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High-energy electron-energy-loss spectroscopy of niobium and niobium-oxygen solid solutions

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Electronic excitations of Nb and Nb-O solid solutions are examined by electron-energy-loss spectroscopy using 250-keV electrons. Distinct differences are observed between Nb and Nb-O. It is found that oxygen in niobium changes the interband transitions and dampens the plasmon excitations.

INTRODUCTION

In recent years, niobium has become an important material of vast technological and theoretical interest. It has the highest transition temperature (T_c) of elemental superconductors and is part of all the useful superconducting alloys and compounds. Its superconducting properties have been related to its band structure, but few spectroscopic measurements have been carried out. Earlier studies using electron-energy-loss spectroscopy[1–4] (ELS) were confined to the reflection mode of operation which utilizes relatively low-energy electrons typically less than or equal to a few hundred eV. Electrons with these energies only penetrate ~ 20 Å into the sample. This raises not only the difficulties of distinguishing the bulk excitations from the surface excitations but also the complexity arising from the sample surface condition. Moreover, the use of low-energy electrons increases the probability of multiple scattering and further complicates the energy-loss spectra making interpretations even more difficult. In this paper we report the first studies of Nb by high-energy transmission electron-energy-loss spectroscopy. Electrons of 250 keV are used in order to minimize multiple scattering effects. Our results (for small momentum transfer) agree well with optical reflectivity measurements,[5] as expected. Our measurements also yield a more accurate value of the bulk plasmon energy than was observed in these optical experiments. We have extended our studies to Nb-O solid solutions in order to understand the influence of oxygen on the electronic structure of Nb. It is known that oxygen in solid solution in Nb, even in the ppm range, causes distinct changes in the superconducting properties ranging from flurxoid pinning[6] to the performance of high-frequency accelerator cavities.[7] It has also been found that oxygen in Nb markedly lowers the superconducting temperature T_c of Nb by ~ 0.93 K per at.% oxygen.[8,9] It has been suggested that the presence of oxygen decreases the electronic density of states at the Fermi level and the electron-phonon coupling constant.[9] (A similar argument has been used to explain the lower T_c of amorphous Nb and of many Nb compounds when disordered.)

Our electron-energy-loss spectra show dramatic changes as the oxygen concentration is increased. We observe that oxygen in Nb affects both interband transitions and collective plasmon excitations.

EXPERIMENTAL

Thin-film samples of Nb were deposited on heated rocksalt substrates in a diffusion pumped system with base pressure $\sim 10^{-7}$ Torr fitted with a magnetron sputtering head. The typical Nb film thickness was $\lesssim 1000$ Å. Self-supporting films were obtained by floating the film off the substrate in water and then mounting them onto specimen holders. Pure Nb films were prepared using research grade 99.9999% purity argon gas. Resistance and inductive measurements on these pure films yielded a T_c of 9.3 K. By admitting oxygen into the magnetron system to a desired partial pressure, Nb-O thin films were made by the same method. T_c depression was not observable until the partial pressure of O_2 during film deposition exceeded 5×10^{-6} Torr. Electron-energy-loss spectra were obtained in the transmission mode using an electron-scattering spectrometer with 250-keV electrons.[10] The energy and momentum transfer resolutions of the spectrometer are 0.3 eV and 0.15 $\mathrm{\AA}^{-1}$, respectively.

RESULTS AND DISCUSSIONS

Pure niobium

The inelastic electron scattering cross section for high-energy electrons is proportional to

$$\frac{1}{q_4} \left| \langle \psi_f | e^{i\vec{q}\cdot\vec{r}} | \psi_i \rangle \right|^2 ,$$

where q is the momentum transfer, and ψ_i and ψ_f are the initial- and final-state wave functions. At small q, the transition matrix element approaches the optical dipole matrix element and therefore the energy-loss spectrum should resemble the results obtained by optical methods. A detailed energy-loss spectrum for $q=0$ in the low-energy region ($\hbar\omega \lesssim 35$ eV) is shown in Fig. 1. For comparison, the energy-loss function, $\mathrm{Im}[-1/\epsilon(\omega)]$, obtained from optical reflectivity measurements[5] is also shown in Fig. 1. Good agreement is observed as expected. The strong resonance peak at 21.7 eV is due to the plasmon excitation involving all the valence electrons in Nb. It is noted that our observed plasmon is about 1 eV higher than that obtained optically. This is due to the uncertainty in the magnitude of the dielectric function $\epsilon(\omega)$ above 21 eV in the optical spectra.[5] Since the electron-energy-loss spectroscopy is a direct measurement of $\mathrm{Im}(-1/\epsilon)$, this technique in general can yield a more accurate plasmon peak position than any other spectroscopic technique. Plasmon peak positions obtained by reflection of low-energy electrons[1–4] are also consistently lower than our observed value. This can be understood if we take into account the surface-sensitive nature of the low-energy-electron measurement and the fact that the surface-plasmon excitation occurs at a slightly lower energy. The peak at 10.3 eV is also a plasmon since $\epsilon_1 \sim 0$ and $d\epsilon_1/d\omega > 0$ around this energy region.[5] However, due to the strong influences of the higher-energy interband transitions this plasmon can not be considered as a free plasmon, but is believed to involve mainly $4d$ electrons with strong screening effects from the $5s$ electrons. The presence of two (or more) plasmon peaks is a common feature for many transition metals due to some degree of localization of d electrons. The small bump at 12.7 eV just above the 10.3 eV plasmon peak has been assigned to interband transitions although the energy bands involved in this transition have not been identified. The small kinks at lower energies (<10 eV) are due to interband transitions and hybrid interband-plasmon excitations. The distinct small peak at ~ 31 eV is a core-level excitation of the Nb electrons.

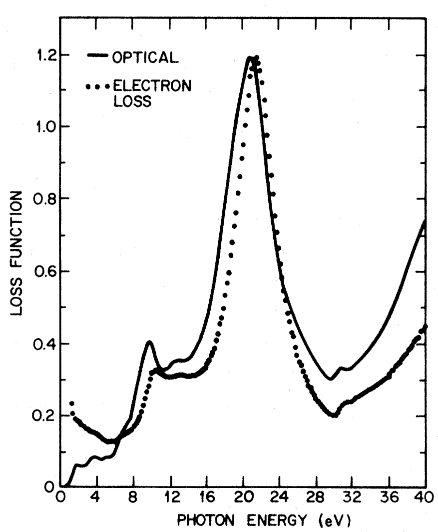

FIG. 1. Electron-energy-loss spectrum of pure Nb for $q=0$, and optical data from Ref. 5.

As we have noted earlier, a unique strength of high-energy electron-loss spectroscopy is its ability to probe the q dependence of electronic excitations. In Fig. 2, we show the q dependence of the energy-loss spectra in the energy range $0 < \hbar\omega \lesssim 100$ eV. First we note that three broad peaks occur above 30 eV with energies falling approximately at the multiples of the fundamental plasmon resonance peak at 21.7 eV. These peaks are most likely due to multiple scattering, and are observed to become very pronounced at large q because of additional scattering by thermal diffuse phonons.[11,12]

When we examine the fundamental plasmon peaks at 21.7 and 10.3 eV, the q-dependent energy-loss spectra yields the dispersion relations of these plasmons. While it is known[11,12] that the plasmon energy increases quadratically in q for a free-electron gas, Fig. 2 shows negligible dispersion for the two plasmons at 21.7 and 10.3 eV. Plasmons in transition metals, however, are expected to be less dispersive than plasmons in a free-electron-gas-like metal such as Al, mainly because of the influence of interband transitions and the extent of localization of the d electrons. Detailed theory to

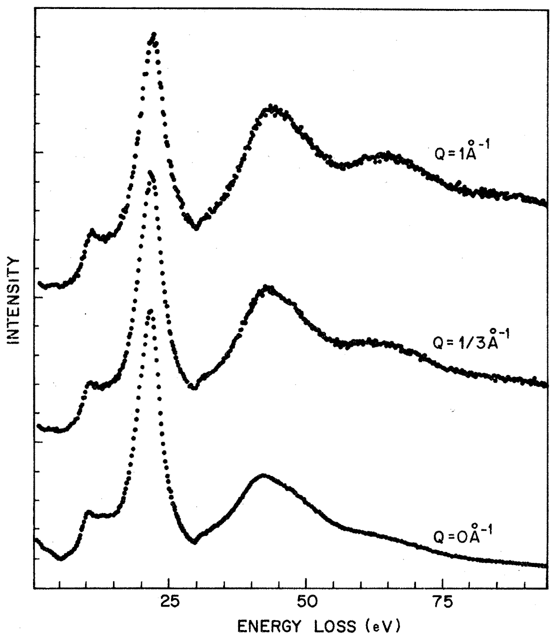

FIG. 2. q dependence of the energy-loss spectra of pure Nb.

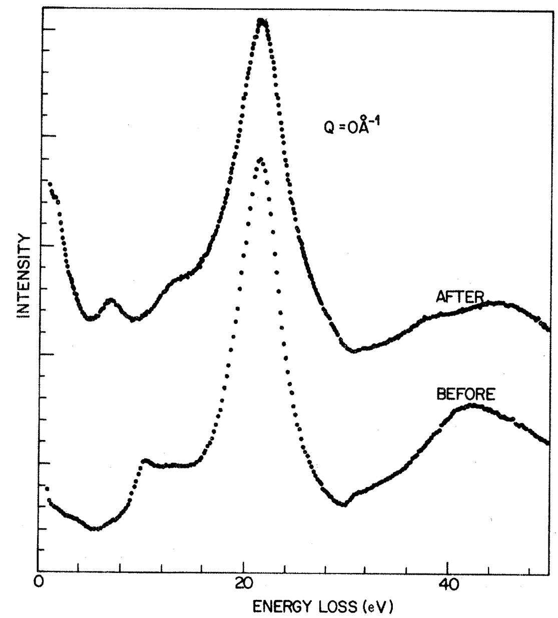

FIG. 3. Electron-energy-loss spectrum of a Nb foil before and after prolonged air oxidation.

account for this phenomena has yet to be worked out. Since the Nb plasmons show no dispersion it is difficult to distinguish the true singly scattered plasmon from the doubly scattered plasmon peak involving scattering by plasmon and thermal diffuse phonons, especially at large q.

Niobium-oxygen solid solutions

As mentioned earlier, the influence of oxygen on the superconducting properties of Nb is marked. We first noticed this effect in our experiment when we took the energy-loss spectra of a pure Nb sample which had been left in the air for about a year. The spectrum of this old sample is shown in Fig. 3. Compared to Fig. 1, we observed that significant changes in electronic structure have taken place. First we note that the large plasmon peak at 21.7 eV has become much broader although its peak position remains unchanged. The 10.3-eV d-electron plasmon is found to have disappeared while a new peak occurs at 6.75 eV. The interband transition peak at 12.5 eV has also broadened considerably. The presence of a thin layer of oxide on the film surface as observed in many thin metal films simply cannot account for the dramatic changes in the energy-loss spectra. It has been shown that a thin oxide layer at the film surface would only affect surface plasmons by moving them to lower energies[13] and should not have any effect on the bulk excitations of the thin-film samples. Our results suggests that oxygen has diffused into the bulk of the thin-film sample and formed solid solutions with Nb. (If so, this has serious implications for the lifetime of thin-film devices based on Nb, but such questions need not concern us here.) The existence of a small amount of oxygen in the sample is confirmed by examining the oxygen $1s$ core level occurring at ~ 530 eV in the electron-energy-loss spectrum as shown in Fig. 4. Also shown in the figure is the core-level spectra of the Nb $3p$ electrons, which appear as two small but rather sharp peaks at ~ 362 and 377 eV.

In order to study the details of the change of electronic structures due to the presence of oxygen, we have examined samples made deliberately with different oxygen concentration. Sample a has a measured T_c of ~ 7.8 K which implies an oxygen content ~ 1.3 at. %, sample b has a T_c of ~ 5.5 K with approximately 3.3 at. % oxygen and sample c has a $T_c < 1.2$ K with more than 7.5 at. % oxygen. The oxygen content was not determined independently. Their energy-loss spectra in the energy region $0 < \hbar\omega < 50$ eV are shown in Fig. 5. For comparison we have also included in Fig. 5 the energy-

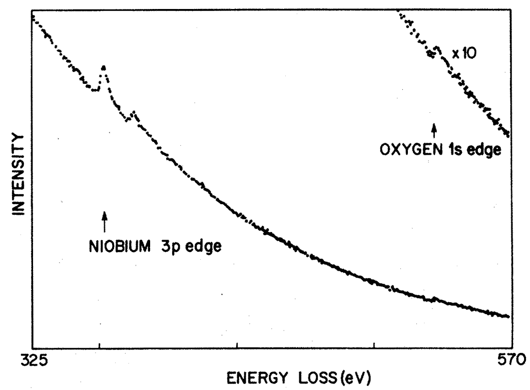

FIG. 4. Core-level spectra showing the existence of oxygen $1s$ excitation. Also shown are Nb$4p$ core excitations.

loss spectrum of the pure Nb sample from Fig. 1. Sample A shows that the width of the 21.7-eV plasmon has increased slightly and the 10.3-eV plasmon has down-shifted a little to ~ 10 eV. With the further increase of oxygen concentration much more drastic changes in the energy-loss spectra are observed as shown in samples B and C in Fig. 5. One observes that as the oxygen content increases the width of the 21.7-eV plasmon peak increases very rapidly, the 12.5-eV interband transition seems to grow in intensity and the 10-eV d-electron plasmon is being gradually suppressed. For sample C with $T_c < 1.2$ K, the 21.7-eV plasmon width has already increased to ~ 15 eV from the 5-eV width of the pure sample. A broad shoulder appears at ~ 15 eV next to the plasmon peak and a pronounced peak is found at 6.75 eV. This suggests that the oscillator strength of the interband transitions with energies higher than 10 eV are weakened considerably as a result of oxygen contamination. The weaker oscillator strength in this energy region tends to lower the magnitude of ϵ_1 and change its slope such that $\epsilon_1(\omega)$ becomes negative and does not cross the energy axis [i.e., $\epsilon_1(\omega)\simeq 0$] around 10 eV. This qualitatively explains why the 10-eV plasmon was first shifted in energy and eventually suppressed with higher oxygen content. The strong shoulder at ~ 15 eV in the energy-loss spectra appeared as a result of this weakened interband transition. It should be remembered that the energy-loss cross section is proportional to $\mathrm{Im}(-1/\epsilon)=\epsilon_2/\epsilon_1^2+\epsilon_2^2$, therefore weak features in ϵ_2, near the plasmon energy where $\epsilon_1\simeq 0$, could be enhanced dramatically in the energy-loss spectra. The loss of oscillator strength at the higher energies seems to be compensated by the strength of the 6.75-eV interband transition peak which grows with increasing oxygen concentration. Comparing Fig. 4 to Fig. 5, we can estimate that the amount of oxygen in the air-oxidized Nb sample is roughly between that of sample B and sample C. The bonding details of dilute oxygen solution in niobium is largely unknown although it is believed that oxygen $2p$ orbitals could form hybridized orbitals with the Nb $4d$ and $5p\,5s$ orbitals and therefore change the electronic structure near the Fermi surface. The changes in the structure of interband transitions can lead to the enormous broadening of the plasmons at 21.7 eV. Of course, electron-impurity scattering can also be a cause for the damping of plasmons in this case. However, a recent optical reflectivity measurement[14] of Nb-based alloys showed that the slope of the plasmon edge in the reflectivity spectra did not change significantly as the concentration of the guest element was varied. In light of this observation, one can probably say that electron-impurity scattering is not an important factor for plasmon damping in Nb.

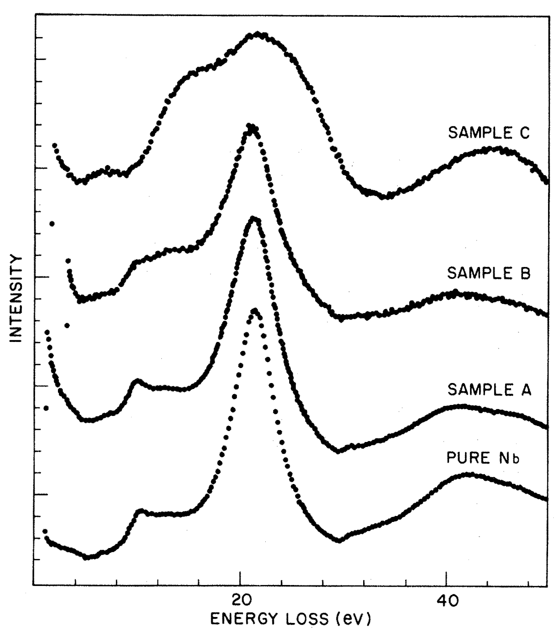

FIG. 5. Energy-loss spectra of Nb-O samples. Samples A, B, and C have superconducting transition temperature at 7.8, 5.5, and < 1.2 K, respectively. For comparison, a loss spectrum of pure Nb (Fig. 1) is also included.

Superconductivity and heat-capacity measurements of the Nb-O system have suggested a monotonic decrease of the density of states at the Fermi surface as the oxygen content is increased. Our data also suggests such a decrease, since the peak at the Fermi surface is smeared as all features become broader when the oxygen content is increased. It is known that the Nb Fermi surface is dominated by states with d-electron character. Examination of the Nb energy-band structure indicates that the high density of states near the Fermi surface mainly comes from a band along ΓN that dips at the Fermi level. Hybridization with oxygen orbitals could move this band upwards slightly and change the density of states at the Fermi level which, in turn, lowers the T_c of the sample. The final states of the Nb $4p$ core excitation at ~ 31 eV are believed to be predominantly states with d character. Hence, transitions of this type can, in principle, yield useful information about the density of states at the Fermi level. Figure 5 seems to indicate that the $4p$ core excitation at ~ 31 eV becomes less pronounced as the oxygen content is increased. However, one should view this with care since the plasmon peak is also getting broader and could smear out the weak $4p$ core excitation.

CONCLUSIONS

We have here presented the first studies of the Nb and Nb-O systems by transmission energy-loss spectroscopy using 250-keV electrons. The strong plasmon observed at 21.7 eV in the present case is about ~ 1 eV higher than the value reported previously by other techniques. We believe this is the most accurate value obtained experimentally so far. Distinct differences are observed between Nb and Nb-O systems. It is found that introduction of oxygen in the Nb metal changes the interband structures and the plasmon behavior. Heavy damping of plasmons is also observed in the Nb-O system. For a detailed interpretation of the present data regarding the effect of oxygen on superconductivity in Nb one has to await further theoretical work in this area.

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