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LATTICE VIBRATIONAL SPECTRUM OF VANADIUM

by

K. KREBS

1963

Joint Nuclear Research Center
Ispra Establishment - Italy

Reactor Physics Department
Experimental Neutronics Service

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LATTICE VIBRATIONAL SPECTRUM OF VANADIUM

SUMMARY

The lattice vibrational spectrum of vanadium is calculated on the basis of four different force models. The comparison with a spectrum measured by neutron techniques shows that none of these "standard" models is completely satisfactory.

I. INTRODUCTION

Inelastic neutron scattering experiments have proven to be a powerful method in investigating the lattice dynamical properties of solids [1]. One of the first substances which had been measured was vanadium. In this case, due to its almost complete incoherent scattering cross section, the measured differential scattering is related directly to the vibrational spectrum.

Already the first measurements [2,3] showed spectra with a double peak as to be expected from general lattice dynamics, but especially at the higher frequency side they were not too conclusive. Since then new measurements [4,5] have been made, which show again the same general structure. In addition to this, also the behaviour at higher frequencies has been clarified to such an extent, that it seems now worthwhile to investigate the relation between the experimental frequency distribution and the results of a theoretical approach based on special force models.

II. THEORETICAL MODELS FOR THE LATTICE VIBRATIONAL SPECTRUM

The lattice vibrational spectrum of a crystal may be calculated from the matrix equation

$$(1) \qquad \left| d_{ik} - T\nu^2 \delta_{ik} \right| = 0 .$$

$M = \{d_{ik}\}$ is the dynamical matrix, the elements of which depend on the lattice propagation vector and on the force constants of the atomic model. ν is the phonon frequency, T a constant depending on the force model considered. The frequency distribution is obtained solving equation (1) for a large number of propagation vectors within the first BRILLOUIN zone and counting the number of times a frequency ν_i occurs in a certain frequency interval between ν_i and $\nu_i + \Delta\nu_i$. In order to find the d_{ik}-values we have to use special force models. This is done in four cases.

A) Born - von Karman Model

For vanadium, a bcc-metal, there are three elastic constants: c_{11}, c_{12} and c_{44}. The CAUCHY relation $c_{12} = c_{44}$ is not fulfilled. If we want to set up the equations of motion, we have therefore to introduce at least three atomic force constants. The relations between these force constants and the three elastic constants follow from the condition that for the limiting case of long waves the equations of motion reduce to the corresponding equations of the elasticity theory.

The simplest model, which contains three constants, is one with non-central interaction between nearest and central interaction between next-nearest neighbours. The corresponding dynamical matrix consists of the following elements [6]:

$$(2) \quad \begin{cases} d_{ii} = P(1 - C_1C_2C_3) + QS_i^2 - T\nu^2 \\ d_{ik} = S_iC_jS_k \end{cases} \qquad (i, j, k = 1, 2, 3)$$

$$P = \frac{2\,C_{44}}{C_{12} + C_{44}}\,, \quad Q = \frac{C_{11} - C_{44}}{C_{12} + C_{44}}\,, \quad T = \frac{2\,\pi^2 M}{a(C_{12} + C_{44})}$$

Here and for the following models we use the abbreviations

$S_i = \sin \pi a k_i$, and $C_i = \cos \pi a k_i$.

k_i is the i.th component of the phonon propagation vector $\underline{k}$ ($\underline{k} = 1/\lambda$), a is the lattice constant (= 3,0396. 10^{-8}cm), M is the mass of a vanadium atom. The elastic constants as measured by ALERS [7] are $c_{11} = 22.795$, $c_{12} = 11.870$ and $c_{44} = 4.255 \cdot 10^{11}$ dyn. cm^{-2} (room temperature values).

The force constants of this model are related to the elastic constants by the following relations:

$$\left.\begin{aligned} \alpha &= \frac{a}{2} c_{44} \\ \beta &= \frac{a}{4} (c_{12} + c_{44}) \end{aligned}\right\} \text{nearest neighbours}$$

(3)

$$\left.\begin{aligned} \alpha' &= \frac{a}{2} (c_{11} - c_{44}) \\ \beta' &= 0 \end{aligned}\right\} \text{next-nearest neighbours}$$

The result of a calculation using these relations is shown in fig. 1 as a histogram. The solid line curve represents the lattice vibrational spectrum which was derived from measurements of the inelastic scattering cross section of slow neutrons [4,5]. A previous calculation by SINGH and BOWERS [8] suffers from the fact that these authors used semi-empirical values for the elastic constants, which differ substantially from the values measured by ALERS [7].
The dashed curves in fig. 1-4 show the DEBYE spectrum, calculated for $\Theta = 388^\circ$ K, the value which corresponds to the elastic constants measured at room temperature.

B) DE LAUNAY's Model

As stated above, the CAUCHY relation does not hold for vanadium. With FUCHS [9] we may assume, that this is due to the presence of free electrons in metals. These electrons have a finite bulk modulus, but as a kind of gas they may not resist to any shear deformation. DE LAUNAY's theoretical approach [10], which considers first and second neighbour interactions, is based on a separation of each wave into a longitudinal and two transverse parts. Each longitudinal part is modified by taking into account the influence of the electron gas. The transverse parts are kept unchanged. The final dynamical matrix is set up in such a way that it reduces for long wavelengths to the one which is valid in the theory of elasticity. In DE LAUNAY's formulation the bulk modulus of the electron gas is then $K_L = c_{12} - c_{44}$.

The elements of the dynamical matrix are:

$$(4) \quad \begin{cases} d_{ii} = 1 - C_1C_2C_3 + QS_i^2 + RR_ip_i - T\nu^2 \\ d_{ik} = S_iC_jS_k + RR_ip_k \end{cases} \qquad (i,\ j,\ k = 1,\ 2,\ 3)$$

$$p_i = k_i/k$$

$$Q = \frac{c_{11}-c_{12}}{2\,c_{44}}\ , \quad R = \frac{c_{12}-c_{44}}{3\,c_{44}}\ , \quad T = \frac{\pi^2 M}{a\,c_{44}}$$

$$R_1 = p_1(1-C_1C_2C_3+S_1^2) + p_2S_1S_2C_3 + p_3S_1S_3C_2$$

$$R_2 = p_1S_1S_2C_3 + p_2(1-C_1C_2C_3+S_2^2) + p_3S_2S_3C_1$$

$$R_3 = p_1S_3S_1C_2 + p_2S_3S_2C_1 + p_3(1-C_1C_2C_3+S_3^2)$$

Force constants:

(5)
$$\alpha = \frac{a}{2} c_{44} \qquad \text{nearest neighbours}$$
$$\alpha' = \frac{a}{2}(c_{11} - c_{12}) \qquad \text{next-nearest neighbours}$$
$$K_L = c_{12} - c_{44} \qquad \text{bulk modulus of the electron gas}$$

Fig. 2 shows the calculated frequency histogram.

C) BHATIA's Model

BHATIA [11] assumes that the forces on any ion in the lattice consist of a) a central interaction between first neighbours, and b) an electronic interaction which in accordance with FUCHS's theory depends on the atomic volume alone.
We remember that the CAUCHY relation becomes invalid if there are interactions which depend only on volume changes. Assumption b) takes therefore the failure of the CAUCHY relation in metals into account.

The effect of b) has been calculated assuming that in absence of any vibration the ionic charge is uniformly smeared out over the entire lattice. The electrostatic potential V of the system is then a constant. Due to lattice vibrations, a change of this potential will occur and the force on each ion due to this change becomes simply -e grad V. The calculation shows that this force is different from zero only for longitudinal vibrations.

So far it seems that there are only two atomic constants for this model, one for the central interaction between first neighbours, and one corresponding to the influence of the electron gas, which itself can be related to the electronic number density by the THOMAS-FERMI-DIRAC-method. However, BHATIA has pointed out the important fact that the lattice, under the central interaction alone, is not in equilibrium, i.e. in a series expansion of the central interaction the first derivative does not vanish. This non-vanishing first derivative introduces a third constant into the theory. The relations of the force constants to the elastic constants are found in the usual way comparing the equations of motion in the long wave length limit with the equations of the theory of elasticity. The constant which is related to the electronic contribution is $K_B = c_{11} - c_{44}$ (for a bcc-lattice). As one can show, this is just the bulk modulus of the electron gas which is therefore related to the elastic constants in a different way than in DE LAUNAY's theory.

The elements of the dynamical matrix for this model are:

$$(6)\quad \left\{ \begin{aligned} d_{ii} &= P(1 - C_1C_2C_3) + \frac{Rk_i^2}{1+Sk^2} - T\nu^2 \\ d_{ik} &= -S_iC_jS_k + \frac{Rk_ik_k}{1+Sk^2} \end{aligned} \right. \qquad (i, j, k = 1, 2, 3)$$

$$P = \frac{2c_{44}}{c_{11} - c_{12} - 2c_{44}}, \quad R = \pi^2 a^2 \frac{c_{11} - c_{44}}{c_{11} - c_{12} - 2c_{44}}$$

$$S = \frac{\pi^2 a^6}{4e^2}(c_{11} - c_{44}), \quad T = \frac{2\pi^2 M}{a(c_{11} - c_{12} - 2c_{44})}$$

(e: electronic charge)

Force constants:

$$(7)\quad \left. \begin{aligned} \gamma &= \frac{3}{16}(c_{11} - c_{12}) \\ \gamma' &= -\frac{9}{16}(c_{11} - c_{12} - 2c_{44}) \end{aligned} \right\}$$ related to the first and second derivatives of the central interaction potential between first neighbours

$$K_B = c_{11} - c_{44}$$ bulk modulus of the electron gas

The histogram, obtained from eq. (1) is plotted in fig. 3.

D) FINE's Model [+)]

With this model the assumption is made that the lattice vibrations are only influenced by forces between ions and not by the interaction with electrons. For the ionic lattice we take into account central forces between first and second neighbours. The electrons are supposed to behave like a gas so that their energy depends only on the volume.

The elastic constants are assumed to be separable into a lattice and an electronic part:

$$(8)\quad c_{11} = c_{11}^{L} + c_{11}^{E}\ ;\quad c_{12} = c_{12}^{L} + c_{12}^{E}\ ;\quad c_{44} = c_{44}^{L} + c_{44}^{E}$$

Since $c_{11}-c_{12}$ and c_{44} specify deformations without volume change, we have further, according to FUCHS [9],

$$(9)\quad c_{11}^{E} - c_{12}^{E} = 0\ ,\quad \text{and} \quad c_{44}^{E} = 0\ .$$

The third assumption which is made is the validity of the CAUCHY relation for the lattice part:

$$(10)\quad c_{12}^{L} = c_{44}^{L}\ .$$

From the usual long wave length limit of the dynamical equations, together with the relations (8), (9) and (10), we find then for the force constants

$$(11)\quad \begin{aligned} \alpha &= \frac{a}{2} c_{12}^{L} = \frac{a}{2} c_{44}^{L} = \frac{a}{2} c_{44} && \text{next neighbours} \\ \alpha' &= \frac{a}{2}(c_{11}^{L} - c_{12}^{L}) = \frac{a}{2}(c_{11} - c_{12}) && \text{next-nearest neighbours} \end{aligned}$$

+) Equivalent to the models of MONTROLL and PEASLEE [13], resp. of BAUER [14].

The elements of the dynamical matrix are:

$$(12)\quad \begin{cases} d_{ii} = 1 - C_1 C_2 C_3 + Q S_i^2 - T\nu^2 \\ \\ d_{ik} = S_i C_j S_k \end{cases} \qquad (k,\ j,\ k = 1,\ 2,\ 3)$$

$$Q = \frac{c_{11} - c_{12}}{2\ c_{44}} \ ; \qquad T = \frac{\pi^2 M}{a\ c_{44}}$$

With equation (10) it is assumed that the CAUCHY relation for the lattice contribution to the elastic constants holds. In this context a serious objection has been raised by BHATIA [11] and by DAYAL and TRIPATHI [15]. These authors emphasize the fact that the CAUCHY relation holds only if the entire interaction is central. They are not necessarily valid for the central part alone of an interaction which comprises also non-central terms. Since in the above model the CAUCHY relation is found to be fulfilled for the lattice part of the interaction, this model stands in contradiction to this principal argument.

The histogram of a calculation for FINE's model in the case of vanadium is given in fig. 4.

III. CONCLUSION

The main difference between the frequency distributions which were calculated for the models A, B, C and D lies in the position of the high-frequency peak. The low-frequency peak seems to be not very sensitive to the kind of model which is used. The more interesting it is to find that the experimental low-frequency peak does not appear at the frequency which the four theories predict.

The second experimental peak does agree with the theoretical one only in one case, namely for FINE's model. However, this is just that model against which one has the principal objection that it implies the validity of the CAUCHY relation only for a part of the total interaction, which itself is not entirely central. To this we may suggest two explanations:

1. The electronic contribution to the lattice vibrations is really neglegible and the failure of the CAUCHY relation for the experimental elastic constants is only a low-frequency phenomenon.

2. The true, yet unknown, model for the calculation of the lattice vibrations agrees accidentally with FINE's model, at least in respect to the approximate position of the two main peaks. One indication to this second possibility may be found from a calculation of the sodium dispersion curves by TOYA [16].

It remains to point out that the experimental curve shows a high-frequency tail and not the expected sharp cut-off. Neither of the four models considered shows the same high-frequency behaviour. The question of the high-frequency tail is therefore still open. This effect might be a matter of the conduction electrons, but there exists also the possibility that it is due to impurity scattering.

Finally we want to state that all the models presented are not able to represent the experimental curve over the whole frequency range. This is an interesting finding, since each of the four models has been used in the literature, e.g. to explain thermodynamic data. At least in the case of vanadium such applications are not justified.

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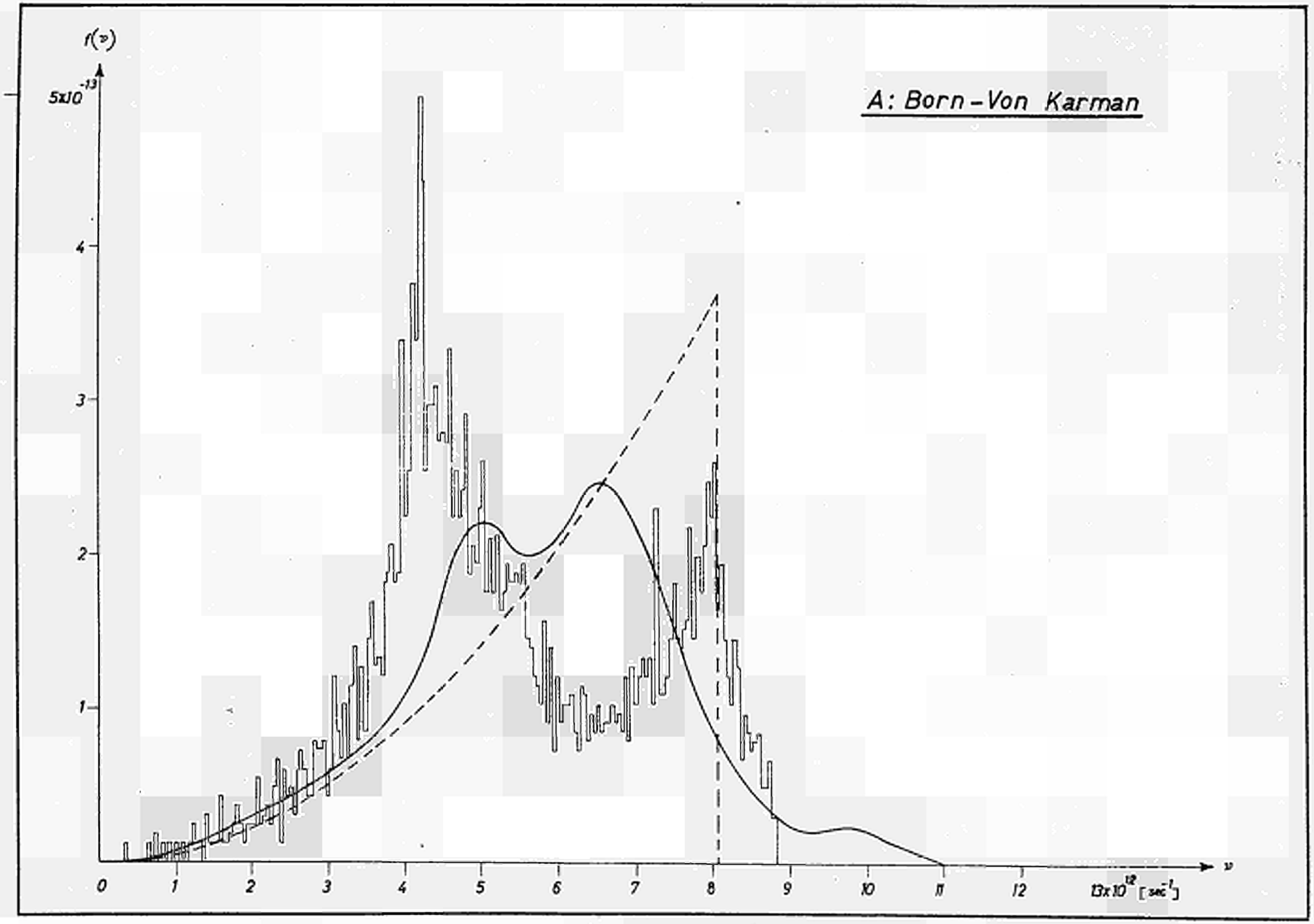

f(ν)
5x10^-13
4
3
2
1
0
1
2
3
4
5
6
7
8
9
10
11
12
13x10^12 [sec^-1]
ν
A: Born-Von Karman

FIGURE 1

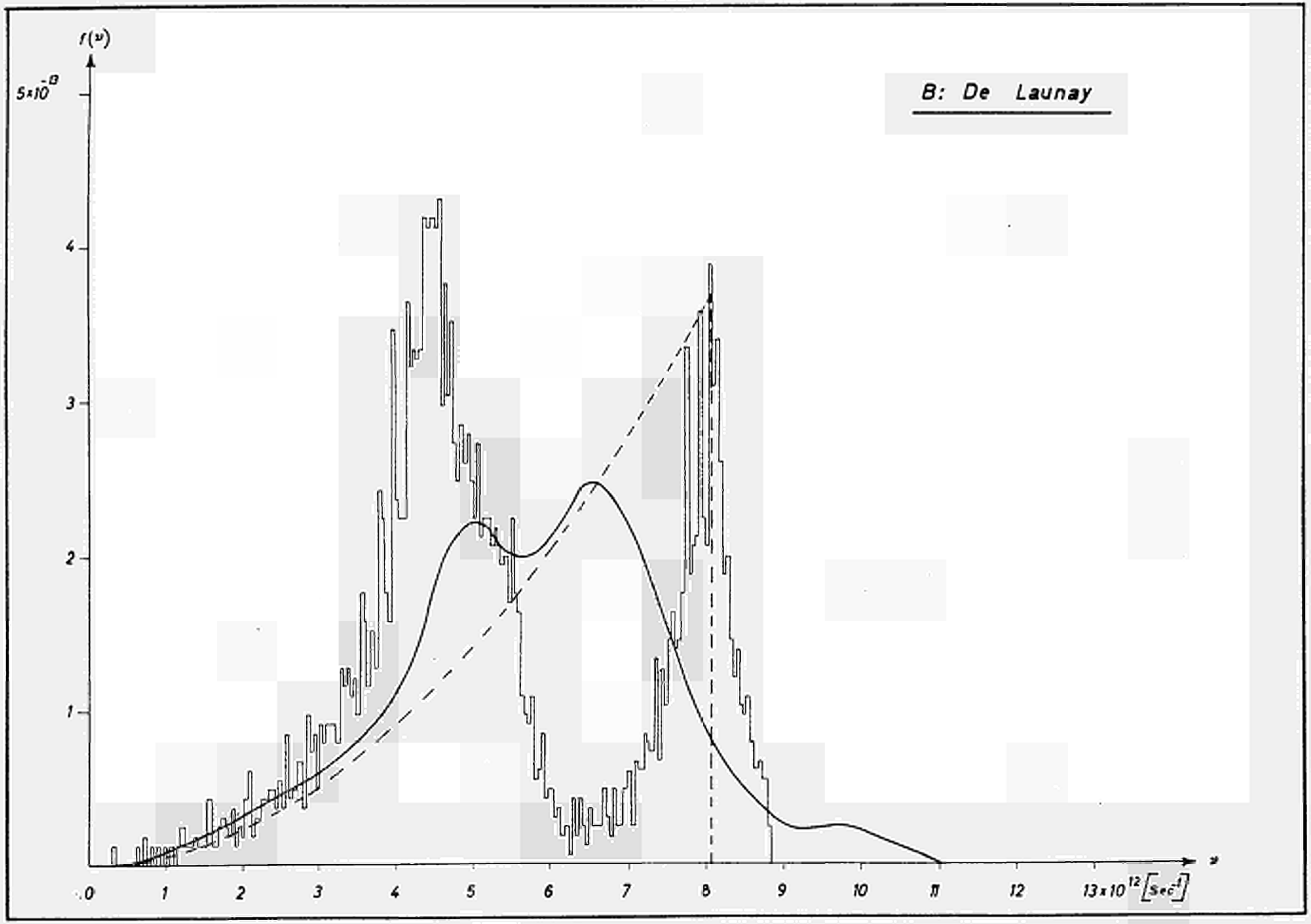

FIGURE 2

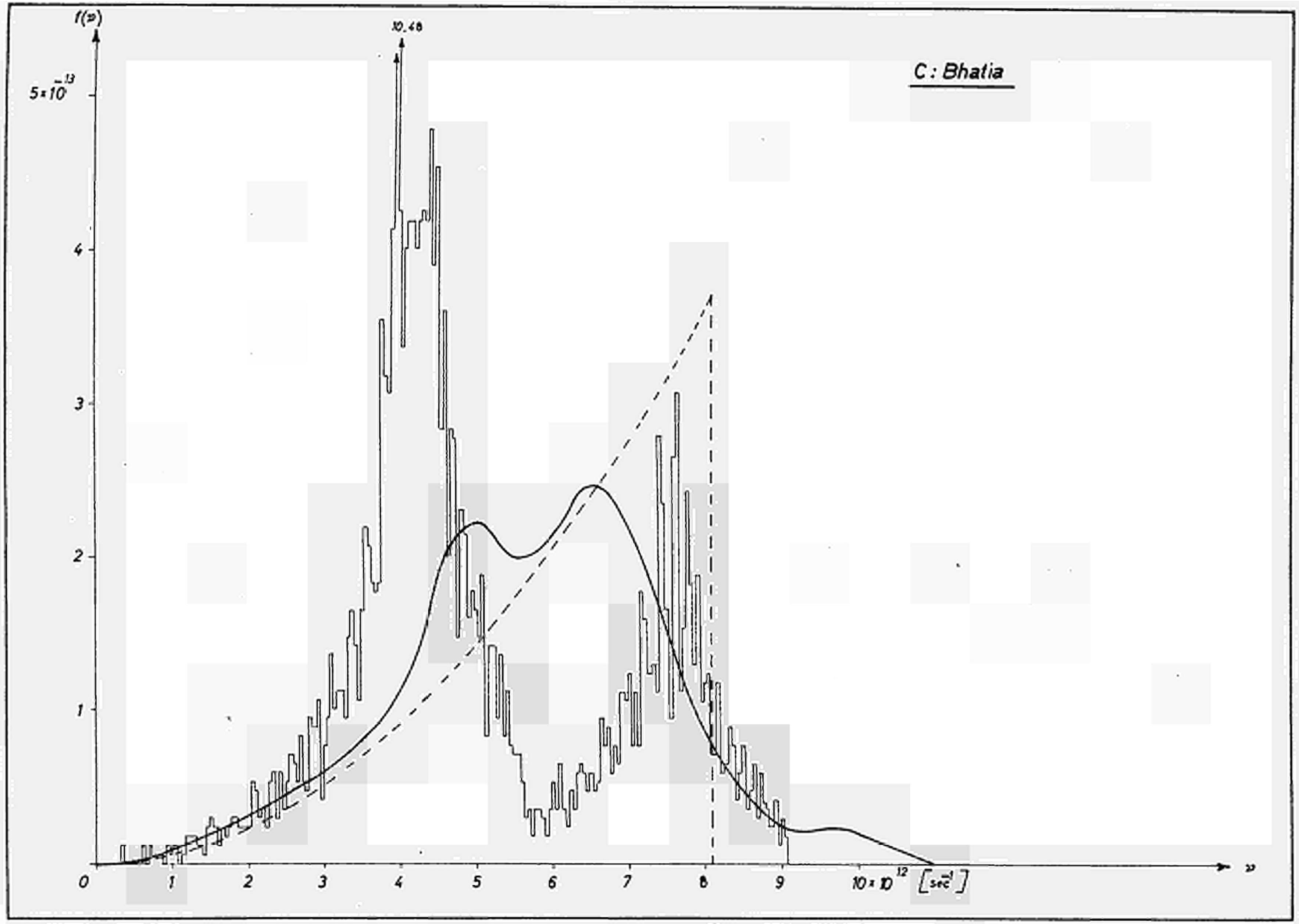

FIGURE 3

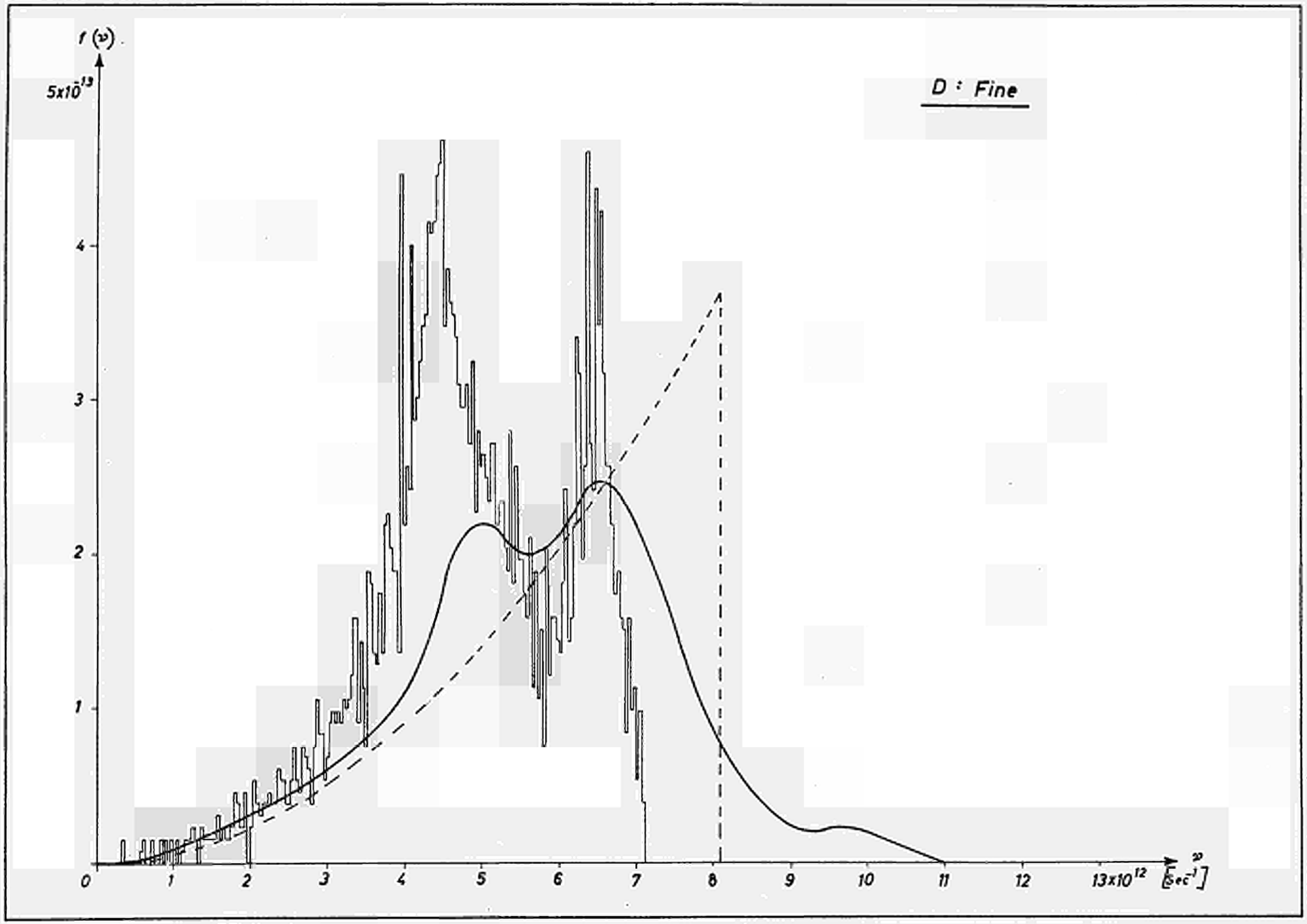

FIGURE 4