

Low-Temperature Dissipation Peak in Niobium*

P. G. BORDONI, M. NUOVO, AND L. VERDINI
Istituto Nazionale di Ultracustica, Rome, Italy

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The energy dissipation coefficient Q^{-1} and the resonant frequency of a circular plate of niobium have been measured as a function of temperature in the range 60–300°K. The measurements have been carried out at four different frequencies from 18 kc sec⁻¹ to 174 kc sec⁻¹ with strain amplitudes smaller than 10⁻⁷. For each vibration mode a pronounced peak is found for the dissipation coefficient while the frequency-temperature curves show a corresponding inflection. The temperature T_m of the dissipation peak depends on the vibration frequency according to an Arrhenius equation which characterizes the thermally activated relaxation effects.

The activation energy \bar{W} and the limiting relaxation time $\bar{\tau}_0$ of the process have been computed and these values [$\bar{W}=0.265$ ev and $(\bar{\tau}_0)^{-1}=61 \times 10^{11}$ sec⁻¹] are in agreement with the values previously found in some fcc metals for the relaxation effect due to the motion of dislocations.

The value of \bar{W} found in niobium shows that the effect cannot be directly produced by the motion of interstitial atoms of hydrogen.

THE peak which has been found by Bruner¹ in the dissipation-temperature curve of niobium seems to be of considerable interest for solid-state physics. If it is due to the motion of dislocations near their equilibrium positions like the peaks found in fcc metals,²⁻⁴ its existence in a bcc lattice would indicate that the mechanism of dislocation motion proposed by Bruner is incorrect. On the other hand, if the peak is produced by the interaction of interstitial hydrogen with dislocations, according to the mechanism introduced by Weiner and Gensamer,⁵ it affords an instance of this mechanism which is much more evident and stable than the peak observed in 1020 steel.

The activation energy \bar{W} , the limiting value $\bar{\tau}_0$ of the relaxation time $\bar{\tau}$, and the logarithmic spectrum width⁴ $\ln(\tau_2/\tau_1)$ have been evaluated by measuring the dissipation coefficient Q^{-1} as a function of temperature in the interval 60–300°K, using the flexural vibrations of a circular niobium plate of 35.96-mm diameter and 3.91-mm thickness.

The measurements have been made at four different vibration modes covering the frequency range 18–175 kc sec⁻¹. The resonant frequencies have also been measured as a function of temperature. The strain amplitude was always smaller than 10⁻⁷, and no amplitude-dependent effect has been noticed. The experimental technique was the same as has been employed in previous investigations on fcc metals.^{3,4}

The niobium was supplied by the Kawachi Chemical Company in sheets of 7.8-mm thickness. No information

is presently available on the impurity content and on the amount of interstitial hydrogen. The specimen was subjected to an axial compression of about 4.5×10^8 kg cm⁻² and its thickness was reduced to 4.9 mm. It was then machined and the measurements were started without any other treatment. No room temperature aging has been noticed, in contrast with what seems to happen in 1020 steel.⁵

For each vibration mode a pronounced peak is found in the dissipation-temperature curves (Fig. 1), while the frequency-temperature curves show a corresponding inflection. The temperature T_m of the peak, the vibration frequency f_m , and the value Q_m^{-1} of the dissipation maximum are listed in Table I.⁶ The fundamental frequency is very near to the single frequency of Bruner's

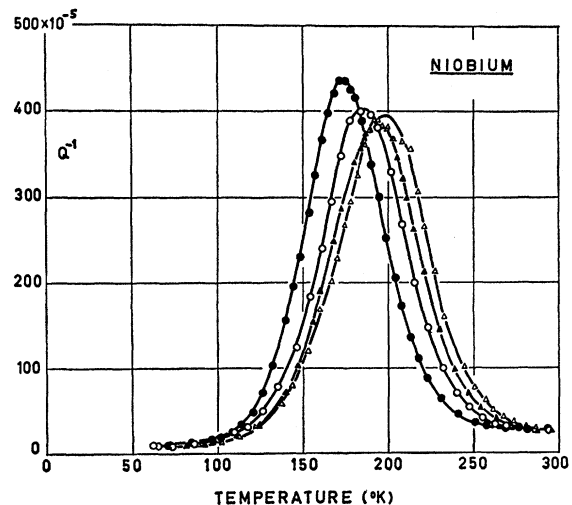


FIG. 1. Dissipation coefficient Q^{-1} as a function of the absolute temperature T for different vibration frequencies: ● 18.62 kc sec⁻¹; ○ 63.73 kc sec⁻¹; ▲ 118.11 kc sec⁻¹; △ 174.38 kc sec⁻¹.

⁶ The symbols are the same as those which have been adopted in the second paper quoted in reference (2); \bar{W} and $\bar{\tau}$ are the central values of energy or time spectra; τ_1 , τ_2 are the values at which the density of relaxation strength is $1/\sqrt{2}$ of its maximum value.

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¹ L. J. Bruner, Phys. Rev. **118**, 399 (1960).

² D. H. Niblett and J. Wilks, Phil. Mag. Suppl. **9**, 1 (1960).
P. G. Bordoni, Suppl. Nuovo cimento **17**, 43 (1960). W. P. Mason, *Physical Acoustics and the Properties of Solids* (D. Van Nostrand Company, Princeton, New Jersey, 1958), p. 266.

³ P. G. Bordoni, M. Nuovo, and L. Verdini, Nuovo cimento **14**, 273 (1959).

⁴ P. G. Bordoni, M. Nuovo, and L. Verdini, Proceedings of the Third International Congress of Acoustics, Stuttgart, September, 1959 (unpublished); Nuovo cimento (to be published).

⁵ L. C. Weiner and M. Gensamer, Acta Metallurgica **5**, 692 (1957).

measurements¹; the agreement between the corresponding values of T_m is good, but the height of the peak in the present case is about twice Bruner's value. When $k \ln f_m$ is plotted against T_m^{-1} the experimental points fall on a straight line, showing that the peak is due to a thermally activated relaxation effect (Fig. 2). The values found for \bar{W} and τ_0 are

$$\bar{W} = (0.265 \pm 0.005) \text{ ev},$$

$$\tau_0^{-1} = 61 \times 10^{11} \times (1.4)^{\pm 1} \text{ sec}^{-1}.$$

The value of \bar{W} is quite near to that previously found for the dislocation peak in palladium⁴ (0.260 ev). In other fcc metals the values are somewhat smaller (aluminum, 0.11; copper, 0.122; silver, 0.124; gold, 0.158; platinum, 0.192). The value of $(\tau_0)^{-1}$ is of the same order of magnitude as that evaluated for dislocation relaxation in fcc metals,^{3,4} being also very near to the Debye frequency $\nu_D = k\theta/h = 52 \times 10^{11}$ cps.

The curves obtained plotting the *normalized* values Q^{-1}/Q_m^{-1} of the dissipation coefficient against the *universal* variable $\bar{W}k^{-1}[T_m^{-1} - T^{-1}]$ are about twice as

TABLE I. Experimental data in the relaxation peak.

| f_m (cps) | T_m (°K) | Q_m^{-1} |
|---------------------------------|--------------------|-----------------------------------|
| 18.62×10^3 | 173.0 | 438×10^{-5} |
| 63.73×10^3 | 184.5 | 404×10^{-5} |
| 118.11×10^3 | 193.0 | 384×10^{-5} |
| 174.38×10^3 | 197.6 | 400×10^{-5} |
| 18.0×10^3 ^a | 173.0 ^a | 211×10^{-5} ^a |

^a Bruner's measurements, reference 1.

broad as the curve for a single relaxation time. They are also slightly asymmetrical, with the low-temperature branch higher than the high-temperature one, like those found for dislocation relaxation in fcc metals.^{3,4} This asymmetry may correspond to the hump noticed by Bruner¹ on the dissipation curve at about 70°K. The experimental evidence is still too limited to decide if the spectrum is an *energy* spectrum or a *time* spectrum.^{4,7} An average spectrum width may be computed for the temperature interval in which the peaks are observed, by means of the Fuoss-Kirkwood approximation,^{3,4,8} taking the values of the high-temperature branch which are less influenced by the low-temperature hump. The value found in this way [$\ln(\tau_2/\tau_1) = 1.85$] is somewhat smaller than the corresponding values obtained in fcc metals (copper, 2.89; silver, 5.30; gold, 3.91; palladium, 7.38; platinum, 3.91).

The value found for \bar{W} shows that the effect cannot be directly produced by the motion of interstitial atoms

⁷ P. G. Bordoni, Proceedings of the Third International Congress of Acoustics, Stuttgart, September, 1959; Colloque sur le frottement interne, Saint Germain en Laye, October, 1960 (to be published).

⁸ R. M. Fuoss and J. G. Kirkwood, J. Chem. Phys. **63**, 385 (1941).

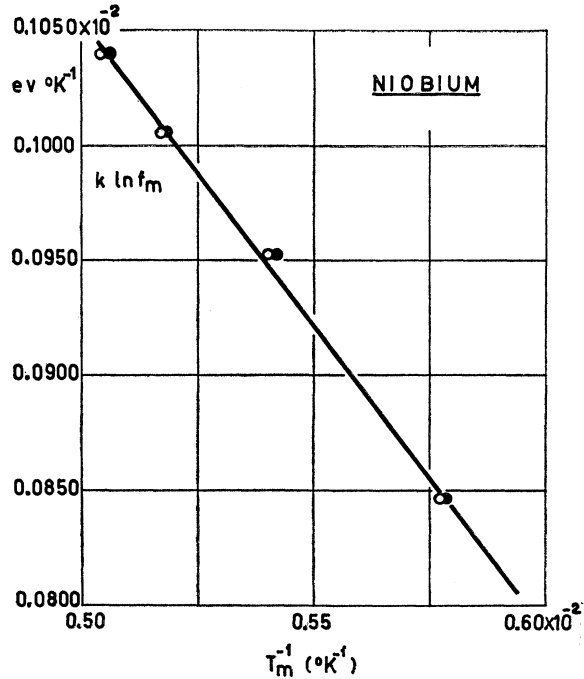


FIG. 2. Relation between the frequency f_m and the temperature T_m corresponding to the maximum energy dissipation: the distance between full circles and open circles gives the experimental error in the evaluation of T_m^{-1} .

of hydrogen, as the activation energy associated with the diffusion of hydrogen in niobium is much larger (0.625 ev) according to Paxton and Sheehan.⁹ Moreover, the motion of interstitials gives rise to relaxation effects with a single characteristic time or with a spectrum narrower than the spectrum observed in niobium, as is shown by the experiments of Powers and Doyle¹⁰ on the diffusion of carbon and nitrogen in tantalum.

It may also be excluded that the small hump at 70°K is due to the diffusion of hydrogen, as was tentatively proposed by Bruner.¹ According to this hypothesis the diffusion constant $D_{H^{Nb}}$ at the temperature of 70°K would take the value¹¹

$$[D_{H^{Nb}}]_{70} = \frac{2}{3} \alpha a^2 / \bar{\tau} = (1/36) a^2 / \bar{\tau} = 0.175 a^2 f$$

$$= 3.4 \times 10^{-12} \text{ cm}^2 \text{ sec}^{-1},$$

where a is the lattice constant $= 3.294 \times 10^{-8}$ cm at 20°C and f is the vibration frequency. For the same temperature Paxton and Sheehan⁹ predict a value of $D_{H^{Nb}}$ many orders of magnitude smaller, according to the

⁹ H. W. Paxton and J. M. Sheehan, Metals Research Laboratory, Carnegie Institute of Technology, Pittsburg, 1957 (unpublished); G. L. Miller, *Tantalum and Niobium* (Butterworths Scientific Publications, Ltd., London, 1959), p. 463.

¹⁰ R. W. Powers and M. B. Doyle, J. Appl. Phys. **28**, 255 (1957). The dissipation-temperature curves of Fig. 2 correspond to a logarithmic spectrum width of 0.17 for carbon and of 0.27 for nitrogen. The activation energies employed in this computation are those given in the same paper (1.72 ev for carbon; 1.63 ev for nitrogen).

¹¹ C. A. Wert, Phys. Rev. **79**, 601 (1950).

following equation:

$$[D_{\text{H}^{\text{Nb}}}]_{70} = 1.61 \times 10^{-3} \exp[-0.625/70k] \\ = 3.0 \times 10^{-48} \text{ cm}^2 \text{ sec}^{-1}.$$

The lack of identification of the 70°K hump with the relaxation effect produced by the interstitial hydrogen destroys one of the main analogies¹ between the niobium peak and the dissipation maximum found by Weiner and Gensamer in steel.^{5,12} Another difference

¹² The value of $D_{\text{H}^{\text{Fe}}}$ computed by Weiner and Gensamer from the experimental data concerning the 50°K peak is wrong by a

between the two effects is that the intricate dependence of the peak's height upon aging which has been observed in steel⁵ finds apparently no parallel in niobium.

The existence of a relaxation spectrum and the close analogy between the values of \bar{W} and $\bar{\tau}_0$ measured in niobium and those found in fcc metals show that, whatever the details of the mechanism may be, the niobium peak is essentially controlled by the dislocations.

factor of 100. The correct value is $2.8 \times 10^{-16} \text{ cm}^2 \text{ sec}^{-1}$, and agrees less well with the value $4.9 \times 10^{-17} \text{ cm}^2 \text{ sec}^{-1}$ obtained from high-temperature experiments.

Interpretation of Low-Energy Electron Diffraction Patterns of Adsorbed Gases

ERNST BAUER

Michelson Laboratory, China Lake, California

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Recent observations of the adsorption of oxygen on nickel are interpreted in terms of double scattering processes instead of the single scattering mechanism which has been used in all previous interpretations. This permits a simple explanation of the observed variation of the intensity of the diffraction pattern with electron energy and provides a plausible understanding of the early stages of adsorption.

IN 1927 Davisson and Germer¹ reported diffraction beams due to adsorbed gases along with the results of their classical experiments on the diffraction of electrons by a crystal of nickel. Since then a large number of low-energy electron diffraction investigations of the adsorption of foreign atoms on single crystal planes have been reported, especially by Farnsworth *et al.* To date the interpretation of the experimental results has been based principally upon the assumption that the diffraction pattern associated with the adsorbed atoms is the result of a single direct scattering by the

adsorbed atoms, as demonstrated in Fig. 1(a). Recent observations² with missing explanations reveal the inadequacy of this assumption. It is the purpose of this paper to report a new assumption which includes *double scattering*, as demonstrated by Figs. 1(c) and (d). This new assumption provides not only the missing explanations but also more reasonable explanations in the case of other observations.

Recently Germer and Hartman² reported the following unexplained observations in the case of oxygen adsorbed on nickel.

Observation 1. Good patterns from two-dimensional arrays of adsorbed atoms appear at certain electron wavelengths only. According to the theory of diffraction of plane waves by a plane grating, the diffraction pattern should be observable equally well for all wavelengths smaller than the lattice constant.

Observation 2. At very low coverage of approximately 0.1 monolayer, the (10) reflections are streaked in contrast to the diffuse (30) reflections. Furthermore, the (10) reflections are occasionally missing.

Observation 1 may be accounted for in the following way. The scattering of slow electrons by oxygen atoms is strongly peaked in the backward and forward directions with the former always less than the latter.³ From accelerating potentials of approximately 50 v on, the backward scattering decreases rapidly with increasing electron energy and the double scattering processes such

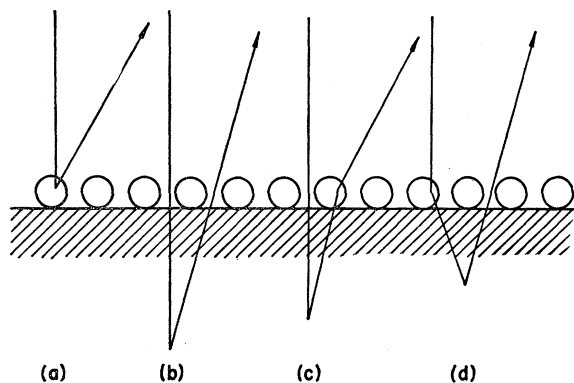


FIG. 1. The different scattering processes: (a) single scattering by gas atoms ("gas beam"); (b) single scattering by crystal ("crystal beam"); (c) double scattering, crystal-gas; (d) double scattering, gas-crystal.

¹ C. Davisson and L. H. Germer, *Phys. Rev.* **30**, 705 (1927).

² L. H. Germer and C. D. Hartman, *J. Appl. Phys.* **31**, 2085 (1960).

³ E. Bauer (to be published).