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INTERNAL FRICTION STUDIES OF THE OXYGEN SNOEK RELAXATION IN GROUP-Va TRANSITION METALS

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Résumé - Les pics de Snoek de O (ou N) dans les métaux Va montrent un élargissement extraordinaire à des concentrations élevées de O (N). Les expériences détaillées de frottement intérieur sur le Nb-0.7% O ultrapure confirment que cet élargissement est symétrique et correspond à une distribution des temps de relaxation continue qui est attribuée à une interaction repoussant des atomes de O qui s'étend à grandes distances ("anticlustering"). Les résultats ne sont pas en accord avec le modèle de "clustering" de Powers et Doyle. En ajoutant des faibles teneurs en N, on observe en plus un élargissement asymétrique du pic de Snoek de O au côté des températures élevées.

Abstract - Snoek peaks of O (or N) in Va metals exhibit extraordinary broadening at higher O (N) contents. Detailed internal friction measurements on ultrapure Nb-0.7% O confirm that this broadening is symmetric and corresponds to a continuous distribution of relaxation times, which is attributed to a long range repulsive interaction of O atoms ("anticlustering"). The results disagree with the predictions of Powers' and Doyle's clustering model. Addition of small amounts of N causes additional asymmetric broadening of the O Snoek peak on its high temperature side.

I - INTRODUCTION

In recent internal friction (IF) experiments on ultra-pure tantalum and niobium doped with oxygen only /1,2/ it was shown that with increasing oxygen concentration the Snoek peak is shifted to somewhat higher temperatures and symmetrically broadened. This observation is not in accordance with an early model derived by Powers and Doyle from IF measurements on Ta-O and Ta-N /3,4,5,6/ which was later also applied to Nb-O and Nb-N /7-9/. The basic assumption of this model is that the Snoek peak in concentrated solutions of interstitial foreign atoms (IFA) is composed of a superposition of several discrete relaxation processes originating from the relaxation of isolated IFA, of IFA-pairs, triplets etc. being formed by a tendency towards clustering. The main consequences of this *clustering model* are (i) an asymmetrical broadening at the high temperature side of the peak, becoming the more pronounced the higher the IFA concentration is, (ii) no marked shift of the peak temperature with the IFA content. Our experimental results on Nb-O and Ta-O on (i) symmetrical broadening and (ii) peak-shift were interpreted with a long range repulsive interaction of IFA, also called *anticlustering* /10/, leading to a continuous distribution of relaxation times. In recent papers on Nb-O /11,12/ these results were questioned and the earlier clustering model was favoured. This controversy prompted us to study Snoek relaxations in Nb-O in more detail /13/. Some of the results are presented in this paper.

II - EXPERIMENTS AND THEIR ANALYSIS

IF measurements were carried out with a computer-controlled inverted torsion pendulum in the frequency range of 1 Hz. IF and related quantities were determined from the free decay of the mechanical oscillations /13,14/. Measurements were taken with increasing temperature at a mean heating rate of 0.5 - 0.8 K/min. To enable reliable data processing about 400 data points were taken for each sample.

The results of two samples are presented in Fig. 1. Sample A was prepared from ultrapure niobium /15/ and carefully doped with 0.7 at.% oxygen /16/ (Fig. 1a). Sample B contained in addition to 0.7% O about 0.05% N (Fig. 1b). It shows a small N-Snoek peak in addition to the O-Snoek peak (higher than for sample A due to different texture). In Fig. 2 the O-Snoek peaks are plotted as $\log [Q^{-1}/Q_m^{-1}]$ vs. $[1/T - 1/T_m + (k/H) \cdot \ln(f/f_m)]$. Q_m^{-1} = height of IF peak, f_m = frequency at the maximum temperature $T = T_m$; $H = 1.23$ eV, see below. The term $k/H \cdot \ln(f/f_m)$ corrects a distortion of the IF curves due to the temperature dependence of $f^2(T)$ (comp. Figs. 1a,b, see /1,14/). The N-Snoek peak in Fig. 1b was subtracted by assuming a Debye relaxation (which should be correct for the low N content of 500 at.ppm) with relaxation parameters from /1,17/. Whereas in Fig. 2 the data points of sample A, being doped only with O, fall very closely on a symmetrical IF curve, the data of sample B, although the N peak is subtracted, exhibit an additional *asymmetrical* broadening on the high temperature side. In Fig. 3 the IF data of sample A are compared with theoretical calculations. Curve (1) is calculated for a Debye relaxation with parameters of dilute Nb-O alloys /14,17/. Curve (2) is calculated according to the clustering model by composing an IF curve of four Debye relaxations, for which the parameters published by Gibala and Wert /7/ for a sample with the same amount of oxygen are used. The data in Fig. 3 are again normalized with respect to peak height and peak temperature.

III - DISCUSSION AND CONCLUSIONS

From the results in Figs. 2 and 3 and from experiments published earlier /1,2/ the following can be stated:

Pure Nb-O. - (i) The Snoek peak is considerably broader than a Debye peak (Fig. 3). Continuous broadening of Snoek peaks for higher IFA-concentrations was already verified for Ta-O and Nb-O /1,2/. (ii) The broadening of the peak occurs rather symmetrically (Fig. 3 /1,2/). (iii) The broadened peak cannot be fitted by curve (2) in Fig. 3, calculated by composing four relaxation processes according to the clustering model. Curve (2) is highly asymmetrical. It coincides at low temperatures with the Debye curve. Above the peak temperature it shows flexures inherent in the (discrete) clustering model in discrepancy with the experimental curve. (iv) With increasing O-content Snoek peaks in Ta-O and Nb-O are shifted to higher temperatures /1,2/ indicating an enhancement of the activation enthalpy H , which, according to /13/, increases from 1.15 eV for Nb with 0.06% O to 1.23 eV for Nb with 0.7% O.

Influence of nitrogen. - Nitrogen causes additional broadening of the oxygen Snoek peak on its high temperature side, which apparently is due to an O-N interaction. At higher N-concentrations this behaviour was already reported by Powers and Doyle /6/ for Ta-O + N, and by Gibala and Wert /18/ as well as by Ahmad and Szkopiak /19/ for Nb-O+N. Whether this O-N interaction is attractive or repulsive is an open question.

Comparison with after-effect (AE)-experiments. - The recent controversy /11,12/ mentioned in the introduction is mainly based on AE-experiments with samples containing *small amounts of nitrogen* /7,12/. Okamoto /12/ reported that their AE-curves of Nb-O could not be fitted with a symmetrical lognormal distribution. This may be explained by the additional O-N interaction. By reanalysing experiments of Gibala and Wert /7/, Cost /11/ derived 3 relaxation times for Nb-O which are approximately identical with those used for calculation of curve (2) in Fig. 2. Cost furthermore analysed AE curves obtained in our laboratory for a dilute, ultrapure Nb-O alloy containing 0.063% O. He essentially obtained a single relaxation time only and argued that the experiments were not carried on long enough for also finding longer relaxation times. However, for the low O-concentration involved O-O interactions (clustering or anti-clustering) are not to be expected at all, and these experiments were used to measure the temperature dependence of the relaxation time for *dilute* Nb-O alloys /14/ and not as an evidence against the clustering model.

In general it is our experience that AE-experiments suffer from two difficulties: (i) The smallest resolvable relaxation strength is in the order of 10^{-4} , whereas IF experiments allow a resolution of 10^{-6} to 10^{-5} . (ii) In AE the strains at zero and infinite time can only be obtained by extrapolation with uncertain assumptions. Therefore, in spite of well established methods for analysing AE measurements in terms of superimposed decay curves with a spectral distribution of relaxation (life-) times we believe in a better resolution of the "fine structure" of relaxation time spectra by IF measurements to discriminate between discrete and continuous distributions.

Conclusions. - The continuous broadening of the IF curves with increasing O concentration reported earlier is thought to be confirmed by the present internal friction experiments on ultra-pure Nb doped with 0.7% O. This broadening is accounted for by a continuous distribution of relaxation times, which is attributed to a long range repulsive interaction of oxygen atoms. The additional asymmetrical broadening of the O peak caused by even small traces of nitrogen obviously indicates an interaction between N- and O-atoms, the nature of which has to be cleared up still.

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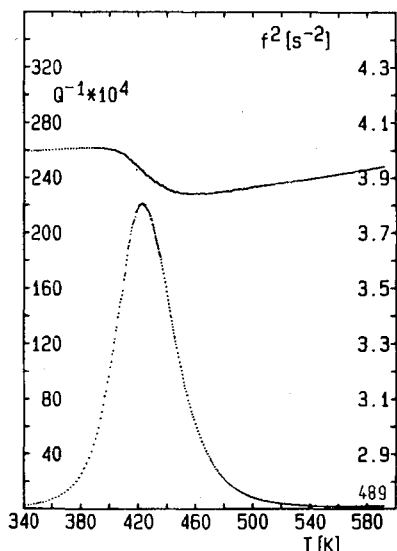


Fig. 1a - IF and f^2 vs. T plots for Nb with 0.7% O (sample A).

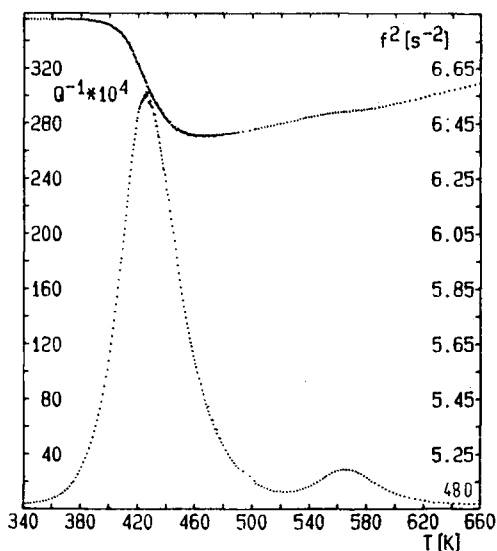


Fig. 1b - IF and f^2 vs. T plots for Nb with 0.7% + 0.05% N (sample B).

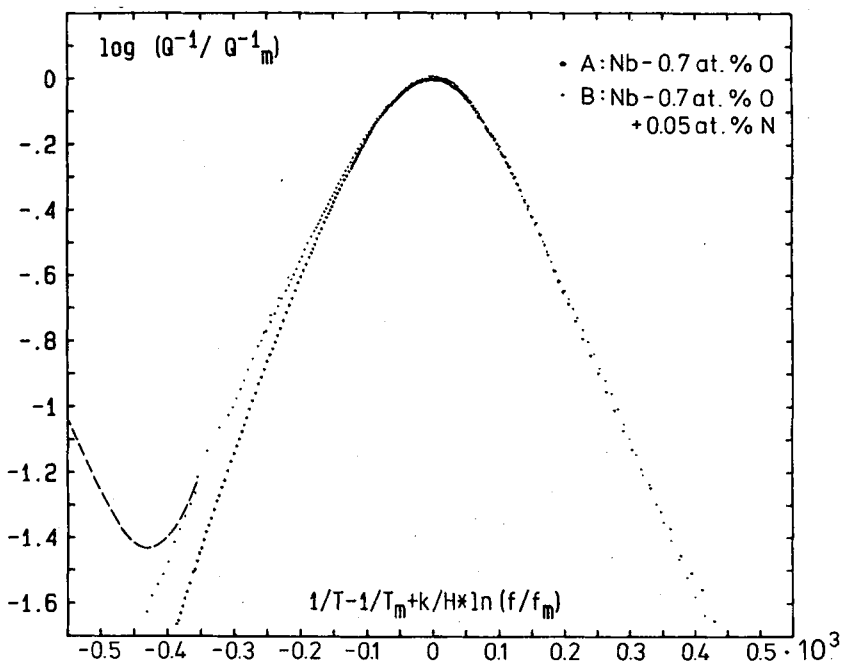


Fig. 2 - $\log [Q^{-1}/Q_m^{-1}]$ vs. $[1/T-1/T_m+(k/H)\ln(f/f_m)]$ - plots for samples A and B. --- without subtraction of the N-Snoek peak.

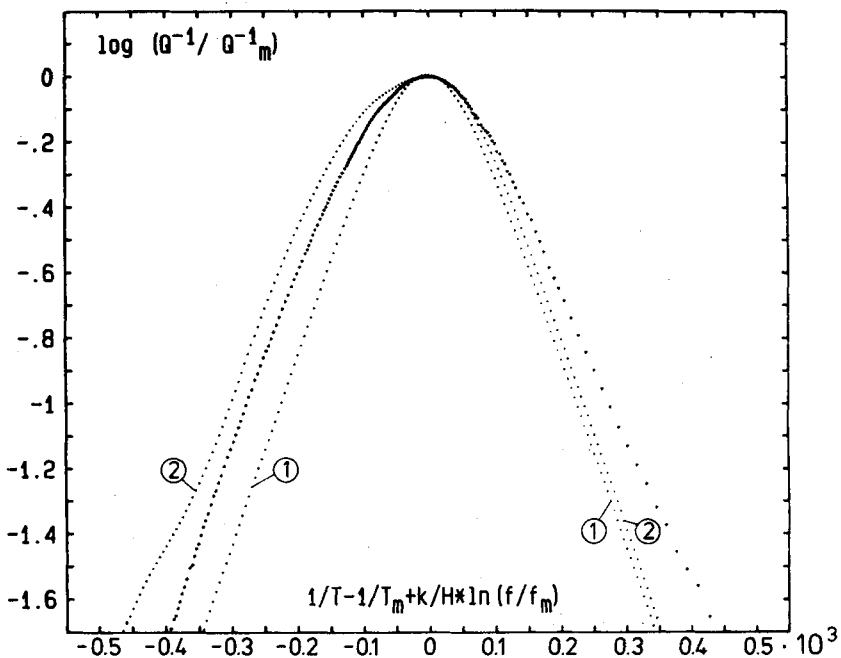


Fig. 3 - $\log [Q^{-1}/Q_m^{-1}]$ vs. $[1/T-1/T_m+(k/H)\ln(f/f_m)]$ - plots for sample A compared with a Debye relaxation (curve 1), and with 4 Debye relaxations acc. to /7/ (curve 2).