Investigation of plasma excitations in technetium by inelastic scattering of electrons

V. D. Gorobchenko, M. V. Zharnikov, E. G. Maksimov, and K. A. Moldosanov

I. V. Kurchatov Atomic Energy Institute

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We report the results of measuring, by shooting through thin films, the characteristic-loss spectrum of fast 25-keV electrons in the transition metal technetium. The experimental spectra obtained at zero momentum transfer are analyzed in detail. A characteristic feature of these spectra is that they contain several resonance peaks, the strongest being at 11 and 27 eV. A phenomenological theory is presented for longitudinal electron-density oscillations, offers at least a qualitative explanation of the observed spectra, and justifies the presence in them of several resonance lines.

1. INTRODUCTION

Study of the fast-electron (energies from 10 to 250 keV) characteristic-loss spectra in solids by the shooting through thin film has diligently continued in the last few years. In such experiments, the inelastically scattered electrons that carry information on the excitation spectrum of the investigated element are analyzed for the energy h lost by them in scattering through an angle θ that serves a measure of the momentum transfer $\hbar\mathbf{q}$. This procedure helped gather extensive experimental information on the characteristic electron-energy losses in metals, semiconductors, and dielectrics (see the reviews by Schnatterly[1] and Raether[2]).

The doubly differential cross section for this scattering takes in the first Born approximation the form

$$\frac{d^2\sigma}{d\varepsilon_{\mathbf{k}_1}\, d\Omega_{\mathbf{k}_1}} = \frac{k_1}{k_0}\left(\frac{e^2}{\varepsilon_{\mathbf{q}}}\right)^2 S(\mathbf{q}, \omega). \qquad (1)$$

Here $\hbar\mathbf{k}_0$ and $\hbar\mathbf{k}_1$ are the momenta of the electrons before and after scattering, respectively; $\varepsilon_{\mathbf{q}} = \hbar^2 q^2/2m$; $\varepsilon\mathbf{k}_1$ is the electron energy after scattering; $d\Omega_{\mathbf{k}_1}$ is the solid-angle element in which the scattered particles are recorded; $\hbar\mathbf{q} = \hbar(\mathbf{k}_0 - \mathbf{k}_1)$ and $\hbar\omega = \varepsilon_{\mathbf{k}_0} - \varepsilon_{\mathbf{k}_1}$ are the energy and momentum transferred to the system in the scattering act; finally, $S(\mathbf{q},\omega)$ is a function called the dynamic structure factor. This function is expressed in terms of the macroscopic dielectric constant $\varepsilon_M(\mathbf{q},\omega)$ of the system as follows:

$$S(\mathbf{q}, \omega) = -[\pi v(\mathbf{q})(1 - e^{-\hbar\omega/kT})]^{-1}\, \mathrm{Im}(\varepsilon_M(\mathbf{q}, \omega))^{-1}, \qquad (2)$$

where $v(\mathbf{q}) = 4\pi e^2/q^2\Omega, \Omega$ is the volume of the system.

The interpretation of electron inelastic-scattering spectra in crystals is based on theoretical premises concerning the properties of the dielectric constant (DC) of the system of interacting particles. The most understandable situation occurs in this case for simple metals, whose electron subsystems have properties similar to those of a homogeneous electron gas of corresponding density. The dominant feature of the characteristic-loss spectrum in an ordinary metal is the strong plasma resonance corresponding to excitation of collective oscillations of the conduction-electron density. The position of this resonance peak is close enough to the frequency at which the dielectric constant $\varepsilon(\mathbf{q},\omega)$ of a homogeneous electron gas vanishes. The theoretical study of the dielectric constant of a homogeneous electron gas has a long history and by now this branch of theoretical physics has been fully explored in general outline (see the review of Gorobchenko and Maksimov[3]). The presence of the crystal lattice exerts a definite influence the location and shape of the plasma resonance, and this influence is quite satisfactorily described for ordinary metals by perturbation theory in the electron-ion pseudopotential, as developed by Sturm (see his review[4]).

The interpretation of the characteristic electron-energy loss spectra in transition metals that contain electrons with appreciable degree of localization near the ion-lattice sites is greatly hindered by the complexity of these spectra, which contain as a rule a large number of frequently overlapping resonance peaks.[5] The nature of the corresponding resonance excitations is not completely clear to this day (see Refs. 1 and 2 for details). Therefore, to interpret fully and correctly all the information these spectra contain, much theoretical and especially experimental work must be done to be able to systematize their features.

We report here the results of an experimental investigation of the characteristic-loss spectra in a transition metal, technetium, on which experiments of this kind have not been performed so far. We present also a phenomenological theory of the longitudinal oscillations of the electron density in transition metals; this theory explains at least qualitatively the observed characteristic-loss spectra in such systems.

2. MEASUREMENT PROCEDURE AND EXPERIMENTAL RESULTS

The measurements were performed with an electron spectrometer intended for an investigation of plasmon dispersion in thin metallic films. In this spectrometer, an electron beam from a gun is made monochromatic in energy by a hemispherical capacitor, is collimated by a pre-acceleration lens, passes through an accelerating capacitor in which the electron energy can be raised to 30 keV, and is incident on the sample. Electron discrimination by momentum transfer is with a pair of deflectors symmetric about the sample and imparting to the electrons a total transverse momentum $-\hbar\mathbf{q}$. Thus, after scattering, only electrons that lost a momentum $\hbar\mathbf{q}$ by scattering land on the axis of the electron-

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optical system. The selected electrons pass through a decelerating capacitor and are focused by a scanning lens on the entrance focal plane of a hemispherical analyzer. At the exit from the analyzer they are recorded by an electronic system based on a channel electron multiplier and a multichannel analyzer. The spectrometer permits operation in the energy-loss interval from 0 to 200 eV at a fixed value of the momentum transfer, which is varied from 0 to 3 Å^{-1}. More detailed information on the construction and characteristics of the spectrometer are published separately.

The technetium sample was a film ~500 Å thick, sprayed in high vacuum on a polished rock-salt substrate by an ion-sputtering method developed by Golyanov and Demidov.[6] The technetium film obtained in this manner was removed from the substrate by "floating in water" and fishing out by the fine-mesh screen of the sample holder.

Figure 1 shows typical spectra of the characteristic losses of a beam of primary electrons of 25 keV energy passing through a technetium sample. The spectra were plotted in energy-transfer ranges up to 40 and 80 eV at zero momentum transfer. The long arrows mark the positions of the peaks that correspond to elastically scattered electrons, and mark the zero of the energy scale. These peaks are well approximated by a Gaussian distribution of width 0.5 eV at half-maximum. As seen from the figure, at energy transfers up to 40 eV the most noticeable details of the spectra occur at 11 and 27 eV. We note in this connection that in Ref. 7, where the x-ray, electron, and conversion spectra of ^{99}Tc in a metallic-technetium matrix are shown, weak satellites were observed, at distances 11 ± 2 and 27 ± 2 eV from the peaks of the conversion and x-ray-electron transitions. These weak peaks were attributed in Ref. 7 to losses to plasmon excitation. This conclusion is confirmed also by our results.

Besides the peaks indicated, the figure shows also a number of other lines. To determine their parameters the experimental spectra were approximated by least squares as combinations of Lorentz peaks with a "background" given by a polynomial of second degree in energy. A fully satisfactory fit could be obtained by approximating the spectra by five lines with the parameters listed in Table I. The first row of this table indicates the position of the E peak, the second gives its width $\Delta E_{1/2}$ at half maximum, and the third the intensity I referred to the intensity I_{27} of the peak at 27 eV.

The number of resonances in the spectrum is undoubtedly not restricted to these five lines. A computer analysis of the spectrum has shown, however, that introduction into the fitting spectrum of additional peaks besides the ones listed in Table I (even including the singularity observed in the spectrum in the region of 7 eV) does not decrease χ^2 noticeably. This allows us to regard the resonances listed in Table I as the most intense spectral lines, whose superposition is a sufficiently good approximation of the experimental spectrum.

The positions of the fourth and fifth peaks are close enough to double the values for the first and third peaks, respectively. Furthermore, a number of supplementary experiments have shown that the intensities of the fourth and fifth peaks increase with decreasing energy of the primary electron beam. This suggests that the indicated peaks are due to repeated creation of plasma excitations and are of no particular interest. As for the fourth peak, it is not excluded that

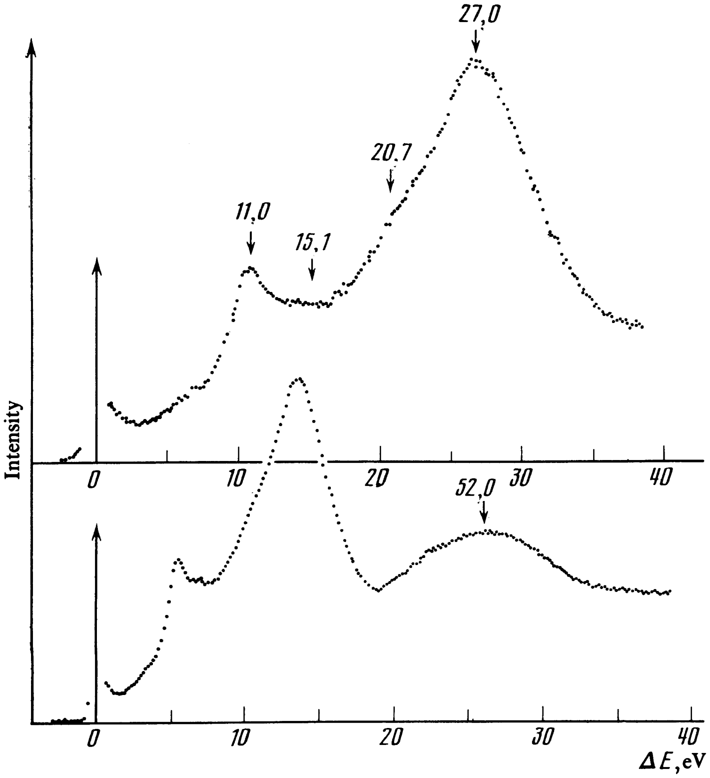

FIG. 1. Characteristic-loss spectra of a beam of primary 25-keV electrons passing through a technetium sample. The spectra were obtained in energy-transfer ranges up to 40 and 80 eV at zero momentum transfer. The long arrows mark the positions of the peaks that correspond to elastically scattered electrons. The small arrows mark the resonance peaks observed in the spectra.

TABLE I.

	1	2	3	4	5
E, eV	11,0±0.1	15.1±0.15	27.0±0.1	20.7±0.2	52.0±0.5
$\Delta E_{1/2}$, eV	2,2±0.2	2.8±0.2	5.0±0.2	3.2±0.2	10,4±0.2
I/I_{27}	0.35±0,02	0.11±0.01	1	0.18±0.02	0,40±0,02

it may also be connected with excitation of a surface plasmon, or at least contains a contribution from this process. A qualitative analysis of the remaining three peaks is given in the next section.

We note in addition that the picture we obtained for the characteristic losses in technetium depends little on the momentum transfer q. This, too, is a characteristic feature observed also by others[5,8] in transition metals.

3. QUALITATIVE ANALYSIS OF THE RESULTS

Technetium, which has in its atomic state an electron configuration $4d\,^5 5s^2$, crystallizes into an hcp lattice with parameters $a = 2.7407$ Å and $c = 4.3980$ Å.[9] If it is assumed that each technetium atom gives up to the conduction band all seven of its outer electrons, and calculate for this case the frequency of the collective plasma oscillations of all the conduction electrons using the classical formula atom gives up to the conduction band all seven of its outer electrons, and calculate for this case the frequency of the collective plasma oscillations of all the conduction electrons using the classical formula

$$\omega_p = (4\pi n e^2/m)^{1/2}, \tag{3}$$

where n is the electron density and m is their mass, we obtain the value $\hbar\omega_p = 25.98$ eV, which agrees quite well with the energy of the third peak of Table I.

A similar situation is observed also for a large number of other transition metals: the energy of one of the peaks in their characteristic-loss spectra correlates quite well with the plasmon energy calculated from Eq. (3), as if we were dealing with a homogeneous electron gas of corresponding density. This circumstance is reflected in Table II.

Here E_1 and E_2 are the positions of the most intense spectral lines, taken from Ref. 5. Owing to the sufficiently good agreement between E_2 and $\hbar\omega_p$, the interpretation of the nature of just this peak never raised any difficulties, and in all investigations of the characteristic-loss spectrum of a transition metal its presence was attributed to excitation of plasma oscillations of the conduction electrons. As for the identification of the other spectral lines—two or more in the case of technetium or one in the metals listed in Table II, or even a larger number of peaks (up to five) in noble metals, difficulties are encountered here.

To understand the appearance of these additional peaks, we consider the expression for the dielectric constant of a crystal in the self-consistent-field approximation[10]:

$$\varepsilon(\mathbf{q}, \omega) = 1 - 2v(\mathbf{q}) \sum_{\alpha\alpha'\mathbf{k}} \frac{f_{\alpha\mathbf{k}} - f_{\alpha'\mathbf{k}+\mathbf{q}}}{\hbar\omega - E_{\alpha'\mathbf{k}+\mathbf{q}} + E_{\alpha\mathbf{k}} + i\delta} \times |\langle \alpha'\mathbf{k}+\mathbf{q} | e^{i\mathbf{q}\mathbf{r}} | \alpha\mathbf{k} \rangle|^2. \tag{4}$$

Here $|\alpha_{\mathbf{k}}\rangle$ is a Bloch state having a band index α and a quasiwave vector $\mathbf{k}$, to which an energy $E_{\alpha k}$ corresponds, while $f_{\alpha k}$ is the Fermi filling function of the single-electron states. We confine ourselves for simplicity to the case of zero momentum transfer. Separating in (4) the contribution from the virtual intraband transitions with $\alpha = \alpha'$ and recognizing that as $q \to 0$ and at $\alpha \neq \alpha'$ we have

$$\langle \alpha\mathbf{k} | e^{-i\mathbf{q}\mathbf{r}} | \alpha'\mathbf{k}+\mathbf{q} \rangle \approx \frac{\hbar}{m} \frac{\langle \alpha\mathbf{k} | \mathbf{q}\hat{\mathbf{p}} | \alpha'\mathbf{k} \rangle}{E_{\alpha'\mathbf{k}} - E_{\alpha\mathbf{k}}},$$

where $\hat{\mathbf{p}} = \hbar\nabla/i$ is the momentum operator, we obtain for $\varepsilon(0,\omega)$ in the case of a polycrystalline sample

$$\varepsilon(0, \omega) = 1 - \frac{\tilde{\omega}_p^2}{\omega^2} - \frac{8\pi\hbar^2 e^2}{3m^2\Omega} \sum_{\alpha\neq\alpha',\mathbf{k}} \frac{f_{\alpha\mathbf{k}} - f_{\alpha'\mathbf{k}}}{(E_{\alpha\mathbf{k}} - E_{\alpha'\mathbf{k}})^2} \frac{|\langle \alpha'\mathbf{k} | \hat{\mathbf{p}} | \alpha\mathbf{k} \rangle|^2}{\hbar\omega - E_{\alpha'\mathbf{k}} + E_{\alpha\mathbf{k}} + i\delta}. \tag{5}$$

In this expression

$$\tilde{\omega}_p^2 = \frac{8\pi e^2}{3\Omega} \sum_{\alpha\mathbf{k}} \mathbf{v}_{\alpha\mathbf{k}}^2 \delta(E_{\alpha\mathbf{k}} - E_F), \tag{6}$$

E_F is the Fermi energy, and

$$\mathbf{v}_{\alpha\mathbf{k}} = \langle \alpha\mathbf{k} | \frac{\hat{\mathbf{p}}}{m} | \alpha\mathbf{k} \rangle = \frac{1}{\hbar} \frac{\partial E_{\alpha\mathbf{k}}}{\partial \mathbf{k}} \tag{7}$$

is the average velocity of an electron in a Bloch state $|\alpha\mathbf{k}\rangle$. The third term in the right-hand side of (5) is the contribution made to $\varepsilon(0,\omega)$ by the interband transitions.

Were we to deal with a system of free electrons with one parabolic band, the integral over the Fermi surface in (7)

TABLE II.

Metal	E_1, eV	E_2, eV	$\hbar\omega_p$, eV	Metal	E_1, eV	E_2, eV	$\hbar\omega_p$, eV
Y	4.0	12.4	11.21	Hf	7,7	15.9	15,71
Zr	8.0	15,6	15.40	Ta	9,4	19.6	19,55
Nb	9.5	19,6	19.60	W	10,3	23,6	22,86
Mo	9.9	22.8	23,06	Re	10.3	26	25.63

could be calculated in explicit form and $\tilde{\omega}_p^2$ would turn out to equal ω_p^2, i.e., to the square of the classical plasma frequency of the electrons (3). For real metals it is customary to express the quantity (6) in the following two equivalent forms:

$$\tilde{\omega}_p^2=\frac{4\pi ne^2}{m_{opt}}=\frac{4\pi n_{eff}e^2}{m}, \tag{8}$$

where $m_{\rm opt}$ is called the optical mass of the electrons on the Fermi surface and $n_{\rm eff}$ is the effective number of the conduction electrons. In metals, $m_{\rm opt}$ and $n_{\rm eff}$ differ substantially from the free-electron mass and from the total conduction-electron density, respectively. The greatest difference is observed precisely in the case of transition metals where, e.g., $m_{\rm opt}$ can reach values $\sim(10\text{–}20)m$.

For the dielectric constant (4) we can easily prove the following f-sum rule:

$$\int_0^\infty d\omega\omega\,\mathrm{Im}\,\varepsilon(\mathbf{q},\omega)=\frac{\pi}{2}\omega_p^2, \tag{9}$$

which can be rewritten in the $q\to 0$ limit in the equivalent form

$$\tilde{\omega}_p^2+\frac{8\pi e^2}{3m^2\Omega}\sum_{\alpha\neq\alpha',\mathbf{k}}\frac{f_{\alpha\mathbf{k}}-f_{\alpha'\mathbf{k}}}{E_{\alpha'\mathbf{k}}-E_{\alpha\mathbf{k}}}|\langle\alpha'\mathbf{k}|\hat{\mathbf{p}}|\alpha\mathbf{k}\rangle|^2=\omega_p^2. \tag{10}$$

This sum rule means, in particular, that at frequencies ω higher than all the characteristic energies E_g of the interband transitions the asymptotic form of $\varepsilon(0,\omega)$ is, exactly as for a homogeneous electron gas, of the form

$$\varepsilon(0,\omega)\underset{\hbar\omega>E_g}{\approx}1-\omega_p^2/\omega^2+i\delta. \tag{11}$$

Generally speaking, in solids the selection rules can allow interband transitions with arbitrarily large values of the energy. Theoretical calculations and experimental data[11] indicate, however, that the oscillator strengths of such transitions decrease with increasing transition energy. This circumstance is qualitatively seen from Eq. (5). In particular, in ordinary metals the most significant interband transitions have energies E_g not larger than several eV. In transition metals, however, the corresponding values of E_g are considerably higher. It is important here, however, that both in ordinary and in many transition metals the quantity $\hbar\omega_p$, which corresponds to the energy of the collective oscillations of the density of all the valence electrons, turns out to be larger than the energies of all the interband transitions that have appreciable oscillator strengths. In this situation the correct estimate for the dielectric constant is (11), and this explains in final analysis the existence, in the characteristic-loss spectra of both ordinary and transition metals, of a resonance peak with energy close to that of the classical plasma oscillations of all the valence electrons.

As for the remaining peaks, it must be noted first that for many transition metals the energy of one of them is quite close to the value $\hbar\tilde{\omega}_p$ given by Eq. (6). Thus, for niobium this value is 7.2 eV (Ref. 11) while the peak energy, as seen from Table II, is equal to 9.5 eV. This circumstance can be qualitatively explained by assuming that at frequencies close to $\tilde{\omega}_p$ the contribution from the virtual interband transitions in (5) can be neglected. We then have

$$\varepsilon(0,\omega)\approx 1-\tilde{\omega}_p^2/\omega^2+i\delta,$$

which means that plasma oscillations with frequency $\omega=\tilde{\omega}_p$ are present in the system. It is also easy to understand the difference between the energy of the corresponding peak and the value of $\hbar\tilde{\omega}_p$. To this end we must consider the following circumstance.

A distinction is usually made in transition metals between two groups with substantially different interband-transition energies. The first is concentrated near the Fermi surface and is characterized by transition energies from several tenths to several electron volts, i.e., by energies as a rule considerably lower than $\hbar\tilde{\omega}_p$. The second group corresponds to much higher transition energies, in the interval $\hbar\tilde{\omega}_p<E_g<\hbar\tilde{\omega}_p$. In accord with the selection rules for the matrix elements of the operator $\hat{\mathbf{p}}$ in d-metals, the transitions of the second group stem from atomic d–f transitions, couple the d and f bands, and have at the same time large oscillator strengths. One can introduce the concept of the effective density $n_{\rm eff}(\omega)$ of the electrons responsible for the transition in the frequency range from 0 to ω by using the rule of partial f-sums[12]:

$$n_{eff}(\omega)=\frac{m}{2\pi^2e^2}\int_0^\infty d\omega'\omega'\,\mathrm{Im}\,\varepsilon(0,\omega'). \tag{12}$$

The experimental data[11,13] show that at $\omega\sim\tilde{\omega}_p$ the value of (12) in transition metals is less than or close to one electron per atom, meaning that the bulk of the effective electron density is concentrated in the d–f transition region.

Taking this circumstance into account we can represent expression (5) for $\varepsilon(0,\omega)$ at frequencies on the order of $\tilde{\omega}_p$ in the form

$$\varepsilon(0,\omega)\approx\varepsilon_0-\tilde{\tilde{\omega}}_p^2/\omega^2+i\delta, \tag{13}$$

where

$$\tilde{\tilde{\omega}}_p^2=\tilde{\omega}_p^2+\frac{8\pi e^2}{3m^2\Omega}\sum_{\substack{\alpha\neq\alpha',\mathbf{k}\\ E_g<\hbar\omega}}\frac{f_{\alpha\mathbf{k}}-f_{\alpha'\mathbf{k}}}{E_{\alpha'\mathbf{k}}-E_{\alpha\mathbf{k}}}|\langle\alpha'\mathbf{k}|\hat{\mathbf{p}}|\alpha\mathbf{k}\rangle|^2, \tag{14}$$

$$\varepsilon_0=1+\frac{8\pi e^2}{3m^2\Omega}\sum_{\substack{\alpha\neq\alpha',\mathbf{k}\\ E_g>\hbar\omega}}\frac{f_{\alpha\mathbf{k}}-f_{\alpha'\mathbf{k}}}{(E_{\alpha'\mathbf{k}}-E_{\alpha\mathbf{k}})^3}|\langle\alpha'\mathbf{k}|\hat{\mathbf{p}}|\alpha\mathbf{k}\rangle|^2. \tag{15}$$

We have subdivided here the virtual interband transitions into two groups having $(E_{\alpha'\mathbf{k}}-E_{\alpha\mathbf{k}})$ respectively smaller and larger than $\hbar\omega$. For the former we have neglected the quantity $E_{\alpha'\mathbf{k}}-E_{\alpha\mathbf{k}}$, and for the latter the quantity $\hbar\omega$. It can be seen from (13) that a resonance peak is expected to appear at the frequency $\tilde{\tilde{\omega}}_p/\varepsilon_0^{1/2}$.

Thus, at least two types of plasma oscillations occur in transition metals by virtue of their distinctive electronic structure and high intensity of the virtual interband d–f transitions. One has a frequency practically equal to that of classical plasma oscillations of all the conduction electrons. The other has a lower frequency and is involved effectively only in electronic states near the Fermi surface.

To explain the presence of three (or more) peaks in the energy-loss spectrum, as in the case of technetium, we need a more accurate analysis of the role of virtual interband transitions than the one presented above. A microscopic analysis of the quantity $\varepsilon(0,\omega)$ using the real band structure and the wave functions of the Bloch electrons is a rather difficult computational problem, and was carried out only for a few transition metals (see, e.g., Ref. 14). No such calculations were performed so far for technetium. We shall therefore use for $\varepsilon(0,\omega)$ in the analysis of the experimental data a simple model in which the two most intense interband transitions are taken into account besides the intraband ones:

$$\varepsilon(0,\omega)=1-\frac{\tilde{\omega}_p^2}{\omega^2}-\frac{\omega_1^2}{\omega^2-\Delta_1^2}-\frac{\omega_2^2}{\omega^2-\Delta_2^2}+i\delta. \tag{16}$$

The quantities ω_i and Δ_i in (16) should be regarded as phenomenological parameters. Within the framework of this model we have in accord with (1) and (2)

$$\sigma(\omega)=I\delta\left(1-\frac{\tilde{\omega}_p^2}{\omega^2}-\frac{\omega_1^2}{\omega^2-\Delta_1^2}-\frac{\omega_2^2}{\omega^2-\Delta_2^2}\right), \tag{17}$$

where I is the proportionality factor. The argument of the δ function in (17), as can be easily seen graphically, vanishes at three values of the frequency which we denote by Ω_1, Ω_2, and Ω_3. If we assume for the sake of argument that $\Delta_1<\Delta_2$, the values of Δ_i satisfy the condition

$$\Omega_1<\Delta_1<\Omega_2<\Delta_2<\Omega_3.$$

Expression (17) can then be transformed into

$$\sigma(\omega)=\sum_{i=1,2,3} I_i\delta(\omega-\Omega_i), \tag{18}$$

where the intensities I_i of the peaks are given by

$$\begin{aligned} I_1&=\frac{\Omega_1(\Delta_1^2-\Omega_1^2)(\Delta_2^2-\Omega_1^2)}{2(\Omega_2^2-\Omega_1^2)(\Omega_3^2-\Omega_1^2)}I,\\ I_2&=\frac{\Omega_2(\Omega_2^2-\Delta_1^2)(\Delta_2^2-\Omega_2^2)}{2(\Omega_2^2-\Omega_1^2)(\Omega_3^2-\Omega_2^2)}I,\\ I_3&=\frac{\Omega_3(\Omega_3^2-\Delta_1^2)(\Omega_3^2-\Delta_2^2)}{2(\Omega_3^2-\Omega_1^2)(\Omega_3^2-\Omega_2^2)}I. \end{aligned} \tag{19}$$

In accord with (18), the scattering cross section is a superposition of resonant peaks at energies Ω_i which must be determined from experiment. It is natural to set the intensities I_i in correspondence with the areas under the experimentally observed peaks. Equations (19) enable us then to determine the parameters Δ_1 and Δ_2, which correspond to the average energies of the most intense interband transitions. This is done with the aid of the formulas

$$\begin{aligned} &\Delta_1^2\Delta_2^2=c[I_1(\Omega_2\Omega_3)^3+I_2(\Omega_3\Omega_1)^3+I_3(\Omega_1\Omega_2)^3],\\ &\Delta_1^2+\Delta_2^2\\ &=c[I_1\Omega_2\Omega_3(\Omega_2^2+\Omega_3^2)+I_2\Omega_3\Omega_1(\Omega_3^2+\Omega_1^2)+I_3\Omega_1\Omega_2(\Omega_1^2+\Omega_2^2)], \end{aligned} \tag{20}$$

where

$$c=(I_1\Omega_2\Omega_3+I_2\Omega_3\Omega_1+I_3\Omega_1\Omega_2)^{-1}.$$

As for the parameters $\tilde{\omega}_p$, ω_1, and ω_2, they are determined from the equations

$$\begin{aligned} &\tilde{\omega}_p\Delta_1\Delta_2=\Omega_1\Omega_2\Omega_3,\\ &\tilde{\omega}_p^2+\omega_1^2+\omega_2^2+\Delta_1^2+\Delta_2^2=\Omega_1^2+\Omega_2^2+\Omega_3^2,\\ &\tilde{\omega}_p^2(\Delta_1^2+\Delta_2^2)+\omega_1^2\Delta_2^2+\omega_2^2\Delta_1^2+\Delta_1^2\Delta_2^2\\ &\quad=\Omega_1^2\Omega_2^2+\Omega_2^2\Omega_3^2+\Omega_3^2\Omega_1^2. \end{aligned} \tag{21}$$

Using the data of Table I and Eqs. (20) and (21) we arrive at the following values of the parameters of our model:

$$\begin{aligned} &\tilde{\omega}_p=17{,}3\pm0{,}2\ \text{eV},\\ &\omega_1=6{,}7\pm0{,}2\ \text{eV},\\ &\omega_2=13.9\pm0.2\ \text{eV},\\ &\Delta_1=14.0\pm0{,}2\ \text{eV},\\ &\Delta_2=18{,}6\pm0.2\ \text{eV}. \end{aligned} \tag{22}$$

We note that the difference $\Delta_2-\Delta_1=4.6\pm0.4$ correlates well with the distance between the outer peaks in the density of the electronic states for the technetium d-band under the Fermi surface. According to calculations[15,16] this distance is approximately 5 eV. We can therefore assume that the virtual interband transitions with average energies Δ_1 and Δ_2 correspond to transitions from these two sections of the d band into the empty f band.

Using (22), we can calculate $(\tilde{\omega}_p{}^2+\omega_1{}^2+\omega_2{}^2)^{1/2}$, which turns out to equal 23.2 eV. This is close enough to the plasma frequency $\hbar\omega_p=26$ eV for technetium and does not contradict the f-sum rule. In addition, using the value of the parameter ω_p from (22) we can estimate from (6) the average velocity of the conduction electrons on the Fermi surface in technetium. Assuming that the density of the electronic states on the Fermi surface is 1.24 eV^{-1} per atom,[17] we obtain the estimate $v_F\approx1.15\times10^8$ cm/sec, which turns out to be of the same order as for most other transition metals. This circumstance can confirm that we have used a reasonable model for the dielectric constant of technetium.

One might ask whether the resonance peaks observed in the spectrum for technetium can be called plasma peaks, i.e,. connected with collective oscillations of the electron density. To answer this question in some manner, we consider the classical picture of collective motion of interacting carriers in the case when there are two such carrier types (e.g., s and d electrons). Assume that for some reason all the s electrons were displaced a distance u_s, and the d electrons a distance u_d. This produces in the system an electric field

$$E=4\pi e(n_s u_s+n_d u_d),$$

that will tend to return the electrons to their initial positions. The result is their collective oscillatory motion described by the system of equations

$$\begin{aligned} &m_s\ddot{u}_s+4\pi n_s e^2u_s+4\pi n_d e^2u_d=0,\\ &m_d\ddot{u}_d+4\pi n_s e^2u_s+4\pi n_d e^2u_d+ku_d=0. \end{aligned} \tag{23}$$

Here n_s and n_d are the densities of the s and d electrons, while m_s and m_d are their effective masses. A similar qualitative treatment of the collective behavior of conduction electrons was used also by Ruvalds in his analysis of the problem of acoustic plasmons.[18] Our approach differs in that we have added to the equation of motion of the d-type electrons an elastic force ku_d, so as to simulate to some degree the fact that the d electrons preserve a definite degree of localization near the lattice atoms. For the system (23) we are interested in solutions in the form

$$u_s=X_se^{i\omega t},\qquad u_d=X_de^{i\omega t}, \tag{24}$$

which correspond to the collective oscillations of the carriers of both types at the same frequency ω. Substitution of (24) in (23) leads to the system of algebraic equations

$$\begin{aligned}&(\omega_s^2-\omega^2)X_s+\frac{m_d}{m_s}\omega_d^2X_d=0,\\&\frac{m_s}{m_d}\omega_s^2X_s+(\omega_d^2+\Delta^2-\omega^2)X_d=0,\end{aligned}\tag{25}$$

where we use the notation

$$\omega_s^2=\frac{4\pi n_se^2}{m_s},\qquad \omega_d^2=\frac{4\pi n_de^2}{m_d},\qquad \Delta^2=\frac{k}{m_d}.\tag{26}$$

Equating the determinant of the system (25) to zero, we arrive at an equation for the natural frequencies of the collective oscillations, which we represent in the form

$$1-\frac{\omega_s^2}{\omega^2}-\frac{\omega_d^2}{\omega^2-\Delta^2}=0.\tag{27}$$

It can be qualitatively seen from (2) that when the condition $\omega_s^2+\omega_d^2\gg\Delta^2$ is satisfied in the classical case the carrier system will resonate at a frequency $\sim(\omega_s^2+\omega_d^2)^{1/2}$ that corresponds by virtue of (25) and (26) to collective in-phase motion of all the electrons. In the case of technetium such a resonance might correspond to the peak observed at 27 eV. The second low-frequency solution of (27) is realized at a frequency close to $\omega_s/(1+\omega_d^2/\Delta^2)^{1/2}$ under the condition that this quantity is much less than Δ. Such a solution corresponds to collective oscillatory motion mainly of s electrons with a frequency ω_s renormalized on account of the d-electron oscillation that is in counterphase and has a much smaller amplitude.

Comparison with (16) and (17) shows that Eq. (27) can be regarded as a particular case of the model used above with the parameter values $\Delta_1=\Delta_2=\Delta$ and $\omega_d^2=\omega_1^2+\omega_2^2$. This suggests that the resonance peaks described by (17) correspond apparently to collective oscillations of the conduction-electron density. The peak observed at 27 eV is due most likely to plasma oscillations of all the technetium valence electrons, while the peak corresponding to 11 eV is connected with the plasma oscillations of the s electrons screened by the d-electron oscillations. The role of the parameter ε_0 [see (15)] that characterizes the degree of screening in the classical case is played here by the quantity $(1+\omega_d^2/\Delta^2)^{1/2}$. As for the peak with energy 15.1 eV, which exceeds somewhat the value 14.0 [see (22)] of the effective energy of the interband transition, its existence is quite readily understood within the framework of the simplified model (16). In fact, at energies somewhat higher than Δ_1 the interband contribution to the dielectric constant is negative, and owing to the divergence of this contribution at $\omega=\Delta_1$ there is always a solution of the equation $\varepsilon(0,\omega)=0$ near Δ_1.

The possibility of existence of specific longitudinal oscillations in electron systems near interband-transition energies was discussed already long ago, and even a special designation, collective band mode, was proposed for them.[19] In experiment excitations of this type are observed usually only in transition and noble metals. In ordinary metals the peaks connected with these modes manifest themselves only in experiments on single crystals[20] and their intensities are in this case quite small compared with that of the basic plasma resonance. The physical reason is that actually there occurs an electron-excitation damping not accounted for in the simplified model (16) and preventing $\mathrm{Re}\,\varepsilon(0,\omega)$ from ever becoming infinite at energies slightly higher than the energy of some interband transition. The contribution to $\mathrm{Re}\,\varepsilon(0,\omega)$ from the interband transitions that have weak oscillator strengths turns out to be negative, but small in absolute value, compared with unity. As a result $\varepsilon(0,\omega)$ can no longer vanish. A similar situation is typical of most interband transitions in ordinary metals also for low-energy transitions in d metals. Only collective band modes whose interband-transitions have a large enough oscillator strength can appear in experiment. It is this which explains why the experimental spectra have a finite number of peaks connected with excitations of this kind.

4. CONCLUSION

Of course, a more detailed description of the form of the characteristic-loss spectrum calls for a consistent quantum-mechanical calculation of the function $\varepsilon(\mathbf{q},\omega)$. Unfortunately, such calculations are extremely complicated for transition metals and have not yet been performed. Recent papers on the optical properties of transition metals (see, e.g., Refs. 11 and 14) contain microscopic calculations of the function $\varepsilon(0,\omega)$, based on Eq. (4) for the dielectric constant of an electron system. We note immediately that this equation itself is quite approximate, since it neglects completely the local-field effects due to the difference between the effective field acting on the electrons and the average macroscopic field (see, e.g., the review by Dolgov and Maksimov[21]). One of the methods of taking into account the corresponding effects in the calculation of the dielectric constant of a crystal was proposed by some of us.[22] Of importance here is only the following: the phenomenological dielectric-constant model proposed in the preceding section for the description of the characteristic-loss spectrum in technetium at $k=0$ is qualitatively in full agreement with the microscopic approach. Of course, the resonance energies Δ_i and the oscillator strengths, which are proportional to ω_i^2, are not at all determined solely by the properties of the single-particle spectrum, as might follow from Eq. (5) for $\varepsilon(0,\omega)$, but must be calculated with due allowance for the effects of the local field. It is also clear that an exact analysis, in contrast to the simple approximation (16), will lead to the appearance of a finite width of the corresponding resonances. All these circumstances, however, do not change at all the qualitative results of the present paper.

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