

Amplitude-weighted density of bulk and surface vibrations of ultradisperse nickel

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(Submitted 21 January 1991)

Zh. Eksp. Teor. Fiz. **100**, 948–960 (September 1991)

Spectra of the amplitude-weighted density of states (AWDS) of bulk and surface phonon modes of crystalline Ni have been studied experimentally and theoretically. Inelastic-neutron-scattering spectra of highly disperse Ni, with an average particle size as small as 200 Å, and also of macroscopic Ni grains, with a particle size greater than 1 mm, were obtained at 80 K.

Sensitization of the surface vibrations of Ni particles by hydrogen atoms of water adsorbed on the surface of these particles made it possible to obtain AWDS separately for bulk and surface states. The same characteristics were calculated in the approximation of a thin plate, for plates with 30 and 50 layers, for three crystallographic configurations of the boundary surfaces: (111), (100), and (110). It is found that from the third layer on into the interior of the crystal the AWDS varies only slightly. It acquires features characteristic of the density of bulk phonons. The density of states for the atoms of the first two layers, in contrast, depends on the surface structure and on the details of the force field near the surface. The experimental AWDS of bulk phonons of nickel can be described well by the calculated value. The experimental results for the surface modes agree qualitatively with the calculated results for a plate with a (111) surface configuration. This agreement is evidence of a predominant faceting of the surfaces of the nickel particles with the (111) plane.

1. INTRODUCTION: STATEMENT OF THE PROBLEM

In the phonon theory of crystals, the amplitude-weighted density of states (AWDS) is conventionally defined in two ways. First, it is the spectral density of states, also known as the dynamic structure factor¹ $S(\mathbf{q}, \omega)$:

$$S_n(\mathbf{q}, \omega) = \sum_j^{3N} |a_j^n(\mathbf{q}, \omega)|^2 \delta(\omega - \omega_j(\mathbf{q})). \quad (1)$$

Second, it is the amplitude-weighted density of states $G(\omega)$, an integral expression for which is

$$G_n(\omega) = \sum_j^{3N} \int_{\mathbf{q}}^{Bz} |a_j^n(\mathbf{q}, \omega)|^2 \delta(\omega - \omega_j(\mathbf{q})). \quad (2)$$

The index j specifies the phonon mode, while the index n specifies both the particular atom and the species of atom in the unit cell. The unit cell consists of N atoms. The quantity a_j^n is the displacement of atom n involved in vibrational mode j , with frequency ω . The spectral density is usually measured by studying the dispersion curves for bulk phonon modes by the method of coherent inelastic neutron scattering or by measuring of the dispersion curves for surface phonons by inelastic electron-scattering spectroscopy (HREELS). Both methods are used for single crystals.^{1,2} The AWDS is the sum of the phonon spectra over the Brillouin zone. It is measured primarily through incoherent inelastic neutron scattering from polycrystalline samples.¹ For bulk phonons, this quantity has been described in detail experimentally and theoretically (Ref. 3, for example). For surface phonons, in contrast, very little is available in the way of experimental observations of the AWDS (see Ref. 4 and the bibliography there). On the theoretical side, there have so far been only two attempts to calculate this quantity in the cluster approximation.^{5,6}

In this paper we are reporting experimental and theoretical studies of the AWDS of bulk and surface phonon modes of a nickel crystal. Incoherent inelastic neutron scattering was used to find the AWDS of highly disperse particles. The AWDS was calculated by the thin-plate method.

In inelastic neutron scattering, the components of the intensity which come from the scattering by bulk and surface nuclei are known to add together, because of the large neutron mean free path. For typical polycrystalline samples, the cross section for the scattering by surface atoms is too small to be measured in the observed spectrum. One might expect a different situation if the surface area of the sample were increased, as it would be if one were to use an ultradisperse powder with an average particle size of 10^3 – 10^2 Å. The first experiment with nickel powders of this sort worked out successfully.⁴ We were able to observe a significant increase in the scattering intensity upon the transition from a macroscopic sample with an average grain size of several millimeters to a microscopic sample with an average particle size ~ 200 Å. To see whether the observed difference in the spectra of the inelastic neutron scattering was linked with an increase in the relative number of surface atoms, we repeated the experiment with particles of a similar size but with a very clean surface. No difference between the spectra of the macroscopic sample and the microscopic sample was found, within the experimental errors. Consequently, an increase in the relative number of surface atoms in the powdered samples studied was by itself clearly inadequate to bring out the surface states.

Analysis of the entire set of data obtained previously⁴ led to the conclusion that the additional scattering from the microscopic sample which was observed was due to water adsorbed on its surface. An adsorbate leads to two effects: the appearance of the vibration spectrum of the adsorbate itself and an intensification of the vibrational spectrum of the substrate because hydrogen atoms of the adsorbed water

molecules are entrained in the vibrational motion of the surface atoms of the substrate (the "horseback-rider effect").

To find confirmation of this conclusion, it is necessary to solve three problems. First, it is necessary to determine just what the spectrum of the amplitude-weighted density of surface states of nickel particles is. Second, it is necessary to determine how the spectrum of this density is affected by the presence of adsorbed water. Third, it is necessary to determine what the spectrum of the AWDS associated with the water is and to determine whether the vibration spectrum of the substrate is being intensified by hydrogen atoms of the adsorbate.

All three of these problems are fundamental and challenging problems in surface spectroscopy. In the present paper, we examine the first of these problems: that of determining the amplitude-weighted density of surface states of a nickel crystal. The two other problems have been the subjects of a detailed study on the basis of computational chemistry and computational spectroscopy.⁷ We refer the interested reader to Ref. 7 for the details; here we will reproduce only the main conclusion of that paper. Calculations which agree very well with experimental data confirm the validity of the approach outlined above in analyzing the role of the adsorbate. Surface vibrations of the substrate become accessible to observation by inelastic neutron scattering when these vibrations are sensitized by adsorbed hydrogen atoms.

2. EXPERIMENTAL RESULTS

The best method for measuring AWDS spectra is the method of incoherent inelastic neutron scattering. This method has been used with the KDSOG-M inverse-geometry time-of-flight spectrometer at the IBR-2 high-pulse reactor at the Joint Institute for Nuclear Research in Dubna.⁹ Scattering spectra were obtained from macroscopic and microscopic samples of Ni (Ref. 4). The spectra for $T = 80$ K are reproduced in Fig. 1. The experimental details are described in Ref. 4.

The spectra of both the microscopic and macroscopic samples are dominated by one-phonon scattering. Figure 2

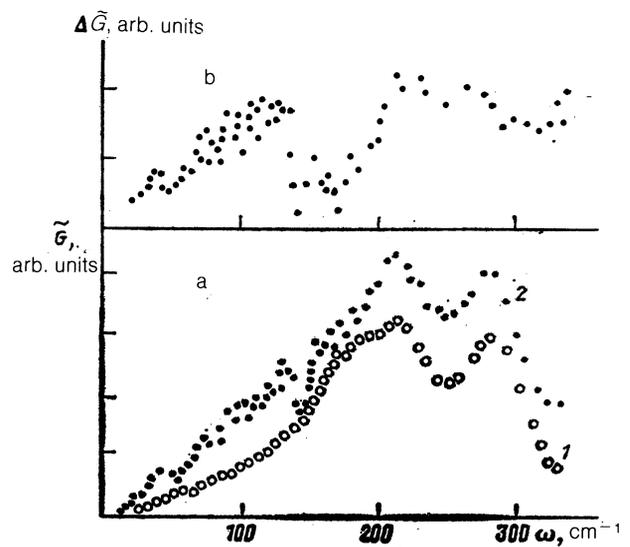


FIG. 2. Experimental amplitude-weighted densities of vibrational states. a— $\tilde{G}_T(\omega)$ for (1) a macroscopic sample and (2) a microscopic sample ($T = 80$ K); b—the difference between 2 and 1, $\Delta\tilde{G}(\omega)$.

shows the AWDS spectra $G_T(\omega)$ observed at $T = 80$ K, as found in accordance with expressions (1) and (2) in Ref. 4. These spectra correspond to the low-frequency regions II and III in Fig. 1, which contain the one-phonon spectrum of the nickel crystal. The lower spectrum in Fig. 2a corresponds to the spectrum of bulk Ni phonons, $\tilde{G}(\omega)_{\text{Ni bulk}}$. The upper curve corresponds to the AWDS spectrum of small Ni particles, $\tilde{G}(\omega)_{\text{Ni part}}$. The difference between the two experimental spectra, $\Delta\tilde{G}(\omega) = \tilde{G}(\omega)_{\text{Ni part}} - \tilde{G}(\omega)_{\text{Ni bulk}}$, is shown in Fig. 2b. The intensity of this spectrum ranges from 30% to 60% of the intensity of the bulk-phonon spectrum.

The small particles which were studied are essentially used as catalysts, and their surface is chemically heterogeneous. According to x-ray structural analysis, the particles are crystalline, consisting of 94% Ni and 6% NiO. Thermal desorption mass spectrometry revealed that carbon monox-

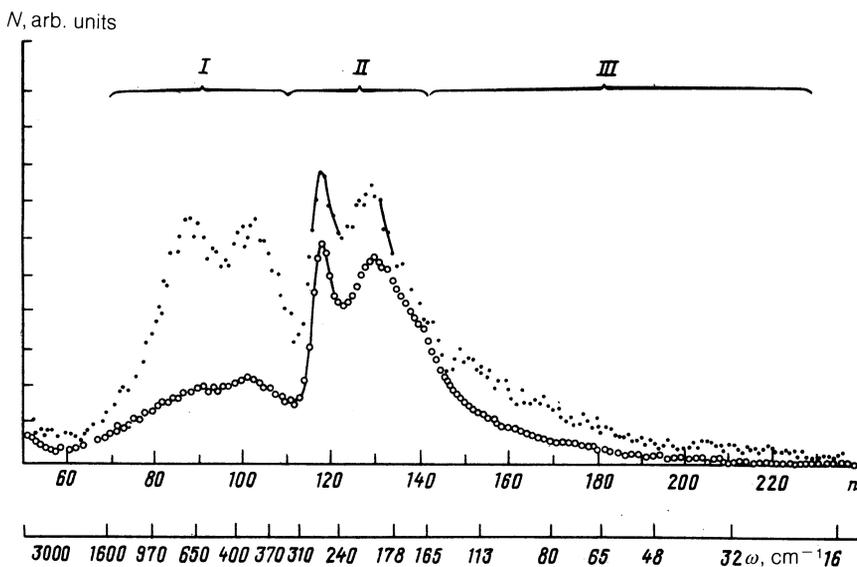


FIG. 1. Normalized time-of-flight inelastic-neutron-scattering spectra of a Ni powder. \circ —Macroscopic sample, with an average particle size ≈ 1 mm; \bullet —microscopic sample, with an average particle size of 230 Å ($T = 80$ K; n is the temporal channel).

ide and water desorb from the surface of the particles in the temperature range 300–600 K. The presence of water means that the surface is not completely oxidized, since water does not adsorb on a NiO surfaces above room temperature.⁸ It can thus be concluded that the surface of the particles consists of regions of Ni and NiO. So far, we have not been able to determine the relative sizes of these regions.

Because of the complex chemical composition of the surface, we need to consider all possible contributions to the difference spectrum $\Delta G(\omega)$ in Fig. 2b. With regard to the vibrations of adsorbed atoms and molecules, such as O, H₂O, and NiO, with respect to the surface, we note that their frequencies are above the frequency region on which we are focusing here, and they make no contribution to the spectrum which we are discussing. However, as we mentioned earlier, all the adsorbate atoms are entrained, to some extent or other, in the vibrational motion of the surface atoms of the substrate. This horseback-rider effect was originally established quantitatively for H, S, O, and Ni atoms;⁵ recently, it has been established for H₂O molecules⁷ adsorbed on Ni clusters. An important point is that in all cases the AWDS spectra induced by the adsorbed atoms are very similar in shape to the AWDS spectra of the surface atoms of the substrate. The observed spectrum $\Delta \tilde{G}(\omega)$ can thus be written in the form

$$\Delta \tilde{G}(\omega) = m_1 \tilde{G}_{\text{H}_2\text{O}} + m_2 \tilde{G}_{\text{O}}(\omega) + m_3 \tilde{G}_{\text{NiO}}(\omega)_{\text{surf}} + m_4 \tilde{G}_{\text{Ni}}(\omega)_{\text{surf}} + m_5 \tilde{G}_{\text{NiO}}(\omega)_{\text{bulk}}. \quad (3)$$

Here m_1 , m_2 , m_3 , m_4 , and m_5 are the numbers of water molecules, oxygen atoms, surface NiO molecules, surface Ni atoms, and NiO molecules in the interior, respectively. Here

$$\begin{aligned} \tilde{G}_{\text{H}_2\text{O}}(\omega) &= 2|b_{\text{H}}|^2 G_{\text{H}}(\omega) + |b_{\text{O}}|^2 G_{\text{O}}(\omega), \\ \tilde{G}_{\text{O}}(\omega) &= |b_{\text{O}}|^2 G_{\text{O}}(\omega), \\ \tilde{G}_{\text{NiO}}(\omega) &= |b_{\text{Ni}}|^2 G_{\text{Ni}}(\omega) + 2|b_{\text{O}}|^2 G_{\text{O}}(\omega), \\ \tilde{G}_{\text{Ni}}(\omega) &= |b_{\text{Ni}}|^2 G_{\text{Ni}}(\omega), \end{aligned} \quad (4)$$

where b_{H} , b_{O} , and b_{Ni} correspond to the neutron scattering amplitudes of the corresponding nuclei. The complexity of expression (3) would seem at first glance to complicate the analysis of the observed difference spectrum. In actuality, however, this situation is simpler. The simplification stems from the following circumstances.

1. The contribution from the last term could not exceed 6% (the NiO concentration in the sample) of the bulk vibrations of Ni, so it could be only a small fraction (less than 10%) of the observed difference spectrum $\Delta \tilde{G}(\omega)$.

2. As we mentioned earlier, we were unable to measure the difference spectrum of the small particles with a clean surface. The contribution from the fourth term in Eq. (3) is therefore very small. The same comment applies to the contribution from scattering from the NiO surface.

3. With regard to the first two terms, we note that since the particles were obtained in an argon atmosphere containing more water than oxygen,⁴ we would assume that the observed increase in the intensity in the inelastic-neutron-scattering spectrum for the microscopic sample in Fig. 1 and the difference spectrum $\Delta \tilde{G}(\omega)$ in Fig. 2b corresponding to it are caused primarily by displacements of hydrogen atoms of water molecules. As was shown in Ref. 7, the shape of the

AWDS spectrum in this case is much the same as the shape of the AWDS spectrum for vibrations of surface atoms of the nickel substrate.

3. CALCULATION OF THE AWDS BY THE THIN-PLATE METHOD

Surface vibrations have been the subject of a large number of calculations over the past two decades.² These calculations have been motivated by the need to interpret the results of HREELS experiments and of experiments on the inelastic scattering of He atoms. The primary goal of this research has been to measure the dispersion curves along various directions of the two-dimensional Brillouin zone. Accordingly, spectra corresponding to a certain value of the component of the vector parallel to the surface, q_{\parallel} , have been recorded. The dispersion curves for a large set of different surfaces have been reproduced successfully in lattice-dynamics calculations.^{9–15} Both a Green's-function method¹⁶ and a thin-plate method¹⁷ have been used to calculate the spectral density of states $S(\mathbf{q}, \omega)$. The two methods are in complete agreement in terms of results; they give the vibration frequencies along with the corresponding eigenvectors. The eigenvectors for each wave vector describe the displacements of the atoms in any layer, so they can be used to classify phonon modes as either surface or bulk modes. Below we use this method for the first time to calculate the AWDS in accordance with Eq. (2), where n and N are the indices of the layer and the total number of layers, respectively; j specifies the eigenvalues ω_j ; and a_x^n , a_y^n , and a_z^n are the components of the displacement vector a_j^n . The squared amplitude of this vector is

$$(a_j^n)^2 = (a_{jx}^n)^2 + (a_{jy}^n)^2 + (a_{jz}^n)^2. \quad (5)$$

These quantities are found through a solution of a dynamic scalar equation for each given value of \mathbf{q} . The elements of the dynamic matrix are calculated in the approximation of a simple model of central forces acting between nearest neighbors. It has been shown that this model leads to agreement to within better than 2% between the bulk phonon dispersion curves (at least in the high-symmetry directions in the Brillouin zone) when a value of $3.79 \cdot 10^4$ dyn/cm is used for the force constant.

An experimental study of the dispersion of surface phonons in the Ni(100) and Ni(110) planes has shown that the calculated results agree better with the experimental results if the force constant between the first and second layers of Ni atoms is increased by 20% from its bulk value.^{11,12} For the Ni(111) surface, the best agreement is found by reducing the force constant by 20% (Ref. 18). To determine the extent to which the calculated AWDS depend on the magnitude of the force constant acting between the first and second layers, calculations were carried out for three values of this constant: the bulk value, 120% of the bulk value, and 78% of the bulk value.

The integration in Eq. (2) was replaced by a summation over the \mathbf{q} values in the region of interest in the two-dimensional Brillouin zone, parallel to the surface of the crystal. The components q_x and q_y for 2500 points were found with the help of a random-number generator. The coordinate system was chosen so that the x and y axes ran parallel to the basic crystallographic directions in the plane of the surface,

while the z axis was directed into the crystal. The broadening function was approximated by a Lorentzian function:

$$F(\omega) = \Gamma^2 / \{(\omega - \omega_s(\mathbf{q}))^2 + \Gamma^2\} \quad (6)$$

with a half-width $\Gamma = 5 \text{ cm}^{-1}$.

The AWDS were calculated from layer to layer from the first layer to the fourth, while at the center of the crystal they were calculated for the 15th and 25th layers for two thin plates consisting of 30 and 50 layers. Under the assumption that the surfaces of the particles might be faceted, but not knowing the exact configuration of the facets, we calculated dynamic matrices for (100), (110), and (111) configurations of the free planes of the plates.

4. RESULTS OF THE DYNAMIC LATTICE CALCULATIONS

Figure 3 shows the results calculated for the (111) configuration of a Ni plate consisting of 50 layers. The data on the 30-layer plate are completely identical to those shown here. The force constant between layers 1 and 2 was increased by 20% from the bulk value of the $3.79 \cdot 10^4 \text{ dyn/cm}$. The results in Fig. 3a show that the density of states, weighted by the squares of the amplitude, obviously depends on the layer index. The greatest difference is observed between layers 1 and 2, on the one hand, and the deeper layers, on the other. The curves corresponding to the third and following

layers are essentially the same. It can thus be asserted that the behavior of the AWDS for the third and deeper layers is similar to the bulk behavior, while the surface has a very strong effect on the AWDS of the first two layers.

Figure 3b-f show the changes in the AWDS with increasing layer index for the displacements of the atoms in the various directions. It can be seen from Fig. 3 that the differences between the surface layers (the first and second layers) and the deeper layers are most obvious for the z direction. For displacements parallel to the surface, the AWDS are similar for all layers. The basic reason for this result is that the number of nearest neighbors at the surface is lowered. This lowering has a strong effect on the component perpendicular to the plane, but it causes a smaller deviation from the bulk behavior in terms of parallel components. This result is in agreement with the results of cluster calculations on the Ni(111) surface.⁵

Figures 4 and 5 show results on the (100) and (110) configurations. Analysis of the behavior of the AWDS as a function of the layer index in these cases leads to similar conclusions. In this case the AWDS differs to the greatest extent from the bulk density for layers 1 and 2. Comparison of results found for layers with the same indices, but with different configurations of the free surface, leads to the conclusion that the AWDS for layers 1 and 2 depends strongly on the surface configuration. This dependence is stronger for the atomic motions perpendicular to the surface and weaker for the displacements parallel to the surface. For the deeper

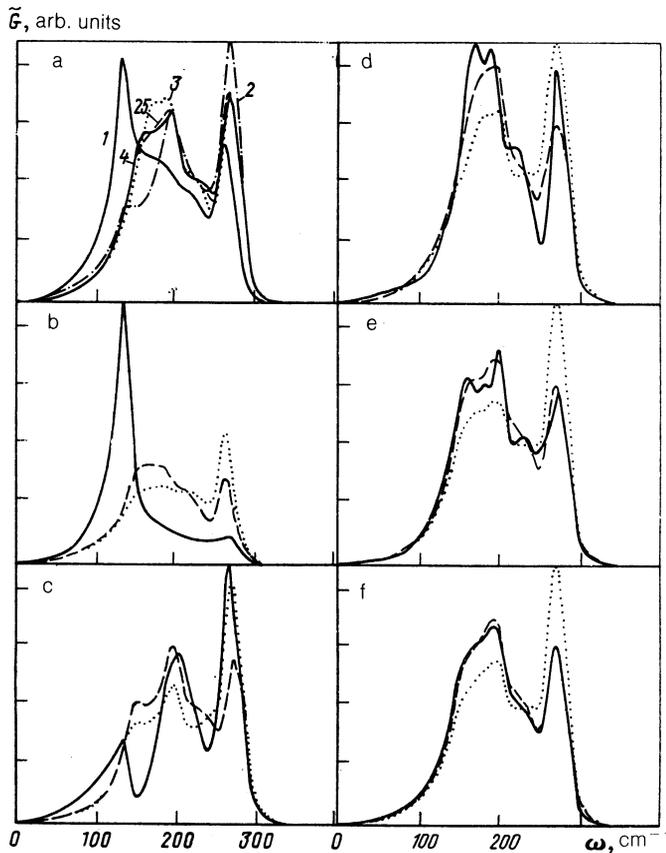


FIG. 3. Calculated amplitude-weighted densities of vibrational states for a 50-layer thin Ni plate with a Ni(111) configuration. a: Total densities, weighted by $|a|^2 = |a_x|^2 + |a_y|^2 + |a_z|^2$. The numbers are the layer numbers. b-f: Densities weighted by the squares of the individual components, $|a_x|^2$ (dotted lines), $|a_y|^2$ (dashed lines), and $|a_z|^2$ (solid lines), for layers 1, 2, 3, 4, and 25, respectively.

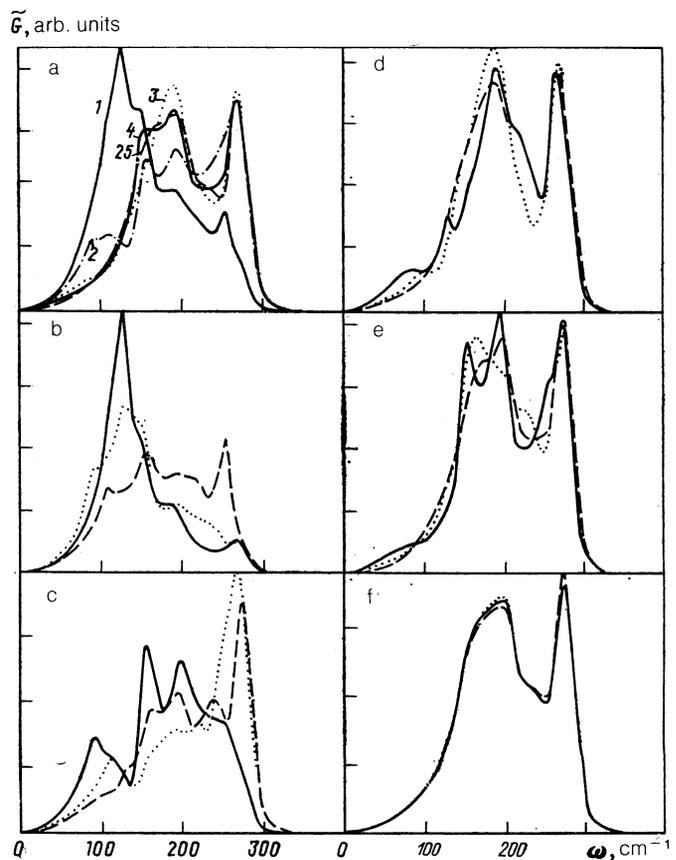


FIG. 4. The same as in Fig. 3, but for a Ni(100) configuration of the plate.

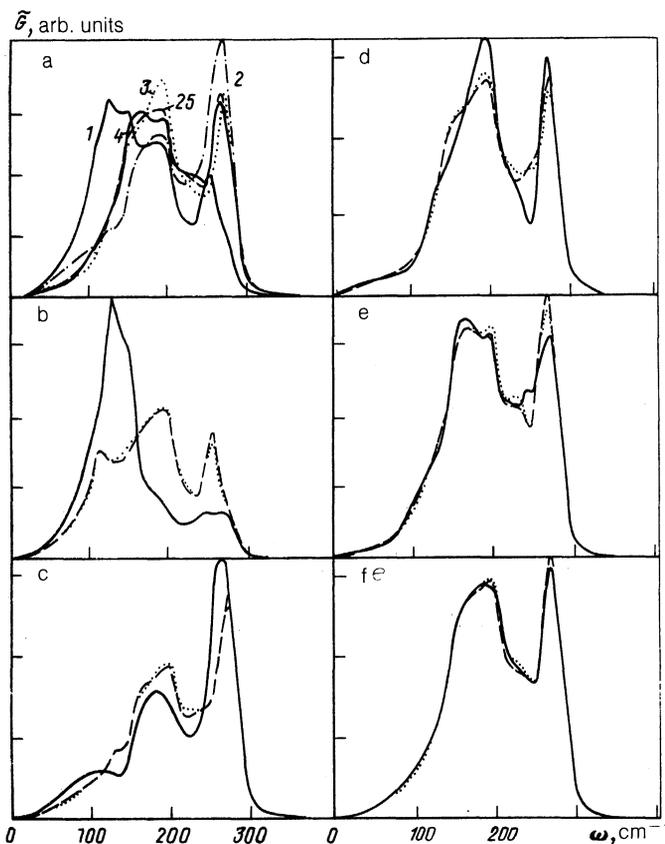


FIG. 5. The same as in Fig. 3, but for a Ni(110) configuration of the plate.

layers, the results are essentially independent of the surface configuration. The change in the value of the force constant between the first and second layers affects only those components of the phonon spectrum which are associated with the surface. Consequently, the AWDS of only the first two layers are affected.

Generalizing these results, we can say that the AWDS for layer 25, which is independent of the surface configuration and independent of the values of the force constants near the surface, is the AWDS of the bulk phonons of the nickel crystal as calculated by the thin-plate method. On the other hand, half the sum of the AWDS's for the first two layers is the AWDS for the surface phonon states of Ni. The complete set of AWDS's for surface phonons, including the results for various configurations of the planes and various values of the force constants, is shown in Fig. 6. The obvious dependence of the AWDS on the surface structure can be utilized as a quantitative test for determining an unknown structure.

5. COMPARISON OF THEORETICAL AND EXPERIMENTAL DATA

5.1. Bulk modes. Figure 7 shows the spectrum of the AWDS of bulk phonons found experimentally from the inelastic-neutron-scattering spectrum of a macroscopic sample, along with AWDS spectra calculated for the 25th layer of a 50-layer thin plate, with three configurations of the free planes. Obviously, there is a very good agreement between the spectra calculated by the thin-plate method and the ex-

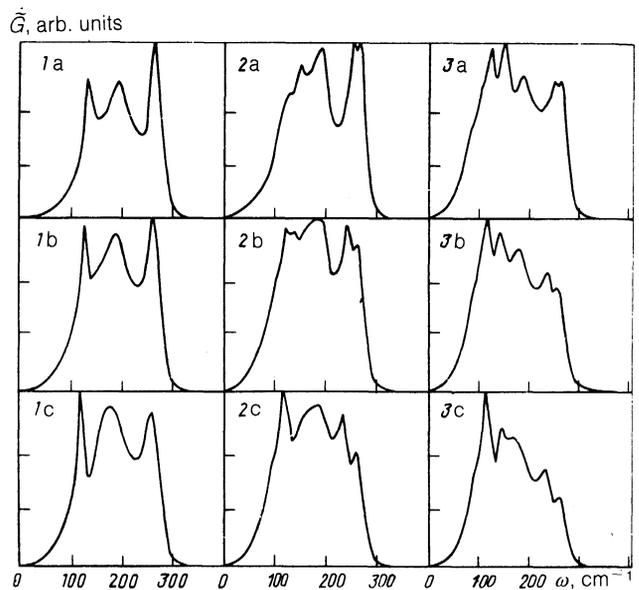


FIG. 6. Half the sum of the calculated amplitude-weighted densities of vibrational states of layers 1 and 2 for a plate consisting of 50 layers. Configuration of the free planes: 1—(111); 2—(100); 3—(110). The ratio of the force constants between layers 1 and 2 to the bulk value is (a) 1.2 [for the (110) configuration, 1.92], (b) 1.0, and (c) 0.78.

perimental spectra, particularly in the main part of the spectrum, between 120 and 300 cm^{-1} .

This agreement might seem surprising since the calculations were carried out in a two-dimensional \mathbf{q} space. However, the absence of the component q_z is offset by the "thickness" of the unit cell, which contains a column of atoms in a number equal to the number of layers.

The slight differences between the calculated results in the low-frequency region occur because the thin-plate calculations can be no better than approximate for infinite sys-

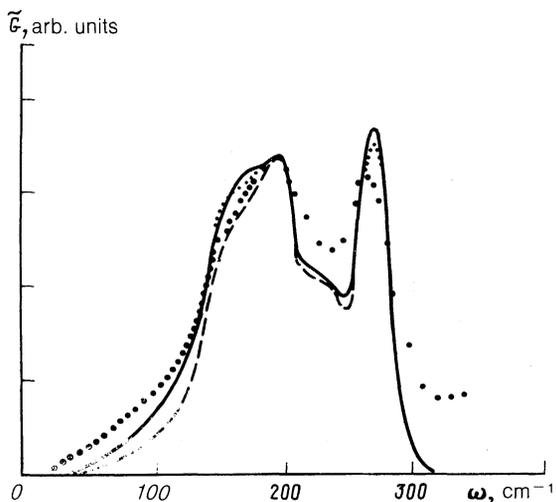


FIG. 7. Amplitude-weighted density of bulk vibrational states of a nickel crystal for several configurations of the free planes: Dashed line—(111); dotted line—(100); solid line—(110). The calculated data correspond to the 25th layer. The points are experimental data for 80 K.

tems. The deviation of the experimental points from the calculated curves in the low-frequency part of the spectrum (the deviation from a parabolic Debye law) is due to a coherent scattering effect. The incoherent approximation,⁴ which smooths out the angular distribution of the scattering intensity, is satisfactory when the difference between the scattering intensities at different angles is far smaller than the intensities themselves. This is not the case in the low-frequency region, so we observe a discrepancy. In the high-frequency region, the discrepancy between the experimental and theoretical results is due to multiphonon scattering.

Curve 1 in Fig. 8 shows the calculated density of bulk phonon states, $g(\omega)$, found from

$$g(\omega) = \frac{1}{N} \sum_j^{3N} \int_{Bz} d\mathbf{q} \delta(\omega - \omega_j(\mathbf{q})), \quad (7)$$

($3N$ is the total number of eigenfrequencies calculated for a 50-layer thin plate). Also shown in this figure, by curve 2, is $z(\omega)$ as calculated in the classical crystal-dynamics approximation.¹⁹ Curve 2 is taken from a handbook,²⁰ in which it represents bulk phonons of the Ni crystal. However, the very good agreement between the experimental and theoretical data in Fig. 7 shows that the density of states of the bulk phonons of this crystal can be described by curve 1.

5.2. Surface modes. A comparison of the experimental data in Fig. 2b with the theoretical curves in Fig. 6 leads to the conclusion that only the curves obtained for the (111) surface agree qualitatively with the experimental spectrum. In Fig. 9, the experimental spectrum is shown along with the AWDS spectrum calculated for the (111) surface with a force constant between layers 1 and 2 reduced by 20%. The theoretical curve, half the sum of the AWDS's for layers 1 and 2, indisputably reproduces the three characteristic peaks in the experimental spectrum as well as the valleys between them. The obvious qualitative agreement between the experimental and theoretical data suggests a predominant faceting of the surface of the particles with the (111) plane.

The question of the shape of the surfaces of small particles has been under discussion for a long time now.^{21,22} Since the structure of small particles in their interior is the same as

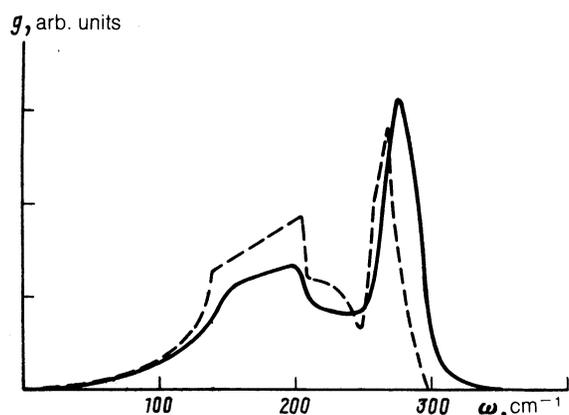


FIG. 8. Density of bulk phonon states of a nickel crystal. Solid line—Calculated for a 50-layer plate; dashed line—calculated in Ref. 20.

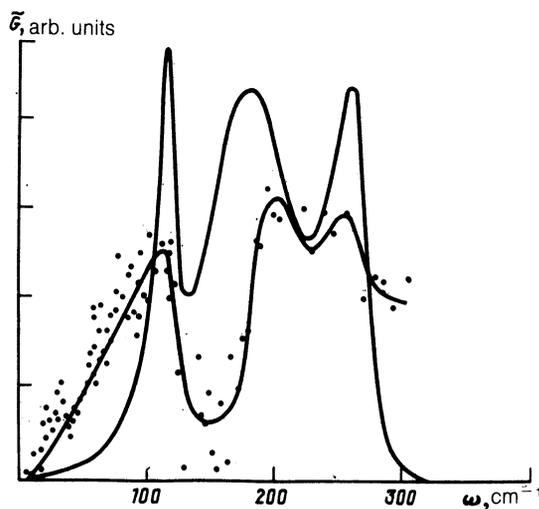


FIG. 9. Calculated half-sums of the amplitude-weighted densities of vibrational states of layers 1 and 2 in the configuration of a (111) free surface. The calculations were carried out for a ratio of 0.78 of the force constants between layers 1 and 2. The points show the experimental $\Delta\bar{G}(\omega)$ spectrum. The solid curve is drawn merely to aid the eye.

that in a bulk sample, the energy per unit volume is the same, so a minimum of the surface energy is the condition for stability of a certain surface shape of the particle.²² The faceting of fcc crystals ~ 200 Å in size should be dominated by the (111) and (100) surfaces (in a ratio of 4:1).²² So far, however, this conclusion has not been verified experimentally. Most of the experimental information about the faceting of particles comes from electron microscopy. The results which have been obtained are largely contradictory.

The surface shape has been found most accurately in a recent study of Pt particles 80 Å in diameter adsorbed on graphite.²² It was shown that the structure of the surface of these particles can be thought of as a sum of different surfaces in the proportions 0.37 (111) + 0.32 (100) + 0.35 (curved surfaces). The results for free particles might be different. Nevertheless, it can be regarded as an established fact that small metal particles with an fcc lattice have surfaces consisting predominantly of the (111) plane. Going back to Fig. 9, we can say that, despite the discrepancies in details, the observed qualitative agreement between the experimental and theoretical results is incontestable evidence that these Ni particles do indeed have a predominantly (111) faceting.

In analyzing the results in Fig. 9 we should bear in mind that they refer to an "unperturbed" Ni surface, while the experimental spectrum is a consequence of a motion of hydrogen atoms of water, "riding" substrate atoms. Possible changes in the substrate structure should also be taken into consideration. As it turns out, however, the surface vibrations of nickel in the (111) configuration are altered only slightly by adsorbed water.⁷ The AWDS spectrum due to the horseback-rider effect, for example, remains very much like the AWDS spectrum of the surface atoms of the substrate.

6. CONCLUSION

From the standpoint of modern surface science, which deals with well-characterized clean surfaces of single crys-

tals, the case of ultrasmall particles, highly active chemically, would hardly qualify as a good model. Nevertheless, these are real catalytic systems, and it is very important to know what happens at them. The results presented here shows that these samples can be studied successfully under certain favorable conditions, even if the results must meet stiff requirements. In the case at hand, the favorable condition is the presence of hydrogen on the surface, which leads to a large intensifying effect in inelastic neutron scattering by surface vibrations of the substrate. This effect is responsible for the difference between the inelastic-neutron-scattering spectra for macroscopic and microscopic Ni samples. It makes possible measurements of the difference spectrum, which corresponds to scattering by surface vibrations.

The calculations carried out here have yielded a very good description of the AWDS spectrum of bulk vibrations for the Ni crystal. The AWDS calculated for surface vibrations shows that the shape of the AWDS spectrum depends on the crystallographic configuration of the planes of the plate. This dependence could be used as a test for identifying an unknown surface configuration. Comparison of calculated and theoretical AWDS spectra has revealed qualitative agreement for the Ni(111) surface. It can be concluded from this agreement that these Ni particles are faceted primarily by (111) planes. This observation is in agreement with thermodynamic predictions of the dominant role of the (111) face in the equilibrium shape of the surface of small particles with an fcc lattice. It also agrees with some results from electron microscopy.

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Translated by D. Parsons