonons in rhenium along the [000 ξ] direction,[2] b—two-phonon spectra of Raman light scattering for the ZZ component of scattering of symmetry A_{1g} at different temperatures: 1—450 K, 2—330 K, 3—120 K.

$\langle 0|P_y|a\rangle$-component of the matix element, should be determined by the change in the component v^Y of the velocity of the electron in the transition between bands a and b in the region of the Fermi level. On the other hand, this change is specified by the matrix element of the EPI, which, in the approximation of Ref. 16, is proportional to $(v_a^Y - v_b^Y)$. Thus, in an anisotropic crystal, the polarization changes can give additional information on the eigenvectors of the investigated phonons if the scattering process takes place with sequential excitation of two phonons and includes the square of the matrix element of the EPI. However, it is not clear whether the observed connectin is possible in the case of simultaneous excitation of two phonons and inclusion of the matrix element of electron–two-phonon interaction.

Returning to the distortion of the frequency distribution of the density of phonon states when account is taken of the factor $[n(\omega/2)+1]^2/\omega^2$, we point out that in comparison with $F(\omega/2)$ (Ref. 11) the ratio of the intensities of the low-frequency and high-frequency peaks decreases here by almost an order of magnitude (Fig. 2). This effect can also be explained with in the framework of the three-band mechansim of scattering with simultaneous excitation of two phonons. The process in this case is similar to first-order scattering, and is determined by the term $[f(E_a)-f(E_b)]/(E_a - E_b + 2\omega_{ph})$.[9] Consequently, the increase in the intensity with increase of the energy of the two-phonon excitation indicates that the basic gap in the region of the Fermi level, (the width of the peak in the Raman density of interband transitions) exceeds 0.05 eV.

The proposed interpretation is confirmed by still another factor: in the Stokes region, we observe a broad peak of scattered light of mixed symmetry, with a maximum in the region of 1500-2000 cm^{-1} (the inset in Fig. 1), which changes weakly upon decrease in the temperature. Its shape varies somewhat for different components of the scattering tensor, and also with change of excitation energy. This scattering can again be connected with transitions between bands split by the spin-orbit interaction, in the region of the Fermi level.

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