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An Examination of a Proposed Experimental Method for Studying Anomalous Snoek Peaks

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It is proposed that an internal friction experiment using frequency as the variable should be capable of furnishing information about the origin of anomalous Snoek peaks. In order to test this proposal an attempt has been made, and is now reported, to numerically analyse synthesised experimental data. The results show that, given suitably precise experimental data, the analysis can return the number of anomalous peaks together with their characteristics. A subsequent choice by the experimenter of a model to explain the concentration-dependence of the peaks, allows interaction energies to be deduced.

1. Introduction

One of the main tools in the investigation of binding energies of foreign atoms, such as interstitials, in a metal or alloy, is the internal friction experiment. Anelastic relaxation processes of these atoms in their matrix produces resonance peaks in the internal friction response at the appropriate frequencies. An analysis of the internal friction spectrum as a function of frequency should therefore yield information on these binding energies. In practice, since the range of frequency obtainable in the laboratory has hitherto been insufficient, frequency has been kept fixed while the spectrum is measured over a range of temperature: this is possible because of the exponential $1/T$ dependence of the relaxation times of the anelastic processes (see equation 2 below). One disadvantage of such a procedure is the difficult spectrum analysis when the peak strengths (as well as the peak relaxation times) depend on the temperature, as we believe they do for certain systems. Such difficulties do not arise when frequency is a variable, with the temperature held constant. Therefore we have set ourselves the task of seeing what can be done with an isothermal variable-frequency experiment, taking into account the fact that the frequency range is severely limited. Since no experimental results are available we have simulated an experiment (including experimental errors) based on a reasonable model for a system where we have good reasons to believe that the peak strengths are temperature-dependent. Having simulated "experimental" data with all the experimental parameters, in particular the frequency range, set to attainable values, we have then analysed these data with the aid of a computer and compared the results with the (known) correct values. The analysis (and its limitations) are discussed in detail; the main conclusion is that an isothermal variable-frequency experiment is feasible and yields a spectrum that can be adequately analysed.

The internal friction Q^{-1} caused by an anelastic process is given by the relation [1]

$$Q^{-1} = \Delta \frac{\omega\tau}{1 + \omega^2\tau^2} \cdot$$

An example of a process which is closely described [2] by this expression is the Snoek relaxation [3] caused by the stress-induced ordering of interstitial atoms between octahedral sites of a bcc lattice. In this instance Δ, the relaxation strength, is a measure of the dissolved interstitial atom fraction, τ is the relaxation time and ω is the atomic jump frequency ($= 2\pi f$, f

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being the oscillation frequency of the specimen).

Internal friction (damping) experiments are usually carried out as a function of temperature: taking some constant value of f and

$$\tau = \tau_0 \exp \frac{E}{RT},$$

we obtain a damping peak which is an even function about the reciprocal of a temperature T_{m} (corresponding to the condition $\omega\tau = 1$) and of a height $\Delta/2 = Q_{\mathrm{max}}{}^{-1}$. By carrying out experiments at different frequencies on an alloy of known dissolved interstitial fraction n_{I} the values of τ_0, E (the activation energy of the process) and the proportionality factor K in the relation

$$\text{atom fraction of interstitials} = \frac{KQ_{\mathrm{max}}{}^{-1}}{100} = \frac{K\Delta}{200},$$

can be determined.

However, the problem of analysis becomes severe if the interstitials can occupy more than one type of site, such as normal lattice sites and those adjacent to substitutional atoms possessing a different E value. Further peaks are then observed at the appropriate T_{p} and the measured internal friction is the sum of terms of the above type with differing τ and Δ. Should the component peaks overlap, then their separation requires special analytical techniques.

In many alloys, substitutional atoms do produce such extra peaks – known as *anomalous peaks* – and typical additions are manganese [4–7], silicon [8–11] (Fast [12] has raised doubt that this element can produce anomalies) or vanadium [13, 14] to iron-nitrogen. The origin of the anomalies, i.e. the location of the interstitials responsible, is under debate, and interest in the problem has increased because manganese-nitrogen groups evidently strengthen the solid solution of iron [15].

A preliminary attempt [16] to analyse the observed anomalous peak in iron-vanadium-nitrogen alloys [13] indicated that it was really made up of at least two anomalous Snoek-type peak contributions which were thought to result from the association of an increasing number of nitrogen atoms with dissolved vanadium atoms forming different types of complexes. An interaction energy was derived but the neglecting of the effect of temperature [16, 17], which alters the distribution of interstitials during the experiment, makes the interaction energy approximate.

When there is more than one peak the spectrum to be analysed is a sum of terms of the type introduced above:

$$Q^{-1} = \sum_r \Delta_r \frac{\omega\tau_r}{1 + \omega^2\tau^2{}_r}, \tag{1}$$

with

$$\tau_r = \tau_{r0} \exp \frac{E_r}{kT}. \tag{2}$$

Here in equation 1 the index r labels the peaks, and τ_r and Δ_r are respectively the relaxation time and strength of the rth peak. Equation 2 expresses the temperature-dependence of τ_r in terms of the constant τ_{r0} and the activation energy E_r for the complex giving rise to the rth peak. As mentioned above, the different complexes considered here are either those consisting of a single isolated interstitial (giving rise to the normal Snoek peak) or those consisting of a substitutional atom grouped with one or more interstitial neighbours (giving rise to the anomalous peaks). Under the assumption that complexes involving the same number of interstitials, contribute to the same peak (the same Δ_r) [16], the relationship between the relaxation strength Δ_r of the rth peak and the interstitial fraction n_r in the complex giving rise to that peak is

$$n_r = \frac{K_r\Delta_r}{200}, \tag{3}$$

The proportionality factors K_r may differ from peak to peak.

As pointed out earlier, the major problem in investigating the origin of the anomalous peaks is the separation of each from the measured spectrum. In an experiment where the temperature is varied at fixed frequency the main reasons rendering the peak-analysis difficult are the following:

(*i*) The relaxation strengths Δ_r may be temperature-dependent so that the peaks are not symmetrical about their centres in the Q^{-1} versus $1/T$ plot; this applies particularly to the anomalous peaks. The primary cause of this is the temperature-dependence of the distribution of interstitials among the various types of complex (i.e. of the set of n_r) which becomes more pronounced as the substitutional-interstitial interaction energy increases. A secondary cause is the inherent temperature-dependence of the proportionality factors K_r, which are proportional to T according to the theory of the Snoek peak due to Polder [18] (however, the experimental verification [19] of this has been doubted [20]).

(*ii*) The values of the K_r in equation 3 are not known for any anomalous peak; they are indeed known to vary with alloying and grain size for the Snoek peak itself [21].

(*iii*) In the case of the anomalous peaks neither the τ_{r0} nor the E_r are known (however see the remarks in section 2 for the τ_{r0}).

As an alternative approach to using temperature as the independent variable at fixed frequency, *frequency* itself can be employed as the independent variable of an *isothermal* experiment. This in itself is not a novel idea but it presents the advantage that the Δ_r and τ_r are then constant over the whole range of the independent variable, in contrast to the case when the temperature is varied. Provided that the peaks are anelastic the damping spectrum can be analysed in terms of equation 1 for varying ω. The strict constancy of the Δ_r and τ_r means that the difficulty (*i*) above in the variable-temperature experiment is here circumvented; in particular the peaks are symmetric about their centres in a Q^{-1} versus $\log \omega$ plot. The spectrum may be analysed to give first the Δ_r and τ_r for each peak, and subsequently the K_r can be derived to give the interstitial fractions n_r.

In using frequency as an independent variable, we are still faced with a serious problem however: only a limited range of frequency is available and so only part of the damping spectrum can be analysed isothermally. It is one of the main objects of the present work to present a method of handling such limited data, in order to be able to define the conditions to be fulfilled in reality, to enable a useful analysis to be made, and to see if these conditions can be achieved. If such a method is feasible, it might prove a powerful tool in investigating the anomalous Snoek peaks.

Unfortunately no experimental data were available to the authors, so we proceeded in the following way. A system was taken for which a *model* has been proposed that provides us with formulae for the fractions n_r as functions of T and other determined quantities (binding energies, total interstitial content, etc.) from first principles; details of the model are given in section 2, below. Then by taking definite values for these quantities and also for the proportionality factors K_r of equation 3 and the E_r and τ_{r0} of equation 2, it is clearly possible to trace curves of Q^{-1} as given by equation 1 as a function either of T or of ω. However, rather than the true curves, we are interested in the "experimental" curves that might result from observations on a system with the same values of the quantities referred to above. To simulate such curves, "experimental data" were computed by adding a randomly generated experimental error to the true values predicted by the model. In this way "experimental" spectra were obtained for Q^{-1} for both the varying-temperature and varying-frequency cases. From the varying-frequency spectra at a fixed (known) temperature, a peak analysis was made to recover the values of the quantities fed into the curves; a comparison was then made with the true values of these quantities. The same was done with the varying-temperature spectra. We shall see that the analysis shows that the frequency-varying "experiments" yield much more accurate values than the fixed-frequency ones; for this reason they would provide the more useful experiment in a practical case.

Finally we should point out that, while of course the details of the method presented here depend on the system chosen, the line of investigation proposed – observation and analysis of a spectrum over a range of frequency at fixed temperature – should be quite generally useful for *any* system giving an anelastic peak spectrum behaving as in equation 1, whatever the damping mechanisms may be. This is particularly true whenever the Δ_r (and τ_r) depend on temperature in some unknown or complicated manner. Furthermore no knowledge of the form of the τ_r or Δ_r (as expressed e.g. through equations 2 and 3) would be required, in contrast to the variable-temperature case.

2. The Model and "Experimental" Data

The system chosen for analysis is the iron–vanadium–nitrogen one already mentioned in section 1 because for this system a model has been proposed [16] to account for some experimental results of Fast and Meijering [13]. The model used in this paper (which differs from the one in reference 16 in only one detail) is the following. The alloy is bcc iron with substitutional vanadium and with interstitial nitrogen atoms which are assumed to occupy octahedral sites. Denoting substitutional atoms by X and interstitial atoms by I, the model postulates that X–I pairs and X–I–I trios are formed in thermodynamic equilibrium under the influence of interaction energies (in the alloy) B_p and B_t

respectively, where the interaction energy is the energy difference between a jump into and out of an associated site. The possible existence of quartets and other complexes is neglected (it is here that this model differs from the one in reference 16; X–I–I–I quartets are allowed in the latter). It is assumed that trios differing only in the placing of the two interstitials in the six octahedral sites around the substitutional atom are anelastically equivalent. More precisely: the two interstitials jump between associated sites independently of one another, and also the binding energy B_t of a trio is the same whatever pair of sites they occupy. Thus there are just three complexes giving rise to peaks: the "free" interstitials responsible for the normal Snoek peak and the pairs and trios responsible for two closely spaced anomalous Snoek-type peaks forming together the observed total anomalous peak. The model then predicts [16] the atom fractions n_1 (free), n_2 (pairs) and n_3 (trios)* of interstitials in these three complexes as obtainable from the equations

$$n_2 = 2n_S n_1 \exp\frac{B_p}{kT}\,, \qquad n_3 = \frac{10}{3}\, n_S n_1^2 \exp\frac{B_p + B_t}{kT}\,, \tag{4}$$

with

$$n_S + n_2 + \tfrac{1}{2} n_3 = n_X\,, \qquad n_1 + n_2 + n_3 = n_I\,, \tag{5}$$

where n_S, n_X and n_I denote the unassociated substitutional, total substitutional and total interstitial fractions respectively. The combinational factors in equation 4 are a consequence of the octahedral siting of the interstitials in the first shell around the substitutional atoms in the bcc metal. A typical behaviour of the three fractions n_1, n_2 and n_3 is shown in fig. 1a (the computation of which is indicated below); it can be seen that there is strong variation with temperature.

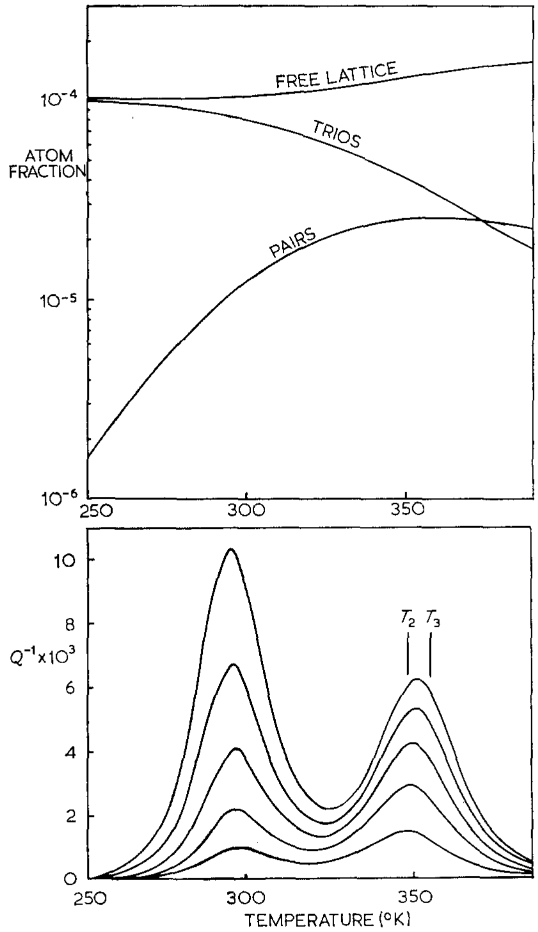

Figure 1 (a) The effect of temperature on the distribution of interstitials in the case of the model discussed in the text. The curves were computed from equations 4 and 5 for the case $n_I = 2 \times 10^{-4}$, $n_X = 10^{-4}$, $B_p = 0.24$ eV and $B_t = 0.29$ eV. (b) Computed internal friction spectra for the present model for the same interstitial fractions as those given in fig. 2.

The damping spectrum of the system is given by equation 1 with $r = 1, 2, 3$ referring, respectively, to the peaks produced by the interstitials in the free lattice, pairs and trios. The relaxation strengths Δ_r $(r = 1, 2, 3)$ are related to the corresponding atom fractions n_r $(r = 1, 2, 3)$ as computed from equations 4 and 5 by 3; and the relaxation times τ_r $(r = 1, 2, 3)$ follow the law 2. The spectra Q^{-1} for varying frequency or temperature at different values of total fractions n_I and n_X can now be computed, once we have assigned values to the basic parameters appearing in the model. These basic parameters are, as is seen from equations 1 to 5, the three proportionality factors K_r of equation 3, the three activation energies E_r and relaxation time

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*The relationship of the interstitial atom fractions n_1, n_2 and n_3 in the three complexes with the atom fractions of the three complexes themselves is $n_1 = n_i$, $n_2 = n_p$ and $n_3 = 2n_t$, where n_i, n_p and n_t denote respectively the free interstitial, pair and trio atom fractions in the notation of the reference 16.

constants τ_{r0} of equation 2 and the two binding energies B_p and B_t of equations 4 and 5. Values for the parameters were of course chosen to be as realistic as possible, and in particular to accord with known anelastic characteristics of the Fe–N system. The three proportionality factors K_r were chosen as unity [21]. For the relaxation times τ_{r0} we accept Stephenson's [22] conclusion that they are all equal to the same constant, universal for Snoek-type processes, in a given metal; from his analysis this constant is 4.225×10^{-15} sec in bcc iron. The activation energy for the normal Snoek peak was taken as $E_1 = 18.350$ kcals/mole from Lord and Beshers [20], and the activation energies for the peaks due to the pairs and trios as $E_2 = 21.800$ kcals/mole and $E_3 = 22.250$ kcals/mole respectively. The last two values are consistent with the position of the total anomalous peak observed by Fast and Meijering [13]. Finally, the binding energies were taken as $B_p = 0.24$ eV and $B_t = 0.29$ eV on the basis of a previous study [16] of the system.

To give an idea of the spectra obtained from the above model we plot curves for Q^{-1} versus T at a fixed frequency of $\omega = 2\pi$ for a temperature range of 250 to 390° K. They are shown in fig. 1b. The substitutional atom fraction n_X was set at 10^{-4} for all curves, and the five different interstitial atom fractions n_I yielding the five curves are in the range 2 to 20×10^{-5} inclusive. The low value 10^{-4} for n_X was chosen, as it corresponds to the amount of vanadium estimated by Fast [23] to be in solution in his study of the Fe–V–N system. Further, the value of n_X should be chosen so that the peaks being investigated are of comparable height, which is the case for $n_X = 10^{-4}$ at the present binding energies. The same value for n_X is maintained throughout the entire work.

The midpoint of the total anomalous peak of fig. 1b is at about 353° K, and this was the temperature chosen for the isothermal variable-frequency spectra. The Q^{-1} versus log ω plots for the above model, at $T = 353°$ K and for the same five values of interstitial fraction n_I as used in fig. 1b, are given in fig. 2 (full lines). The "frequency peak" occurs roughly in the middle of the log frequency range of 0.5 to 50 Hz at this temperature. For two of these spectra the three component curves representing the free interstitial, pair and trio contributions are also indicated (broken lines).

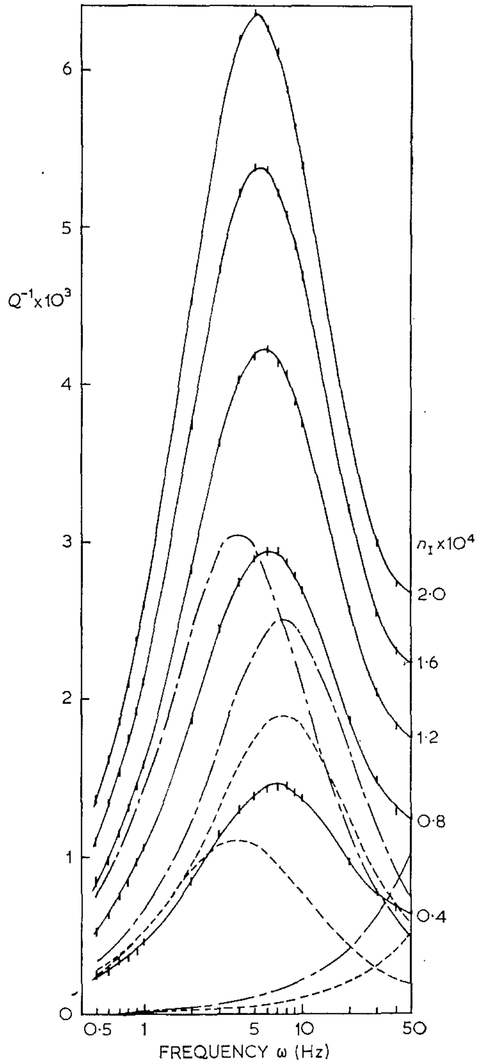


Figure 2 Some of the computer-produced internal friction spectra, taken as a function of frequency, used in the analysis discussed in the text. The spectra were evaluated at a temperature of 353° K and the component curves of two of the spectra, n_I equal to 0.8 and 1.6×10^{-4}, are shown as dashed and dash-dot curves respectively. The error bars indicate the "experimental" data for the case when $\alpha = 2 \times 10^{-5}$.

Knowing the exact spectral curves for the model (as given e.g. in figs. 1b and 2), we now wish to simulate the spectra such as an experiment might give for the same system, and analyse these spectra to recover the values of the parameters. We can then compare these values with the correct ones to get an idea of the accuracy of the results such an "experiment" would yield. We are principally interested in isothermal "experiments" at variable frequency, for reasons given in section 1 (strong temperature-dependence of the Δ_r). Our programme is the following:

(*i*) Simulation of experimental data for Q^{-1} versus $\log\omega$ spectra. This is done from the exact curves (such as those in fig. 2) by applying a randomly generated error to the correct values. The error function must correspond to reality as much as possible; a study of the literature convinced us that it was reasonable to assign a maximum tolerance to a given experiment and add a random error to each computed Q^{-1} value. The limiting tolerances chosen were $\pm 10^{-5}$, $\pm 2 \times 10^{-5}$ and $\pm 3 \times 10^{-5}$, thus giving three "experimental" sets of data of differing "accuracy", each for ten different values of n_{I}. These sets of data with their associated tolerances are hence those which would remain to be analysed, after the subtraction of background damping in a real experiment.

Some of the computer-produced data is shown in fig. 2 for five of the n_{I} values. One object of taking a range of tolerances was to discover the upper limit which the analytical technique could handle.

Representing these data as "experimental" obviously implies that the frequency range, temperature and values of n_{I} will already have been chosen by the experimenter. We cannot expect to measure the whole internal friction curve isothermally as a function of frequency and must therefore work within a limited frequency bracket. The equipment developed by Martinet [24] for example, covered only one decade of frequency, taking about 30 sec to stabilise a new frequency. However, two decades are possible, though perhaps at the limit, using equipment of this type; therefore we take 0.5 Hz to 50 Hz as our frequency range and consider this to be experimentally realisable. With this frequency range fixed by the equipment, the temperature (which can presumably be set to any desired value) must be set to allow study of the most useful part of the damping spectrum. We want to include as much of the anomalous peak as possible; and in fact we need only include sufficient of the normal Snoek peak "tail" to permit an accurate estimate of its height, because in practice its relaxation time is always known (i.e. in our notation τ_{10} and E_1 are known, and τ_1 can be calculated from equation 2 for any desired temperature). We shall therefore, here and henceforth, assume that τ_1 is known for any T and shall use this fact in the data analysis below. To fix the temperature of the "experiment" in accordance with these remarks, it is supposed that a preliminary run has been made for fixed frequency and variable temperature; the temperature is then chosen to be at about the middle of the anomalous peak, here at $T = 353°$ K. Finally, the values of n_{I} are always known by the experimenter, as is also the value of n_{X} which is the same for all "runs", and is given above.

(*ii*) The analysis of the "experimental" data is described in detail in section 3. There are two steps. At first we only assume the spectra are describable by equation 1, and derive "best" values for the strengths Δ_r and times τ_r for each curve (i.e. at each of the ten values of n_{I}) together with their estimated "experimental" errors. This is done for the three sets of "data" with different tolerances. As stated under (*i*) above we know only the time τ_1 for the normal Snoek peak. Not only are the remaining τ_r and all the Δ_r unknown, but the number of terms in the sum in equation 1 is unknown; the analysis must also recover this number – here, 3.

So far the analysis is quite general in the sense that the method (below) allows us to resolve under certain conditions spectra describable by equation 1, whatever the system producing them (given the one value τ_1). The second step relates the model to the data. For each tolerance, we use the set of data from the ten spectra to deduce the proportionality factors from equation 3 and the second of equations 5. Thus we have

$$\sum_{r=1}^{3} \frac{K_r \Delta_r^{(i)}}{200} = n_{\mathrm{I}}^{(i)} \quad i = 1, 2, \ldots, 10 \qquad (6)$$

where $\Delta_r^{(i)}$ is the relaxation strength of peak r as obtained from the analysis of the spectrum "observed" for an interstitial content $n_{\mathrm{I}}^{(i)}$. The "best" values of K_1, K_2, and K_3, together with their errors, are computed from these equations (see section 3). Finally equations 3, 4 and 5 are used to get the "best" values for the binding energies B_{p} and B_{t}. The results for the three K's and two binding energies are compared with the exact values, for each tolerance.

To obtain values for the τ_{r0} and E_r from the "experiments", we must repeat the above process for several different temperatures; then they may be obtained from the "observed" τ_r using equation 2. In fact this was done for only one tolerance (2×10^{-5}) and one value of n_{I}, as shown below. It is noted that the range of temperature which can be employed depends directly on the frequency range.

(*iii*) An analogous procedure was used to generate varying-temperature "experiments" at a fixed frequency of $\omega = 2\pi$. Data were simulated to give plots for the same ten values of n_I as above, but only for one (intermediate) tolerance $\pm 2 \times 10^{-5}$. The exact curves from which these data are generated are shown in fig. 1b for five values of n_I.

In analysing these data one proceeds from the same assumption as would be necessary in a real experimental situation. The peak relaxation strengths are taken to be constants, independent of temperature, i.e. the peaks themselves are supposed to be symmetrical about their centres (as functions of $1/T$); the relaxation times follow the law 2. The data were therefore analysed to find the "best" fit by three symmetrical peaks, and give values for the three Δ_r and the three peak temperatures (we assumed the fact of three relaxation processes to be known) for each n_I. The binding energies B_p and B_t were then obtained from the Δ_r (using the previous B_t method of reference 16) and again compared with the correct values. The values for B_p and B_t obtained by the varying-temperature "experiment" are considerably worse than those obtained by the varying-frequency "experiment". This difference is due to the assumption of symmetric curves in the curve analysis; while it is evidently correct in the latter case it is not in the former, because of the strong temperature-dependence of the Δ_r.

3. Derivation of Δ and τ Terms

The data shown in fig. 2 are some of the calculated "experimental" damping spectra and are imprecise, $Q^{-1} \pm \epsilon$. At first we assume known that there are three peaks. In order to fit these to equation 1 for three peaks and n experimental points, we can define

$$\beta^2 = \sum_{j=1}^{n} \left[\frac{\dfrac{Q_j^{-1}}{\omega_j} - \displaystyle\sum_{l=1}^{3} \frac{\Delta_{lj}\dfrac{1}{\tau_{lj}}}{\dfrac{1^2}{\tau_{lj}} + \omega_j^2}}{\dfrac{\epsilon}{\omega_j}} \right]^2 \qquad (7)$$

which is to be minimised to obtain the desired values of the three Δ and two τ terms. Equation 7 was found to be the most convenient way of curve-fitting the "experimental" data. The use of $1/\tau$ in place of τ reduced computation and since the former was returned by the curve-fitting technique it is this which is discussed in the results given below. The actual values of $1/\tau$ for the anomalous peaks were 3.932 and 7.468 sec^{-1} i.e. one greater and one less than 2π. The technique of curve-fitting employed throughout this work was a method of steepest descents using conjugate directions due to Powell [25]. This technique has the advantages that derivatives of the function with respect to the five unknowns are not required, and also that an estimate of the standard deviations can be made [25].

Whilst the "experimental" damping values are known the error ϵ in each is in practice not known, thus making the minimal β^2 difficult to find. To overcome this difficulty we replaced ϵ with the known maximum tolerance α of all

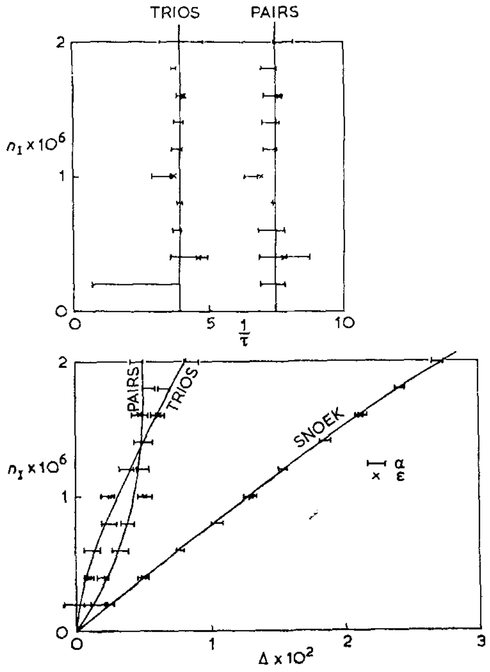


Figure 3 Results of curve-fitting the "experimental" data of a variable frequency experiment at 353° K, with the experimental error α set at 2×10^{-5} for all ten values of n_I assuming that there are two contributions to the anomalous peak. The crosses refer to cases where the correct value of ϵ, the error in each experimental point, was included in equation 7. The error bars are the standard deviations where α was substituted for ϵ in equation 7. The full curves are the theoretical ones based on the model, given in the text, which was used to compute the original "experimental" data.

points. This approximation obviously affects the minimum β^2 with respect to the five unknowns, but our tests showed (fig. 3) that it does not alter the resulting five values significantly. The fact that the true β^2 fit deviates slightly from the real minimum indicates that rounding incurred in outputing the error ϵ in the original computed data is in any case significant. Other preliminary tests showed both that the final minimum point achieved was independent of starting values and also that the known true values of the five unknowns are returned by the computer if the known "perfect" data are used, with an arbitrary value of α, for a given set of data. Having established that the curve-fitting technique using α in place of ϵ can return a unique and acceptable result for any input data, we can proceed to examine the analysis of the "experimental" data, the synthesis of which was discussed in the previous section.

The first series of calculations proper, investigated the effect of the maximum tolerance α on the results and on their standard deviations, assuming the anomalous peak to have two components. The results showed, as one might expect, that the lower the value of α the better the "fit". For any given value of α, the results for a complete set of data, that is for all ten n_I when considered together as in fig. 3, support the existence of two contributions to the total anomalous peak as can be seen by the constancy of $1/\tau$. Also shown in fig. 3 are the theoretical curves derived directly from the present model; the agreement between the curve-fitting "experimental" data results and the original model is quite reasonable.

Whilst this result is clearly satisfactory we must remark that we did assume the correct number of anomalous peaks, whereas in practice their number is not known. We applied the obvious test and tried to analyse some of the "experimental" data assuming that the total anomalous peak is made up of first one, and then three contributions. The result of the first of these tests is shown in figs. 4a and the non-constancy of $1/\tau$ for all n_I is in itself sufficient evidence that more than one process contributes to the total anomalous peak. It is interesting that the curve of $1/\tau$ versus n_I should appear to intersect the abscissa at the value for the relaxation of the interstitials in X–N pairs. However this certainly cannot be cited as evidence that only one relaxation process occurs at infinitesimal concentration.

The three-peak analysis (in the discussion here we refer only to anomalous peaks) also showed some interesting characteristics. The curve-fitting procedure produced one of two situations:
(i) Two of the three relaxation processes had the same relaxation time and the sum of their Δ's was equal to one of the peaks in the two-peak case (i.e. the computer superposed the two peaks). The third process was correctly allocated (in $1/\tau$ and Δ) to the second of the peaks in the two-peak case.
(ii) One of the three Δ values was returned as zero with its associated $1/\tau$ value set at some arbitrary value, i.e. the computer found that this peak was not necessary to fit the "experimental" data. The remaining two peaks were correctly allocated to the two peaks of the two-peak analysis. In only one case was a spurious minimum, i.e. a fake set of data, returned by the curve-fitting procedure.

Taking the results in fig. 4 together with those in fig. 3, one could reasonably conclude that there are only two components in the total anomalous peak. This in itself is a remarkable result, but we are not sure that this would be true independently of the number of anomalous components.

4. Derivation of the *K* and *B* Terms

From the data in fig. 3 it is now possible to deduce the proportionality constants K in equation 3. We have about eight values of the Δ terms with reasonable precision as a function of n_I (fig. 3), the total interstitial atom fraction in the alloy. The standard deviations in $1/\tau$ and Δ at low n_I were too large (for all α) to allow us to place any reliance on the Δ values and these were discarded in the following analysis. Selecting the eight equations 6 for the remaining values of the $n_I^{(i)}$, we rewrite them in matrix form:

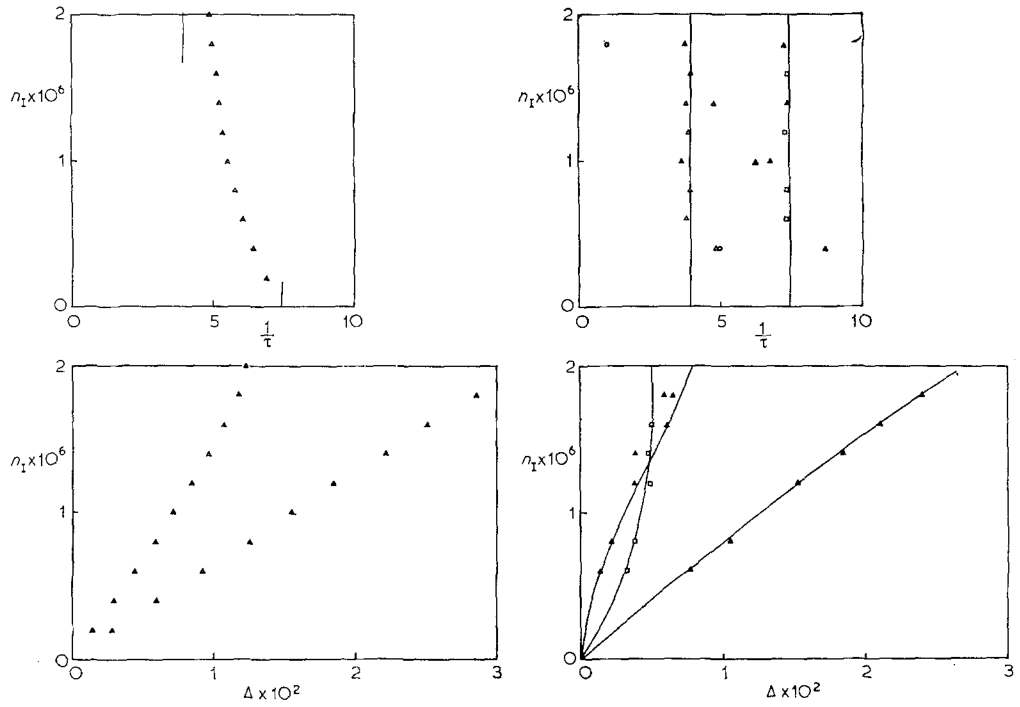
$$\frac{1}{200}\,\Delta \boldsymbol{K} = n_I$$

where Δ is an 8 × 3 matrix. If Δ' is the transpose of V, then

$$\frac{1}{200}\,\Delta'\,\Delta \boldsymbol{K} = \Delta'\,n_I$$

which can be solved using standard methods [26] for the K's thus allowing the fractions of interstitials responsible for each relaxation process to be found immediately from fig. 3.

It is only at this point that for a real experiment a decision would have to be taken about the



(a) (b)

Figure 4 Results of curve-fitting the "experimental" data of the variable-frequency experiment at 353° K assuming that the total anomalous peak is made up of (a) one and (b) three contributions. The input data for analysis are the same as those used in fig. 3 where the correct number (two) of contributions to the total anomalous peak had been assumed. The results are discussed in the text. Δ single relaxation time; □ sum of two Δ with identical τ values; ○ time with zero Δ.

model to interpret the results*. In this instance we naturally assumed the model used as a basis for generating the experimental data, to apply, and from equations 4 and 5 we derived values for the B terms which are given in table I together with the K's. The deviations were derived using standard methods as given, for example, by Margenau and Murphy [27], under the assumption that the errors in the Δ and K terms are independent. In a practical case, when applying this technique to real experimental data, several models may have to be tried to see which gives the best fit with the damping behaviour of each mechanism having to be known.

Table I illustrates the effect of overestimating the Δ values using equation 7 (evident in fig. 3), on the derived K_2 and K_3 data, and their concomitant influence on the B values. It is clear that no great reliance can be placed on the values of K. On the other hand the results obtained for the B values together with their errors can be considered satisfactory (evidently, partly because B_p and B_t are related logarithmically to the measured quantities).

We can now consider what other information is available to us from the frequency experiment. At a given temperature we now know Δ and τ for each peak and, further, the curves in fig. 1a can be computed because the interaction energies B_p and B_t are also known. If the temperature of the "computer experiment" is now varied within the available frequency bracket, the temperature-dependence of both the Δ and τ terms can be studied. The appropriate "computer experiments" were therefore carried out with $\alpha = 2 \times 10^{-5}$ and $n_I = 1.6 \times 10^{-4}$ and the results are presented in fig. 5. This will give us values for the E_r and τ_{r0} via equation 2.

These results show that whilst Δ_I for the Snoek peak is always returned accurately when sufficient of the tail is available for analysis (presumably because τ_I is given), the range of temperature

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*Of course our simulated experimental data were based on a model; what we mean here is that the procedure so far could be applied directly to peak analysis of actual experimental data, and does not require any model to interpret the data.

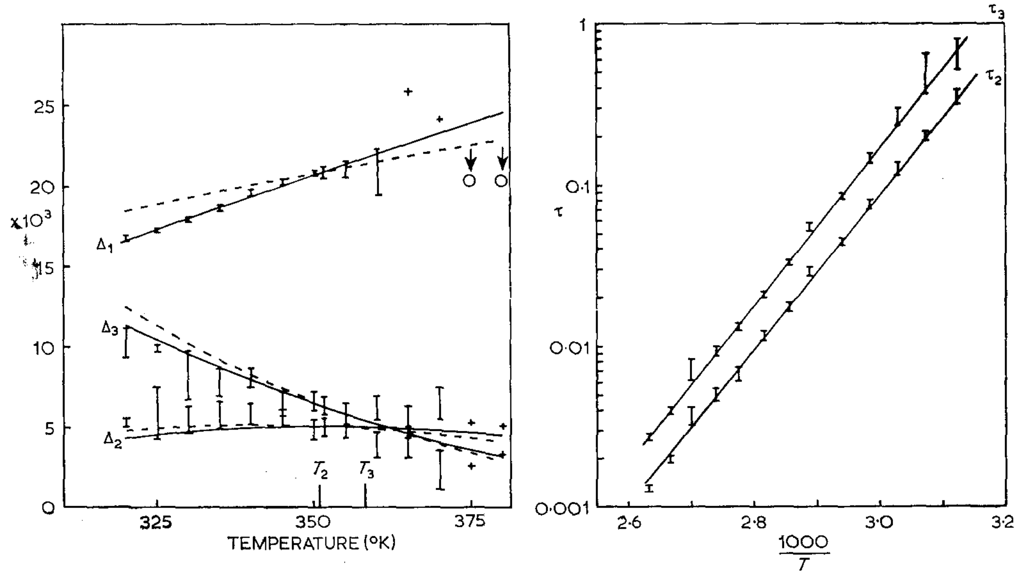
TABLE I

Data	K_1	K_2	K_3	B_p (eV)	B_t (eV)
"Model"	1.0	1.0	1.0	0.24	0.29
$\pm 10^{-5}$	0.866 ± 0.423	1.120 ± 0.456	1.351 ± 1.166	0.245 ± 0.025	0.278 ± 0.034
$\pm 2 \times 10^{-5}$	0.896 ± 0.602	1.021 ± 0.943	1.324 ± 1.375	0.241 ± 0.046	0.278 ± 0.041
$\pm 3 \times 10^{-5}$	0.887 ± 0.460	1.112 ± 0.712	1.305 ± 1.144	0.245 ± 0.035	0.275 ± 0.040

which is available to return useful values of the Δ's for the anomalies is very limited, although their relaxation times are given with reasonable precision. The inherent temperature-dependence of the Δ terms is however not available for study in the case of the anomalies (Δ/T curves are shown in fig. 5a relative to Δ at 353° K), whereas that for the Snoek peak is. The temperature-dependence of the τ's for the anomalies can however be analysed (fig. 5b).

On the basis of the results presented we can make some comment on the frequency range necessary to analyse successfully the damping spectrum. The spectrum which is necessary depends on the relative locations and number of the anomalous peaks. In the present case (fig. 5), a low frequency ω cut-off at about 1 Hz will be the maximum which can be tolerated. At the high frequency end, practically no reduction can be countenanced without reducing the amount of "tail" of the Snoek peak to a value which could not return an acceptable result. We would add that on the basis of the present work we cannot state quantitatively what an acceptable Snoek peak tail represents, as it will depend partly on the number of experimental points.

Finally, for comparison purposes, we used the above curve-fitting method to study data from a variable-temperature "experiment", as mentioned in (*iii*) of section 2. The "experimental" data are computer-simulated in the same way as above, from the exact curves, some of which are shown in fig. 1b. The frequency is fixed at $\omega = 2\pi$ for all "experiments" and the temperature varies in the range 315 to 390° K inclusive. The resulting spectra are analysed to obtain the binding energies from the model. As would have to be done in a practical case, we assume that the peak relaxation strengths are constants independent of temperature, i.e. that the peaks themselves are symmetrical about their peak temperatures in a Q^{-1} versus $1/T$ plot. The peak temperatures for the anomalous peaks are indicated in fig. 1b (for the exact curves) as T_2 and T_3 for the pair and



(a) (b)

Figure 5 The effect of curve-fitting "experimental" data taken from a series of variable-frequency experiments carried out at different temperatures but maintaining the same frequency range 0.5 to 50 Hz. The results are presented showing (a) the variation of the three terms as functions of temperature; the full curves show the theoretical variation calculated from the model and the broken curves show how these curves would shift if Δ varied as $1/T$ (relative to the value at 353° K); (b) the variation of τ_2 and τ_3 with reciprocal temperature.

trio peak respectively. The τ_r for the peaks are supposed, as before, to vary with temperature according to equation 2 with the three τ_{r0} equal to the universal constant 4.225×10^{-15}.

The analysis gives "best" values for the three Δ_r, now constants, and the three E_r. In actual practice, rather than the E_r, we obtain the three peak temperatures T_r; the relationship between the two for any peak follows from equations 1 and 2, by noting that the maximum occurs at

$$\omega\, \tau_{r0} \exp \frac{E_r}{kT_r} = 1$$

where ω and τ_{r0} are known. The results of the analysis are presented in fig. 6; they are very misleading as a comparison with fig. 3 shows. Further, the interaction energies we derive from this "experiment" via equations 3 to 5, and using the method of reference 16 are $B_p = 0.453$ eV and $B_t = 0.067$ eV, which are therefore completely unrealistic, as one would expect. It is interesting to note that, whilst these curve-fitted results are widely divergent from reality, they do show an internal consistency in that the curve-fitted peak temperature appears constant and a smooth variation of the Δ's with n_I is obtained. This consistency is clearly misleading.

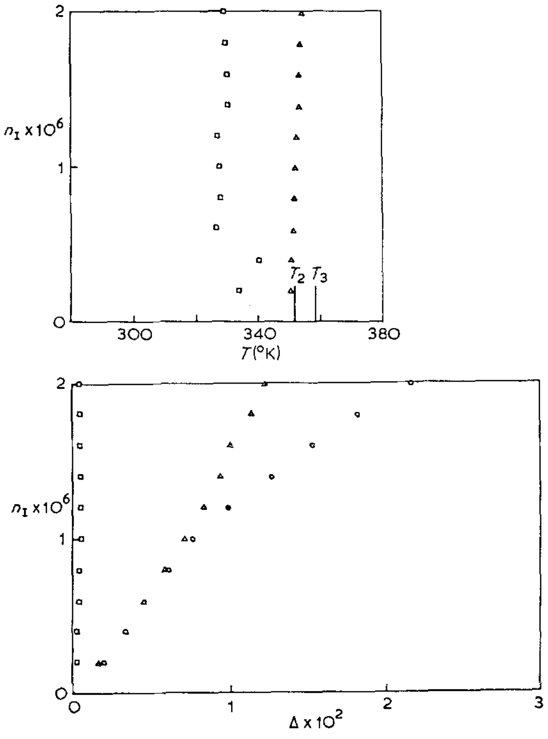


Figure 6 Results of curve-fitting "experimental" data for a variable-*temperature* experiment, with $\alpha = 2 \times 10^{-5}$, assuming that the damping peaks are even about their peak temperatures in a Q^{-1} versus $1/T$ plot. These results should be compared with those in fig. 3 for the corresponding variable-frequency experiment.

5. Discussion

The results presented above show that an experiment using frequency as a variable is capable of giving useful information about the origin of anomalous Snoek peaks, at least in the type of system discussed here.

The strength of the approach results from the fact that we can derive the apparent distribution of the interstitials from experimental observations before a specific model has to be applied to derive interaction energies. At this point we must insert a cautionary comment. The observed damping behaviour depends not only on the distribution of interstitials but also upon their ability to respond to an alternating stress, i.e. the interstitials must be able to "jump" to be seen by the experiment. As an example where this may not be true, the interstitials sequestered by the substitutional atoms may not always be placed within the lattice in such a way that they can freely contribute to the damping, and hence affect the appropriate Δ. Thus the derivation of the K's in section 4 is not necessarily independent of a model invoked to explain the internal friction; a knowledge of the damping behaviour of any subsequently used model is therefore required at that point in the analysis.

There are several other aspects of the proposed experiment which warrant further discussion. In the present work we have investigated a case where the available frequency range includes the anomalous peaks, together with the tail of the Snoek peak. The frequency bracket required for any specific case can be estimated from a classical experiment (we have tacitly assumed an experiment using temperature as a variable to be a necessary preliminary). We query whether the frequency experiment is worthy of consideration in a case where the frequency bracket is not sufficiently broad to include, for example, the tail of the Snoek peak when the temperature is set to study an anomalous peak. This experiment should only be done under conditions where the Δ values taken for one peak (single or composite) can be *reliably* extrapolated to the temperature range over which the second peak has been studied thus allowing a true isothermal comparison. It would appear from fig. 6a that the (normal) Snoek peak, being the most precise, should be extrapolated in preference to anomalous peaks.

The degree to which the actual separation of the anomalous peaks affects the ability of the analytical technique to return acceptable results has not been investigated specifically here. However, considering the curves in figs. 1b and 3, we feel that in any example where a total anomalous peak temperature shift with increasing interstitial fraction is observable in a temperature experiment, the system should be amenable to analysis by the frequency experiment. This separation would seem to be in the region of 4° C.

It is interesting to note in passing that this minimum separation of about 4°C in a variable-temperature experiment corresponds to a ratio of relaxation times of the total anomalous peak components of about 1.5 at 353° K. The ability of the variable-frequency experiment to resolve contributions to an internal friction peak is therefore comparable to that of isothermal elastic after-effect experiments, where a minimum ratio of 2.5 is reported [28].

The experimental precision required depends upon the peak separation: the more widely separated are the peaks the less precision is strictly necessary for separation, although we note that this would result in more imprecise values of Δ and τ. From the present work a precision of better than $\pm 3 \times 10^{-5}$ in the damping measurements is desirable. Some subsidiary runs using $\alpha = 4 \times 10^{-5}$ showed such a wide scatter that no conclusions could be drawn from them.

Finally we consider whether the effect of precipitation can be allowed for in the present work. Isothermal precipitation not only alters the total interstitial fraction n_I but is also likely to affect the substitutional fraction n_X, as one would expect the X atoms to form a compound with the interstitials if an appreciable interaction energy exists in solution in the matrix. Precipitation will thus affect all Δ terms as a function of time during the experiment and precludes the assumption of peaks which are even about their relaxation times. The problem is then analogous to the situation in which the interstitial fractions vary during the classical temperature experiment because of the interaction energies. Thus by the same analogy it does not appear that the frequency experiment is worth while under such conditions.

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