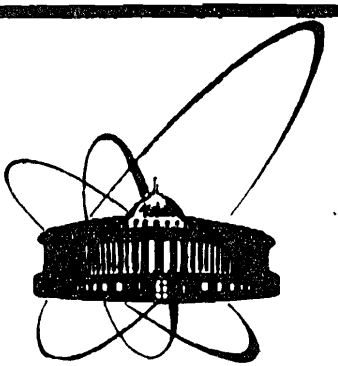

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A NEW APPROACH TO THE GLASSY BEHAVIOUR OF DISORDERED SOLIDS

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1. Introduction

Now it is well established that the low-temperature phenomena found in glasses can also occur in crystals (Ackerman et al. 1981; Fischer et al. 1981). For a large group of disordered solids the results of thermal, ultrasonic, dielectric and other measurements do not confirm the current Debye-theory. It has been thought that these anomalies can be attributed to the amorphous structure itself by the lack of long-range order. However, topological disorder is not sufficient for glassy behaviour (Gardner and Anderson, 1981; Löhneysen et al., 1981), and the magnitude of various effects is not decisive for characterizing its general physical origin (Fischer, 1983). Besides the existence of certain localized excitations, the correlation of different low-temperature phenomena appears to be the most important characteristic of glassy behaviour.

A phenomenological tunneling model is usually favoured to explain the effect, although there is no reliable information about the nature of the tunneling entities (Phillips, 1981). Therefore, any interpretation of experimental results in a long run means their conversion to certain assumptions concerning the properties of low excitation spectra. On that account ferroelectric crystals serve as excellent samples for an investigation of glassy behaviour due to a high sensitivity of dielectric constant to low-lying excitations and a strong correlation of glassy anomalies to characteristic lattice properties (Fischer, 1983) suggesting an important role of the disorder of the domain structure.

A recent paper deals with an analysis of dielectric and thermal properties of relaxation ferroelectrics (Fischer, 1986). For temperatures $T \lesssim 1K$ it has been found that the glassy anomalies can be

explained using the tunneling model with a constant density of states. However, no confirmation was found for the presence of any energy-dependent density of tunneling states at higher temperatures. It is the purpose of the present paper to give a further analysis of these low-temperature phenomena in dielectric constant and thermal conductivity at $T > 1K$ and to show some substantial results of a new approach to understanding the physical origin of the glassy behaviour (Fischer, 1983).

2. Experimental Results and Discussion

The general behaviour of the complex dielectric constant of disordered solids is similar to the results obtained for a $Sr_{0.5}Ba_{0.5}(Nb_2O_6)$-single crystal (fig.1): The logarithmic dependence $\Delta\varepsilon/\varepsilon = A_1 \ln \frac{T}{T_1}$ can be explained by relaxation scattering on two-level system with a constant density of states P_o.

The upper logarithmic dependence $\Delta\varepsilon/\varepsilon = A_2 \ln \frac{T}{T_2}$ (1a) at $T \gtrsim 10K$ is suggested to be caused by a process not adhering to the tunneling model, and thus the intermediate dependence

$$\Delta\varepsilon/\varepsilon \sim T^2 \qquad (1b)$$

is the cross-over between the two different mechanisms. The upper process is characterized by a broad peak in dielectric losses, and it is thought to be thermally activated. Such peaks are also known in ultrasound attenuation for a large amount of amorphous solids.

Usually these effects are explained by the standard Debye-model where the imaginary part susceptibility is given by:

$$\chi''(\omega,T) \sim \frac{1}{T} \cdot \frac{\omega\tau}{1 + (\omega\tau)^2} \qquad (2)$$

with thermally activated relaxation time

$$\tau = 1/\omega_p = \tau_o \exp(\tilde{E}_a/K_B T) ,$$

where ω is the measuring frequency,

$\tilde{E}_a$ is an activation energy and τ_o some "attempt-to-jump" time. Thus, any concrete process can be characterized by its activation energy $\tilde{E}_a$. However, a large amount of experimental results shows that the peaks are much wider than those predicted by (2). Analogous to the tunneling states model, it becomes necessary to postulate a broad distribution of activation energies $g(\tilde{E}_a)$, again without any reasonable justification. Often the distribution $g(\tilde{E}_a)$ required to fit the data is unphysical. This current treatment of experimental results by Debye-response does not add new information to our knowledge of glassy behaviour although intuitively it seems to be justified owing to the disorder in glasses.

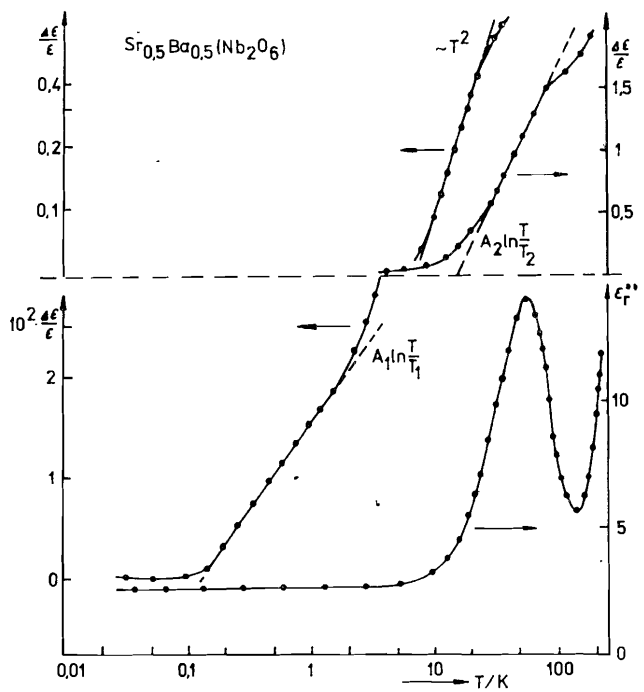

Fig.1. Variation of the complex dielectric constant of a $Sr_{0.5}Ba_{0.5}(Nb_2O_6)$-single crystal with temperature; measuring frequency $f = 1{,}6$ kHz

3. Glassy Behaviour and Universal Dielectric Response

An alternative approach to the "Non-Debye" behaviour in dielectric relaxation is given in the conception of universal dielectric response (UDR) theory (Jonscher, 1977a). It has been found that the dielectric response of a wide range of solids strongly departs from the Debye model showing a remarkably common pattern.

This can be characterized by the dielectric losses χ'' obeying

$$\chi''(\omega) \sim \omega^{n-1} \quad \text{at} \quad \omega > \omega_p \quad \text{with} \quad 0 \leq n \leq 1. \qquad (3)$$

This anomalous behaviour regarding Debye-theory is largely independent of the type of physical structure, chemical type, chemical bonding, polarizing species or geometry. The empirical law (3) has the unique property that its Kramers-Kronig transformation gives the same functional form leading to the "universal" law of dielectric response:

$$\chi''(\omega) / \chi'(\omega) = \cot(n \cdot \pi/2)$$

serving as general criterion of dielectric relaxation in solids. Owing to thermal activated relaxation, equation (3) can be completed to the empirical formula:

$$\chi''(\omega, T) \sim \frac{1}{T} \left[\left(\frac{\omega}{\omega_p}\right)^{1-n} + \left(\frac{\omega}{\omega_p}\right)^{-m} \right]^{-1}. \qquad (4)$$

It was suggested that m is a function of n, and so the complete loss peak is a unique function of the parameter n only (Ngai, 1979a; Ngai and White, 1979). A schematic representation of the various observed types of dielectric response over the range of solids shows that the value of n characterizes the interaction strength between the polarizing species (Table 1). The universality of this "Non-Debye" relaxation suggests that the general mechanism is due to many-body interactions. For the discussion of a possible mechanism, first a "screened-hopping" model was proposed interpreting the loss peak as a result of sequential interplay of two different types of decay process in the time domain (Jonscher, 1977b). The reorientation of certain charged particles or dipoles is accompanied by the

reaction of the surroundings relaxing into a new equilibrium. It has been postulated that such a behaviour can be described by an infrared divergence mechanism associated with the existence of some ubiquitous low-energy excitations in the system (Ngai and White, 1979).

Table 1. Systematization of Dielectric Response of Solids (Ngai and White, 1979)

n	Polarization Unit	Interaction	Types of Solids
0	dipoles	non-interaction	-
< 0.3	dipoles	nearest-neighbour (liquid-like)	liquids, p-n junctions, ferroelectrics at high frequences, cryogenic polymers, liquid crystals
≈ 0.5	dipoles	nearest-neighbour (liquid-like)	polymers glasses } > Tg
> 0.6	dipoles	many-body interactions (solid-like)	polymers glasses } < Tg
			clathrates, ferroelectrics at low frequencies ≷ T_c
$n_1 < 0.3$	hopping	many-body interactions (electronic hopping, ions)	Me-β-alumina
$n_2 > 0.6$	charges		
n ≈ 1	lattice dipoles	many-body interactions	highly pure lattices

Taking into account an assembly of two-level systems, the interaction between the local units will give a complete description of the susceptibility data (Dissado and Hill, 1979).

A detailed analysis of the complex of experimental results and of the various theoretical conceptions leads to the conclusion that the UDR and glassy behaviour are two aspects of a common and quite universal relaxation mechanism not adhering to Debye-theory and typi-

cal for a wide range of solids (Fischer, 1983). Therefore it is not surprising that Table 1 includes all solids showing glassy behaviour.

4. Calculation

It appears that the broad maximum in dielectric losses as a characteristic of glassy behaviour should be analysed in terms of the UDR-concept. For the first calculations it is appropriate to use the simple empiric formula (4) irrespective of any theoretical model. For example, the fit for the above SBN (50% Ba)-sample is shown in fig.2. A three level fitting scheme was used to determine n, m and $\omega_o = \frac{1}{\tau_o}$. The value found for n (= 0.83) corresponds to the schematic representation of Table 1 and emphasizes the high degree

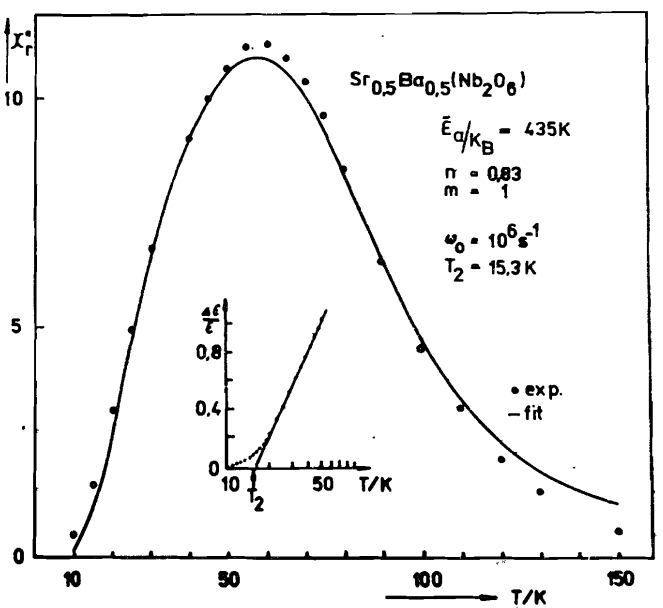

Fig.2. Dielectric loss peak of $Sr_{0.5}B_{0.5}(Nb_2O_6)$. The solid line is a fit of Eq.(4) to the data. The fitted parameters (n, m, ω_o) are indicated in the figure.

of dipole-dipole interaction in this single crystal. From these results an activation energy $\tilde{E}_a/K_B$ = 435K is deduced. However, as was shown by Ngai (1979a) $\tilde{E}_a$ is only an apparent activation energy related to the actual activation energy E_a :

$$\text{by } E_a = (1 - n)\tilde{E}_a \quad \text{giving } E_a/K_B = 74K.$$

The Kramers-Kronig transformation gives the variation of the real part of dielectric susceptibility shown in the inset of fig.2. For $T < 50K$ numerical calculations produce the variation

$$\frac{\Delta\varepsilon}{\varepsilon}(T) = A_2 \cdot \ln T/T_2, \quad (A_2 = 0.86; \quad T_2 = 15.3K)$$

in confirmation of the experimental results (A_2 = 0.90; T_2 = 15.6K). Thus, a good agreement with the experimental results is found by analysing this characteristic glassy anomaly with the use of the UDR-concept.

5. Correlation of Low-Temperature Phenomena

A strong correlation between thermal conductivity λ and dielectric relaxation was found by Fischer (1983). Thus, for instance, λ shows the well-known plateau-behaviour just in the same region of temperatures where ε obeys (1b). It was suggested that Eq.(1b) is due to the cross-over to the relaxation mechanism characterized by the broad peak in dielectric losses with increasing temperature. The correlation can be also illustrated by the striking agreement between the temperature T_2, fitting the results corresponding to (1a), (Fig.2), and the mean temperature T_p of the strong phonon scattering (plateau) in thermal conductivity. Table 2 shows that this correlation

was found in both amorphous and crystalline materials, and it is thought to be a general one. The two PLZT-samples show that the correlation retains regardless of large structural relaxation effects. It was found by Ackerman et al. (1981) that the specific heat C also appears to be correlated with the plateau in λ . From the dielectric results we can extrapolate to an analogous correlation for acoustic relaxation.

Table 2

		T_2/K	T_p/K
single crystals:	SBN(50% Ba)	15.6	15
	$SrTiO_3$	2	2
	KH_2PO_4	9	10
polycrystals:	PLZT 8.5/65/35	7.5	8
	PLZT 8/65/35	45	40
	$Pb_xSr_{1-x}TiO_3$		
	x = 0	2	2
	x = 0.005	2.4	2.2
	x = 0.055	6.5	7.5
	x = 0.12	8	7.5
amorphous solids:	Cenusil (a)	9	7
	BK7 (b)	10	10

* (a) - from Scheibner (1983), (b) - from Anthony and Anderson (1979).

6. Generalization of the UDR-Conception

For all solids exhibiting glassy behaviour in general a broad peak in dielectric, acoustic and mechanical relaxation can be found although, in particular, the effect may be masked by some additional excitations.

Thus, the above consideration and the results of numerical calculations obtained for SBN suggest a generalization of the UDR-interpretation for the other solids.

For the mechanical and electrical relaxation peaks in β-alumina an analogous interpretation was given by Almond and West (1981). For a theoretical interpretation the UDR was attributed to a universal mechanism similar to infrared-divergence response (Mahan, 1974). The unifying features of other low-frequency fluctuation, dissipation and relaxation phenomena were demonstrated by Ngai (1979b). The strong correlation of thermal, dielectric and acoustic anomalies suggests for thermal conductivity data an interpretation in terms of the universal response concept (Fischer, 1983).

Thus, the typical plateau-behaviour can be explained as a result of phonon scattering at excitations seen in the broad dielectric and acoustic relaxation peaks. These excitations are characterized by the well-defined activation energy E_a, without any need of a broad spectrum $g(E_a)$. The phonon mean free path $l(\omega)$ is given then by the fluctuation-dissipation theorem:

$$l^{-1}(\omega, T) \sim (\exp \frac{\hbar\omega}{K_B T} - 1)^{-1} \cdot \chi''(\omega, T). \qquad (5)$$

At present there is no satisfactory explanation of the plateau in λ . However, regarding the dominant phonons ω_{Dom}, Eqs.(4) and (5) immediately give a simple physical explanation:

$$\hbar\omega_{Dom}(T_p) \approx E_a \quad ! \qquad (6)$$

i.e., the plateau at T_p is due to strong phonon scattering on the characteristic excitation E_a. So it is not surprising to find additional contribution to specific heat data at T_p. The value of $E_a/K_B = 74K$ obtained from the dielectric results for the SBN sample is in good confirmation with the main Einstein-mode ($\Theta_E = 73$ K) found in specific heat measurements on a SBN (55% Ba)-single crystal (Henning et al., 1982). Taking into account Eqs.(4) and (5), the

"nonresonant" scattering on tunneling states (Zaitlin and Anderson, 1975) with an energy-dependent density of states P(E) becomes no necessary for an interpretation of λ . Thus, it was suggested to use a resonant term tunneling state scattering, ℓ_{Res}^{-1} with constant density P_o, a relaxation process according to Eqs.(4) and (5) and the scattering on point defects to explain the characteristic glassy behaviour in λ (Fischer, 1983). Using for the first examination the relaxation term (4) with parameters found by the χ''-fit for the SBN(50% Ba)-crystal (fig.2),a three-level fit with the above scattering processes gives a good agreement with the thermal conductivity results obtained for a SBN(39% Ba)-crystal (Hässler, 1984). In general, various results of λ for different materials can be simulated by changing the contribution of the scattering processes being under discussion as seen in fig.3.

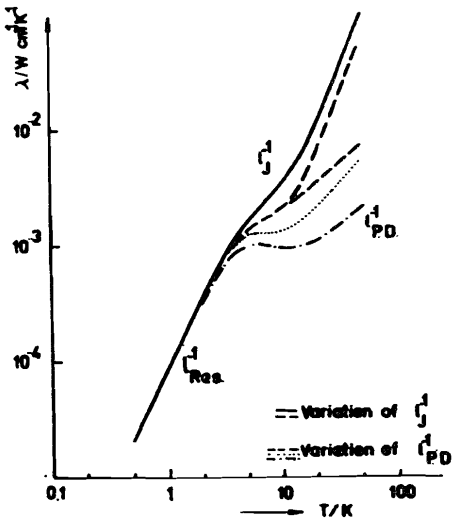

Fig.3. Simulation of different λ -curves by changing the contribution of phonon scattering due to universal response (l_J^{-1}) and point defects ($l_{P.D.}^{-1}$).

Conclusions

The analysis of the dielectric results of crystalline ferroelectrics shows that the broad relaxation peak found in amorphous solids can be explained by a universal Non-Debye-relaxation process caused by a certain mechanism of many-body interactions. A single activation energy is efficient for characterizing the process, and it is proposed that this parameter is correlated with the structural excitations decisive for dynamic phase fluctuations in the short range order. Thus, for instance, in the case of the SBN-crystal one can propose that E_a describes the configuration tunneling of the NbO_6-octahedra between the T1 and T2 phase (Ngai and Reinecke, 1977). The obtained strong correlation between the thermal conductivity and dielectric results is found to be a substantial feature of glassy behaviour. The generalization of the universal response conception to the thermal conductivity gives a simple explanation of the plateau in λ and of the corresponding correlation between dielectric, thermal and acoustic anomalies in disordered solids. Eqs. (4) and (5) are confirmed by a special experiment dividing this interpretation from the two-level model (or similar conceptions) in a principle manner. This question will be considered in the following paper.

References

Ackerman D.A., Moy D., Potter R.C., Anderson and Lawless W.N. 1981 Phys.Rev. B23, 3886.

Almond D.P., West A.R. 1981 Phys.Rev.Lett. V.47, 432.

Anthony P.J., Anderson A.C. 1979 Phys.Rev. B20, 763.

Dissado L.A., Hill R.M. 1979, Nature 279, 685.

Fischer E., Hässler W., Hegenbarth E. and Fritsberg V.I. 1901 phys.stat.sol.(a), 66, K169.

Fischer E. 1983, Dissertation, TU Dresden.

Fischer E. 1986, phys.stat.sol.(a), to appear

Gardner J.W., Anderson A.C. 1981, PhysRev. B23, 1988.

Hässler W. 1984, Dissertation, TU Dresden.

Henning I. et al. 1982, phys.stat.sol.(a) 73, K105.

Jonscher A.K. 1977a, Nature 267, 673.

Jonscher A.K. 1977b, phys.stat.sol.(b) 84, 159.

Löhneysen H.V. et al. 1981, J.de Phys.Coll. C6, 193.

Mahan G.B. 1974, sol. state phys. 29, 75.

Ngai K.L. 1979a, Comm.Sol.State Phys. 9, 127.

Ngai K.L. 1979b, Comm.Sol.State Phys. 9, 141.

Ngai K.L., Reinecke T.L. 1977, Phys.Rev.Lett., V.38,74.

Ngai K.L. White C.T. 1979, Phys.Rev. B20, 2475.

Phillips W.A. (Ed.) 1981. Topics in Current Physics, 24.

Scheibner W. 1983, TU Dresden, private communication.

Zeitlin M.P., Anderson A.C. 1975, Phys.Rev. B12, 4475.

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Фишер Э. E8-86-235

Новый подход к проблеме стеклообразных свойств сильно дефектных твердых тел

Диэлектрическая релаксация и тепловые свойства сегнетоэлектрических кристаллов при низких температурах проявляют такие же аномалии, как и у неупорядоченных твердых веществ. При $T > 1K$ эти аномалии можно объяснить в рамках универсального процесса релаксации недебаевского типа, который предположительно является следствием некоего общего механизма многочастичного взаимодействия. Одна энергия активации E_a достаточна для описания и широкого максимума в температурной зависимости диэлектрических потерь, и плато в теплопроводности. Этот новый подход дает в частности простую физическую интерпретацию причин, обнаруженных у аморфных веществ корреляций между разными тепловыми, диэлектрическими и акустическими аномалиями.

Работа выполнена в Лаборатории высоких энергий ОИЯИ.

Препринт Объединенного института ядерных исследований. Дубна 1986

Fischer E. E8-86-235

A New Approach to the Glassy Behaviour of Disordered Solids

At low temperatures the dielectric relaxation and thermal properties of ferroelectric crystals exhibit the same behaviour known for disordered solids. At $T > 1K$ these anomalies can be explained by a universal Non-Debye relaxation process due to many-body interactions. A single activation energy is efficient for characterizing both a broad peak in dielectric losses and a plateau-like slope in thermal conductivity. The new approach gives a simple physical explanation of the correlation between thermal, dielectric and ultrasonic anomalies in disordered solids.

The investigation has been performed at the Laboratory of High Energies, JINR.

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