NEAR-DEBYE ACOUSTIC RELAXATION DUE TO Cr^{2+} IN $GaAs^{1)}$

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We have studied the acoustic relaxation peak associated with Cr²⁺ impurities in GaAs, in order to investigate the deviations of the loss behaviour from that predicted by a simple Debye model. Within the limitations imposed by the local systematic errors associated with coherent ultrasonic methods, the relaxation loss can be described by a single Debye response. The temperature dependence of the relaxation time indicates weak one-phonon processes and an excited state at about 90 K.

I. INTRODUCTION

Defect centres often cause elastic or dielectric losses to an oscillating probe field. The non-resonant or "relaxation" losses are often interpreted as being due to the dynamic repopulation of energy levels associated with the defects. Simple models of such repopulation processes lead to the well-known Debye response.

In recent years the use of the Debye response has been criticized on two fronts. The first criticism concerns the use of the rate equations to describe the dynamics of population response implicit in obtaining the Debye expression. Although the rate equations are widely used, they ignore the off-diagonal elements of a full density matrix treatment [1]. Attempts at a general density matrix treatment have been made, but to date have either been so complex that no practical elastic or dielectric response functions have been obtained or approximations have been used which seriously reduce the validity of the method [2]. The second criticism, due to Jonscher [3] and Ngai [4], is more empirical in nature. They note that in a wide range of polymer and glass materials, both the elastic and dielectric response are non-Debye like in the frequency domain, corresponding to a Curie von-Schweidler, rather than to an exponential response in the time domain. However, in almost all such cases the experimental loss can be empirically parametrised using a simple form with few

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system dependent parameters. This "Universal" form. Jonscher argues, does not naturally follow from a distribution of "Debye" responses but indicates the action of a more fundamental loss mechanism which must be common to a wide range of systems [3].

sado and Hill [8], [9], [10], take up the idea of s trongly coupled "corof the probe field with a set of "correlated states" resulting from interacting observed high frequency power law dependences can result from the interaction systems which exhibit the degree of self-similarity needed for the ideas of fractals are related to the internal "order" of the system. There are however very few related states". The later papers on a "cluster" model introduce ideas similar to correlated states from which Ngai's results follow. Later models by Disficiently strong interaction general statements can be made about the density of centres. Wigner [7] had shown previously that under conditions of sufinteractions between the centres themselves [3]. Ngai [6] pointed out that the interacting with its surroundings. Later Jonscher introduced the concept of tail of the loss response in terms of the screened response of a defect centre "screened hopping" model of Jonscher [5] explained the high frequency physical explanation for the "Universal" response. The earliest of these, the to be fully developed those of fractal theory, where the parameters n and m of the universal response A number of different models have been devised in an attempt to provide a

These theories each have two major weaknesses when it comes to application. In each it is difficult to relate the parameters of the theory to physical properties of a real system, and in each the limits of applicability of the theory are unclear. In those theories which introduce correlated states, for example, it is not clear what concentration of relaxing centres is necessary. Although dilute concentrations of magnetic ions in a crystal lattice have been included in the lists of systems exhibiting the non-Debye behaviour [11] it is unclear how in practice such systems can be intercorporated into the theory.

Gallium arsenide containing chromium impurities is a system which is known to exhibit a single relaxation peak in its elastic response [12]. The peak attributed to Cr²-, is readily measurable in samples with chromium concentrations of order 10 ppm and occurs at about 15 K for measurements made at low microwave frequencies. We have carried out very careful measurements over a wide range of temperatures and frequencies since it is clear that not only is the quality of the previous data relatively poor, particularly in the wings of the response, but that the interpretation, based only on the peaks of the responses, is incorrect. At the same time Cr²- centres provide an interesting opportunity to examine a Debye-like behaviour in a system which is typical of those classed as "dilute" and for which the standard application of classical repopulation theories which treat the centres as sufficiently far apart to be non-interacting would

yield a Debye response. We have therefore used a least-squares fitting routine to examine how well data covering a wide range of frequency and temperature can be fitted by a single Debye relaxation peak. We have also considered deviations from the Debye behaviour, and examined the degree to which data of this type can be said to provide evidence for the non-Debye behaviour.

II. EXPERIMENTAL METHODS

The measurements were conducted on *n*-type GaAs in which chromium in the Cr^{2+} state is known to predominate. The material used was cut from boule CT770A which contains $(8 \pm 2) \times 10^{16}$ cm⁻³ Cr_{2+}^{2+} centres and has a silicon concentration between 2×10^{17} and 10^{18} cm⁻³, and form boule 5CSWC24 assessed as having a Cr^{2+} concentration of 5.4×10^{15} cm⁻³. Samples were cut in the from of rods with their long axes aligned along either the (100) or the (110) direction. Conventional pulse-echo techniques using CdS transducers were used to make attenuation measurements over the temperature range 4.2 to 50 K, at a number of frequencies in the range 59MHz to 1.65 GHz. All the measurements reported here are of longitudinal modes. As expected both from theory and from the results of To kum oto and I shiguro [12], no evidence was found for a relaxation peak associated with the (100) transverse mode.

(110) data. Above these temperatures the rapidly weakening relaxation losses. na, which are satisfactory up to 35 K for the (100) data and up to 30 K for the frequencies. This method enabled us to obtain data for the relaxation phenomewhile for the (110) longitudinal mode $a = 3.04 \times 10^{-19}$, b = 1.27 and c = 3.7For the (100) longitudinal mode $a = 4.08 \times 10^{-18}$, b = 1.11, c = 4.0 was used squares method over the temperature range for which the expression is valid The constants a, b and c were obtained by fitting the available data by a leastcorrections were applied by using an attenuation expression of the form $a\omega^{h}T^{h}$ measurements made in our own laboratory on chromium free material. The GaAs is well known from previous measurements by Helme [13], and from contribution from the raw data. Fortunately the thermal phonon attenuation in the relaxation data could be analysed it was necessary to subtract this thermal towards higher temperatures due to the onset of thermal phonon losses. Before background which was flat at temperatures below the peak, but which rose measured as a function of temperature. The peak was superimposed on a combined with the uncertainty in the thermal phonon loss make the analysis of found to extend to 40 K for frequencies below 200 MHz and to 50 K at higher The attenuation is then given in dB cm⁻¹. The useful temperature range was the data unprofitable. At each frequency a single relaxation peak was observed in the attenuation

The results of an extensive series of measurements on a (100) sample cut from CT770A are shown in Figure 1. The data shown have been corrected for the thermal phonon contribution, and the data sets have been matched in the low temperature limit. Corresponding data for the (110) longitudinal mode and for the dilute material of boule 5CSWC24 have been obtained.

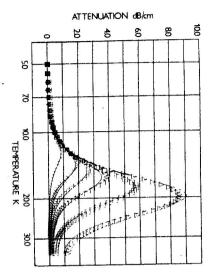


Fig. 1. GaAs: Cr^{2+} sample CT770A (100) axis. The data set upon which the fitting procedures described in the text were performed. The low temperature attenuations at each frequency have been made to be co-incident and the errors assumed in the fitting routine are indicated by vertical bars. Key: | 59 MHz. \times 140 MHz. + 214 MHz. ∇ 316 MHz. \cap 572 MHz. \wedge 1005 MHz.

The results have been subjected to least-squares fitting routines based on an algorithm given by Bevington [14]. X^2 methods require an estimate of the error of each data point, and treat these errors as uncorrelated. A close study of coherent ultrasonic and microwave acoustic techniques indicates that the errors in attenuation measurements seldom meet the criteria for being uncorrelated, but are frequently dominated by systematic effects due to tuning and coherent phasing. Our present measurements are no exception. We have, however, estimated plausible errors by considering the consistency of comparisons of different echo pairs, and by examining the effects of electronic retuning and electronic noise. These errors have then been treated as if they were uncorrelated. An indication of the errors assumed in our analysis is given as vertical bars in Figure 1. Rather than give estimates of the plaussibility of a particular fit, which will be erroneous due to assuming uncorrelated errors, we give X^2 divided by the number of degrees of freedom, referred to here as Q.

III. THEORY

a number of different charge states including Cr2+. The 5D ground state term for the free ion is split into a T_2 groundstate triplet, and an upper E doublet by the er model would not be coupled by E-type phonons, the static model is the basis cannot be strictly correct, since in the static limit the three wells of the Jahn-Tellcoordinated site. While their explanation in terms of a static Jahn-Teller effect exhibit tetragonal symmetry rather than that expected from a tetrahedrally Cr^{2+} centres couple to the E-type but not T_2 distortions and that the centres spin resonance measurements of Krebs and Strauss [15] indicate that the tetrahedral crystal field provided by the surrounding arsenic atom. The electron tion relaxation between three wells whose energies are perturbated by the strain to and Ishiguro [12] (hereafter referred to as T&I). They consider populafor the interpretation of the acoustic relaxation measurements by Tokumo. tion along either the (100) or the (110) directions appear as two-level systems strains, and for a coustic probe fields induced by longitudinal modes propaga--phonon and two-phonon Raman process transitions between the wells. The field of an acoustic wave, and following Sussman [16] allow both one- Cr^{2+} centres then behave as simple three-level systems split only by E-type T&I show that the resulting attenuation can be written in terms of a Debye Chromium substitutes for gallium in the GaAs lattice, where it can exist in

$$\alpha = 4.34 \cdot [N(T) \cdot G^2/(\varrho \cdot v^3 k T)] \cdot [\omega^2 \cdot \tau/(1 + \omega^2 \cdot \tau^2)]. \tag{1}$$

In Equation (1), N(T) is the population. G is the coupling coefficient appropriate to the acoustic mode, v is the acoustic velocity, ϱ is the density of the medium, and τ is the relaxation time. T&I treated N(T) as temperature independent in the absence of a large applied strain and for τ used the expression:

$$\tau^{-1} = A \cdot T + B \cdot T^{7}.$$
 (2)

Here the first term represents the contribution due to one-phonon transitions and the second term represents the two-phonon Raman transitions. At each frequency of measurement T&I used the data near the peak to obtain the temperature at which the attenuation peak occurred and then used the expression ω . $\tau = 1$ to obtain the value of τ at that frequency. The τ data and Equation (2) were then used to obtain $A = 1.0 \times 10^7$, and B = 4.7. The fit has thus been derived from the peaks of the acoustic response, rather than from an overall fit to the data. Equations (1) and (2) indicate that at sufficiently low temperatures the attenuation should assume the value:

$$a = 4.34 \cdot N(T) \cdot G^2 \cdot A/(\varrho \cdot v^3 \cdot k).$$
 (3)

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If, following T&I, N(T) is taken as temperature independent, the low temperature attenuation should take a fixed value independent of frequency and temperature while at high temperatures the relaxation attenuation drops to zero. Since this low temperature plateau is not observed in either the data of T&I or in our own data, it is clear that either the use of a temperature independent N and the form of τ given by Equation (2) is incorrect in the low temperature limit, or the estimate of A is incorrect, or there is some more fundamental fault in the theory.

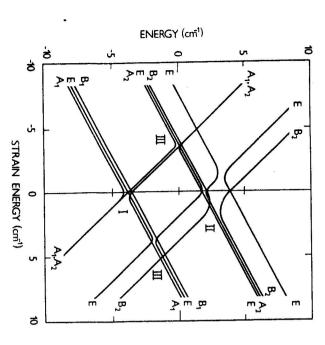


Fig. 2. Energy level splitting for the Cr^{2+} centre in GaAs as a function of strain energy for tetragonal strains along the (001) direction in zero magnetic field. The levels are labelled according to their transformations under D_{2d} and the Roman numerals indicate those regions of particular interest in this study (after Abhvani et al. [17]).

Abhvani et al. [17], [18], have produced a series of papers describing a full dynamic Jahn-Teller model of the Cr²⁺ centre, by a method which includes the influence of spin-orbit coupling and strain distortion of the site surroundings. They have also given comprehensive details of how the 15 ground-state levels are split in terms of the two *E*-type distortions of the surrounding atomic cluster. These two components of strain are used to define a "strain plane". Typical results for a particular strain direction within this plane are shown in Figure 2, where the "strain energy" is a scaled elastic strain. Although the 15

strain. Loss will not result, for example, from the parallel regions of Figure 2, behaviour being over narrow ranges of strain where the level cross. We note that group of ten parallel levels may be identified, the only deviation from parallel three-level system of the static model may be seen in that a group of five and a levels are split apart in an apparently complicated fashion the relation with the or from the regions of very high strain where only the lowest levels would be strains are not well known but are expected to form a Gaussian distribution with attenuation will result from an average over all sites. The "random" lattice acoustic wave but to the much larger lattice strains at that site. The observed populated. Each site is subject not only to the perturbing influence of the losses occur only when levels, both of which are populated, are split apart by a "strain energy" width corresponding to about 5 cm-1 [18]. In predicting the regions such as II at higher energy. Regions I should produce losses at low strain each contain low-lying regions such as those marked I in Figure 2, and expected to be greatly site dependent. Energy-strain diagrams for a particular sites save for those in the narrow cross over regions, which will contribute little. Figure 2 we note that the coupling factor G will be the same for all contributing relaxation loss from a distribution of sites subject to strains such as those of as the temperature is lowered and cease to contribute. The temperature below Raman transitions and Orbach transitions involving excited states are not strain distribution will also depopulate and cease to contribute at the lowest marked III representing sites whose numbers are depleted by the Gaussian which this occurs will correspond to 5 cm⁻¹ or 8 K. Regions such as those temperatures. Regions such as II, however, will depopulate into the lower levels expected to be of order 100 K above the ground state. temperatures. The excited states of these central have not been calculated but are

IV. ANALYSIS OF THE DATA

Initially the attenuation data were examined for the presence of the low temperature plateau discussed in the previous section. If such an effect existed, it would be noticeable in the low frequency (100) data from the more concentrated sample where the thermal phonon attenuation is less important. After a lengthy statistical analysis it was concluded that the low frequency attenuation is in the range $0.02 \pm 0.04\,\mathrm{dB/cm}$. It is not improbable therefore that the effect is zero it is certainly so small that it will not greatly influence overall fits to the data.

IV.1. Fitting the data using the Debye expression

Least squares fits to our data were carried out using the single Debye expression of Equation (1). Following T&I the population N(T) has been taken

as temperature independent. The possibility of N(T) containing Boltzmann factors, which will in general have a far lower temperature dependence than $\tau(T)$ will be discussed later.

Two methods of fitting were used, each yielding $\tau(T)$. The first method uses an overall fit to the data for a particular material and mode, using as parameters the amplitude factor M=4.34. $N\cdot G^2/(\varrho\cdot v^3\cdot k)$, and parameters characterizing $\tau(T)$. An attempt at a fit using the form of Equation (2) gave much the same magnitude as that obtained by T&I for the T^7 term and a finite one-phonon term but an extremely unsatisfactory overall fit ($\varrho=3$). Analysis showed that while the temperature dependence of τ needed to be T^7 at 10 K, at higher temperatures the dependence on temperature needed to be lower. Although several expressions for τ having no physical basis were found to give satisfactory fits, we restricted our analysis to terms having some basis in theory. These included the Raman expression T^7 and the Orbach terms of the form $C/\exp(D/T) - 1$), where D has the dimensions of temperature. The expression

$$\tau^{-1} = B \cdot T^7 + C/(\exp(D/T) - 1)$$
 (5)

gave the following fits for sample CT770A:

(110)	(100)	Directions
1.07×10^{-8}	5.71×10^{-8}	M
2.58	2.08	В
1.60×10^{11}	1.90×10^{11}	c
82.8	82.4	D
0.5	0.9	9

The ratio of the amplitudes for the two directions, 5.4 is in very good agreement with the theoretical ratio of 4. $(v(110)/v(100))^3 = 5.38$. The quality of fit for the (100) data is shown in Figure 3. While the fit at low temperatures is excellent, deviations occur close to the peaks and in the upper tail at some frequencies. The systematic trends in these discrepancies and those for the (110) data are, however, hard to identify, suggesting that many more parameters in the fitting functions would be needed to much improve the fit. Measurements made on the dilute sample indicated that the peak magnitudes scaled with Cr^{2+} concentration, thus confirming the identification of the centre.

The second method of analysis was to take the data at each temperature and to obtain τ at that temperature by fitting the data versus frequency. The value of M obtained from the various functional forms of τ used previously did not greatly vary, and the values quaoted above were used in this procedure. The results for the (100) data are shown in Figure 4. The results are plotted in the form $\tau' = \tau$. 10. T^7 for ease of presentation and to show the comparison with the $\tau(T)$ of T&I. It is seen that while the present results and those of T&I cross

at two points and do not greatly differ in the region of 12 K to 20 K, at low temperatures our result reflects the apparent absence of a one-phonon term while at high temperatures our results rise steadily above the T&I result reflecting the need for a temperature dependence lower than T^7 .

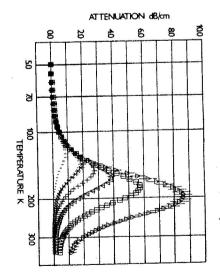


Fig. 3. GaAs: Cr^{2+} sample CT770A (100) axis. The solid lines indicate the fit to the data set of Fig. 1 obtained using the Debye model with a temperature dependent relaxation time given by $\frac{1}{1+r} = RT^2 + C/(e^{D/T} - 1)$ where the parameters are as given in the text.

 $1/\tau = BT^7 + C/(e^{D/T} - 1)$ where the parameters are as given in the text. Key: | 59 MHz, \times 140 MHz, + 214 MHz, ∇ 316 MHz. \square 572 MHz, ∇ 1005 MHz.

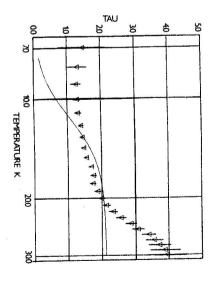


Fig. 4. GaAs: Cr^{2+} sample CT770A (100) axis. The points indicate relaxation times derived at individual temperatures in order to build up a representation of $\tau(T)$, the vertical bars indicate the error in τ' at each point. The solid curve is the relaxation time function obtained by Tokumoto and Ishiguro [12].

IV.2. The use of non-Debye fitting functions

Most of the "Universal" fitting functions propose power law variations with frequency which differ from those of Debye both above and below the peak in the response and which may be represented in their most elementary form by replacing ω^2 . $\tau/(1+\omega^2$. τ^2) of Equation (1) by the functional form $\omega/((\omega,\tau)^n+(\omega,\tau)^{-m}]$. The Debye form obtains if n=m=1. n determines the low temperature behaviour where ω . $\tau \geqslant 1$ while m determines the behaviour when ω . $\tau \leqslant 1$. Fitting our data from CT770A using this non-Debye form and the relaxation time expression of Equation (5), gives the following results.

(110)	(100)	Direction
1.06	5.82	$M = (x 10^{-8})$
4.04	0.73	В
0.70	1.90	C (x 10^{11})
76.9	80.3	D
1.0	1.0	n
0.83	1.35	m
0.4	0.4	9

The fits obtained, although a slight improvement on the Debye fits are visually little different, for example, from that of Figure 3, the reduction those in Q resulting from improved fitting in the high temperature wings. The magnitude parameters M are very little changed. The parameter n is seen to closely retain its Debye value. Although m differs from unity in each fit the deviations are in an opposite sense and the mean differs little from unity. The fits for the two propagation directions are optimized by different relative amounts of Raman and Orbach terms. As for the Debye fits Q is relatively intensitive to small variations in the two contributions.

V. DISCUSSION AND CONCLUSIONS

We have subjected data for the Cr²⁺ relaxation peak from a wide range of temperature and frequency to a detailed statistical analysis. The use of a single Debye peak, a temperature independent population and a three parameter relaxation time expression gives a fit to the data which is adequate but which displays a range of discrepancies from the data which are complex and local in frequency and temperature. The use of two Debye terms does not improve the quality of fit, which suggests that we are studying a system where the relaxation time does not greatly vary between contributing centres.

The use of non-Debye fitting functions produces somewhat improved fits for both the (100) and the (110) data sets. The fits are, however, Debye-like in the low temperature wings and only vary greatly from Debye in the high temperature wings. Moreover, they are in an opposite sense for the two data sets. The comparison between the (100) and the (110) data is crucial since if the centre couples to E distortions only, and there is considerable evidence that this is so,

the two sets of data should vary only by a calculable amplitude. It is for this reason that the two sets have been interpreted separately. However, the nature of the deviations between the fit and the theory is different for the two propagation directions. This suggests that local systematic errors are responsible for the major remaining contributions to the Q. Such local errors are common in "ultrasonic" measurements which use coherent detection, and are evident for example in the wings of the data of T&I. These systematic errors make it extremely difficult to estimate small deviations from the Debye behaviour from the Debye behaviour from high frequency elastic measurements which use coherent techniques.

analysed the data close to their peaks, our wide-ranging analysis clearly indicastates exist, this value is consistent with the position of an excited state estimated relaxing levels. Although no detailed calculation of the positions of the excited time which implies an excited state or group of excited states 82 K above the times smaller than they estimated. The dynamic Jahn-Teller model itself present values for τ and those of T&I differ little over the range for which T&I by Krebs and Stauss from their EPR measurements [19]. Although the depopulation into weakly loss-producing lower levels would apparently remove energy-strain diagram such as II and III of Figure 2. At low temperatures the Cr2+ centre, or that most of relaxation loss occurs from regions of the modifies $\tau(T)$. It is possible that either the direct processes actually are weak for temperature as N(T)/T. $\tau(T)$. Thus an incorrect assumption concerning N(T)terms. At low temperatures such that $\omega \cdot \tau \gg 1$ the attenuation varies with provides a possible explanation for the apparent absence of the direct process tes that the magnitude of the one-phonon term, if it exists, must be at least ten the direct process in a treatment which assumed N(T) constant. The results of the fit using a Debye function yield a form for the relaxation

Handling a full dynamic Jahn-Teller model incorporating lattice strains is difficult. However, we have re-analysed the data assuming N(T) contains the simplified Boltzmann factor $2/(2 + \exp(8/T))$ that would result from ten relaxing levels 8 K higher in energy than five lower levels. A best fit to the data yields a direct process term of $\sim 4 \times 10^5 \, \mathrm{s^{-1} \, K^{-1}}$, still very weak compared with the value deduced by T&I. We conclude therefore that even on this model the direct processes are weak.

This reanalysis with a temperature dependent N(T) does not greatly modify the prediction concerning the excited state, or improve the overall quality of fit and our conclusion that small deviations from the Debye form are difficult to detect using coherent techniques still stands.

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АКУСТИЧЕСКИЕ РЕЛАКСАЦИИ ПОЧТИ ДЕБАЕВСКОГО ТИПА В GaAs, ОБУСЛОВЛЕННЫЕ Сг²⁺

и возбужденном состоянии при температуре около 90 К. мость времени релаксации свидетельствует о присутствии слабых однофононных процессов потери могут быть описаны при помощи простого отклика Дебая. Температурная зависи кими ошибками, обусловленными методами когерентного ультразвука, релаксационные целью исследовать отклонение характера потерь от предсказаний, полученных на основе простой модели Дебая. В рамках ограничений, которые заданы локальными систематичес-В работе изучается пик акустической релаксации, связанный с примесями Cr2+ в GaAs с