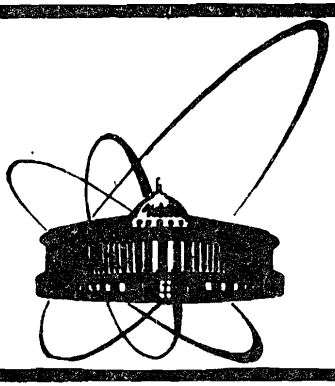

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GLASSY BEHAVIOUR OF ORDER-DISORDER TYPE FERROELECTRIC SINGLE CRYSTALS AT LOW TEMPERATURES

Submitted to "Journal of Physics C"

1986

Introduction

In the recent years the research of low-temperature properties of amorphous solids has played a growing part in solid state physics. However, to date we are far away from any satisfactory understanding of the microscopic mechanism causing a variety of anomalies obtained in thermal, acoustic, dielectric and other measurements.

Even phenomenological models fail in considering a large amount of experimental results (Phillips 1981; Fischer 1983). A further advance in this direction is rendered more difficult by the experimental fact that with increasing structural disorder the glassy behaviour of different solids gets quite similar independent of individual properties of the crystalline modification.

But simple disorder is not sufficient for explaining the effect. Consequently, investigations of an analogous behaviour of ordered crystalline solids are needed with facilitating the identification of decisive excitations.

Glassy behaviour is well established in a variety of crystalline materials. In particular, measurements of ferroelectric crystals are important owing to advanced structural investigations and high sensitivity of the dielectric constant for low-lying excitations (Fischer, 1983). The character of phase transition is thought to be important for nature, concentration and kinetics of localized excitations. There are displacive type and order-disorder type ferroelectrics characterized by different strength of the potential anharmonicity describing the energy of atoms and dipoles rearranging at phase transition.

Some displacive type ferroelectrics exhibit a high degree of structural and compositional disorder causing a diffuse phase tran-

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sition. For such relaxation ferroelectrics the glassy behaviour was first found for PMN (Ackerman et al. 1981), PLZT polycrystals (Fischer et al. 1981) and SBN single crystals (Fischer et al. 1982). Analogous results are obtained for $Pb_xSr_{1-x}TiO_3$ ceramics and for the quantum paraelectric single crystal $SrTiO_3$ (Fischer, 1983).

In order-disorder type ferroelectrics the phase transition is caused by the condensation of a soft tunneling mode. In KDP-type crystals in the paraelectric state the protons tunnel between the two minima a double-well potential along the hydrogen bonds. Above the Curie-temperature T_c the proton motion within different bonds is uncorrelated. This corresponds to a high degree of disorder in the proton system. At $T > T_c$ measurements of thermal conductivity on such crystals show similar results as known for glasses (Suemune 1967). At phase transition the glassy behaviour appears to be finished. For $T < T_c$ the dipolar interaction causes a long-range order in the proton system and in the lattice coupled to it. The tunneling motion of protons is localized within one potential minimum. However, a certain disorder remains due to the domain structure. Therefore it is promising to study the influence of this kind of disorder on thermal and dielectric properties of these crystals.

Experiment

For measurement of the thermal conductivity and the dielectric constant monocrystalline samples with large T_c (TGS, T_c=322K), intermediate T_c (KDP, T_c=123K) and low T_c (DLTlT, T_c= 1.8K) were chosen. The thermal conductivity was measured at $0.1K < T < 4K$ by a usual stationary two-heater method in a ^3He-^4He dilution refrigerator. The temperature was determined by a calibrated Ge-thermometer checked by a second one mounted on a sample holder. The present paper deals with the results of thermal conductivity. The dielectric data and all

details of preparation and measuring accuracy are summarized by Fischer (1983).

Results

For a KH_2PO_4 single crystal ($6.5 \times 7.3 \times 30$ mm^3) λ was measured along the c-axis. In this direction the phonon propagation is more sensitive to the scattering by proton motion localized mainly in a plane normal to the ferroelectric c-axis (Hegenbarth 1980). The results are shown in fig.1. The low temperature data ($T < 4.2K$) make a good extrapolation to the higher temperature data though the results are obtained for different samples with unknown defect concentration and domain structure.

For comparison the results for KP_2PO_4, and the calculated variation of $\lambda(T)$ due to crystal surface, dislocations, point imperfections, and Umklapp processes are also illustrated.

At $T < 4.2K$ the results obey:

$$\lambda = 1.0 \cdot 10^{-2} \cdot T^{2.05 \pm 0.1} \quad (W/cmK)$$

In $LiTlC_4H_4O_6 \cdot H_2O$ (LiTlT) the phase transition is also determined by the kinetics of proton tunneling. The Curie-temperature of LiTlT (T_c=10K) is shifted to lower temperatures by deuteration (T_c=1.8 for DLiTlT, (Brezina et al.1970)). Figure 2 presents the thermal conductivity results for a DLiTlT single crystal (2x2x15 mm^3) at $0.1K < T < 4.2K$. The heat flow was along the a-direction parallel to the spontaneous polarization axis. Again there is a good extrapolation to the high temperature values ($T > 4.2K$).

For $T < 1K$ one obtains:

$$\lambda = 9.7 \cdot 10^{-3} \cdot T^{2.0} \quad (W/cmK).$$

At T_c there is a distinct discontinuity in slope.

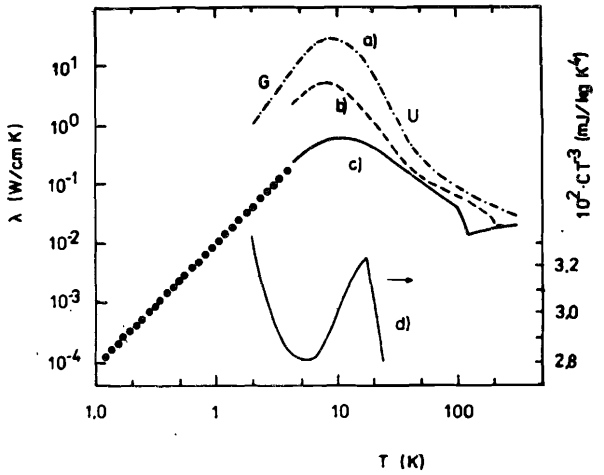

Fig.1. The thermal conductivity λ of a KH_2PO_4 polydomain single crystal. For $T > 4K$ results are taken from (Suemune 1967).
a) The calculated variation with the temperature of λ due to phonon scattering on the crystal surface (G), dislocations, point imperfections and Umklapp processes (U);
b) and c) thermal conductivity of KD_2PO_4 and KH_2PO_4, respectively;
d) specific heat, divided by T^3, of a KH_2PO_4 single crystal (Lawless 1976).

In $(NH_2CH_2COOH)_3 \cdot H_2SO_4$, (TGS) there is a second-order phase transition at $T_c = 322K$. The changes in dielectric properties by deuteration are negligible in comparison with the two other samples (Lines and Glass 1977). Thermal conductivity was measured along the c-axis, i.e. perpendicular to the polar b-axis. The results for two different samples are shown in fig.3. At $0.1K < T < 3K$ the first sample ($0.5 \times 0.7 \times 30$ mm^3) obeys:

$$\lambda = 2.96 \cdot 10^{-2} \cdot T^{2.6} \quad (W/cmK) .$$

The small cross section of the sample and the high absolute value of λ suggest that this behaviour is due to the influence of boundary scattering at these temperatures where the mean free path is of the order of 0.1 ... 1 mm. Thus, for clear deduction of any contribution from low-lying excitations the boundary scattering should be eliminated. So measurements were continued for a larger sample ($5 \times 10 \times 35$ mm^3, sample 2). The results show a well-defined T^2-dependence at $0.1K < T < 1K$.

Discussion

The thermal conductivity of the three ferroelectrics shows the T^2-dependence at low temperatures suggesting phonon scattering typical for glasses. However, for these single crystals the absolute values of λ are advanced by 2 ... 3 orders of magnitudes. On account of this, a maximum in λ is obtained for $T \approx 10K$ known for crystals. Yet the value of λ_{max} is reduced by more than two orders in comparison with the results expected by calculating the phonon scattering as usual for dielectric crystals (fig.1). Above the maximum in λ the Umklapp processes ($\lambda \sim T^n \exp(\Theta/\alpha T)$) do not limit the thermal conductivity in KDP and DLiTlT (Suemune 1967, Hegenbarth 1980):

KDP: $\lambda \sim T^{-1.5}$ at $20K < T < 100K$
DLiTlT: $\lambda \sim T^{-1}$ at $10K < T < 30K$.

Therefore, it appears unreasonable to suggest that the reduced maximum in λ is due to the low-temperatures scattering process (T^2-dependence) alone. There is rather a second phonon scattering at $T \gtrsim T_{max}$ other than the Umklapp process. It is obvious to identify this scattering process as a typical one causing the plateau in λ

in glasses. Owing to the low intensity of this scattering mechanism in these ferroelectric crystals, it could not influence significantly the slope in $\lambda(T)$. This discussion in terms of glassy behaviour is confirmed by available specific heat and dielectric data. It is well-established that the specific heat of amorphous materials exhibits a minimum-maximum behaviour in C/T^3 against T representation. Usually this effect is explained by the contribution of low-lying localized states (two-level systems and Einstein-modes). These anomalies in specific heat are also found for KDP and TGS crystals (Lawless 1976). For KDP this is shown in connection with thermal conductivity results (fig.1). It has been found by Ackerman et al. (1981) that the peak in C/T^3 is correlated with the plateau in λ both for amorphous and crystalline materials. So the typical phonon scattering mechanism responsible for a plateau-like slope, if sufficently strong (as in amorphous materials), for KH_2PO_4 is expected around 17K. This is confirmed by the above discussion concerning the reduced λ at these temperatures. Another interesting feature of λ should be pointed out. For KDP-type crystals it has been found by Suemune (1967) that the thermal conductivity peaks λ_{max} increase proportionally to the fourth power of the Curie-temperatures T_c as:

$$\lambda_{max} \approx 2.6 \cdot 10^{-9} \cdot T_c^4 \ (W/cm \cdot K) \qquad (1).$$

The present results show that below the peak λ obeys: $\lambda = A \cdot T^2$. It is easy to show that the correlation can be also expressed concerning A as $A \sim \lambda_{max} \sim T_c^4$ within the same accuracy. In the current tunneling model (Phillips 1981): $A \sim (n_0 \cdot \gamma^2)^{-1}$ (n_0 is a constant density of two-level systems and γ the coupling constant). It is known that γ is not very sensitive within the same class of materials. Thus, eq. (1) gives a correlation between low-lying states and lattice dynamics: $n_0 \sim T_c^{-4}$. The analogous relationship is known for amorphous solids with $n_0 \sim T_g^{-1}$ (T_g is

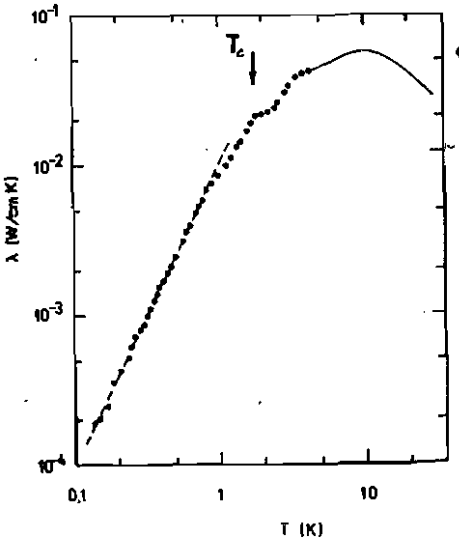

Fig.2. Thermal conductivity of DLiTlT. •, present data (- -, $\lambda \sim T^2$); —, data from (Hegenbarth 1980).

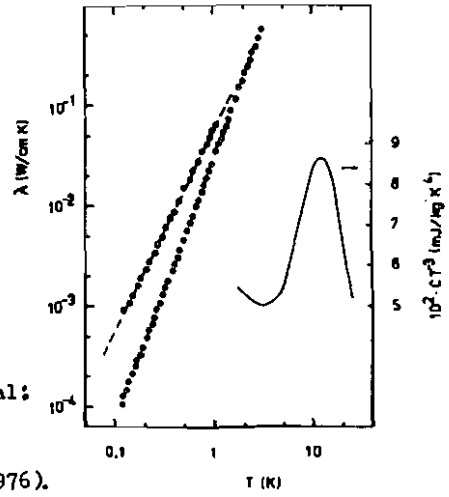

Fig.3. Thermal conductivity of a TGS polydomain single crystal: •, sample 1; o, sample 2, (- -, $\lambda \sim T^2$); —, specific heat divided by T^3 of TGS (Lawless 1976).

the glass transition temperature), (Raychandhuri and Pohl 1982). This relation was the subject of some speculations in the framework of two-level system spectra. Such a type of correlation is also known for antiferromagnetic monoxides with the NaCl-type structure where $\lambda_{max} \sim T_N^{4/3}$ (T_N is the Neel-temperature). Suggesting glassy behaviour and $n_0 \sim T_N^{-4/3}$ for these crystals with magnetic order. It is interesting to prove these correlations for other groups of ferroelectrics and ferromagnetics. The glassy behaviour of order-disorder-type ferroelectrics is confirmed by the dielectric measurements. Figure 4 shows, for example, the variation of dielectric constant for a KDP single crystal. There is a distinct minimum in $\Delta\varepsilon/\varepsilon$ at $T \approx 1.5K$, and the logarithmic temperature dependence for $T < T_1$

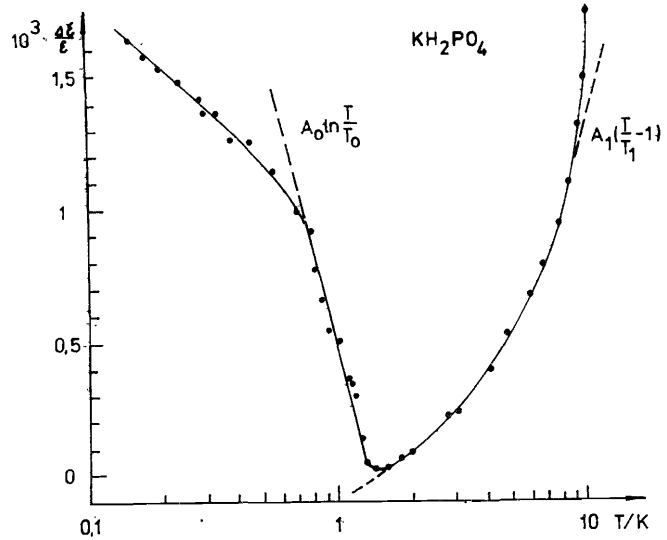

Fig.4. Variation of $\Delta\varepsilon/\varepsilon$ with temperature for a KDP single crystal.

is well known for glasses. For the measuring frequency f = 1.6 kHz, the value of T_{min} is approximately one order of magnitude larger than that usually observed in amorphous materials and other disordered solids. The lineary dependence $\Delta\varepsilon/\varepsilon = A_1(T/T_1 - 1)$ ($A_1 = 2.1 \cdot 10^{-4}$, $\varepsilon'(T_1) = 14.7$) for $T > T_1$ is also a substantial feature of the universal mechanism causing glassy behaviour (Fischer 1983).

Conclusions

Measurements of thermal conductivity, specific heat and dielectric constant at low temperatures show the glassy behaviour of order-disorder-type ferroelectric single crystals.

Analogous results are known for relaxation ferroelectrics and quantum paraelectrics.

An analysis of thermal conductivity data in terms of two-level systems gives values for $n_o \gamma^2$ or n_o lying in the same range as for other disordered and amorphous solids (see the Table).

Table. Analysis of Thermal Conductivity Data:
1) from (Fischer 1983),
2) from (Anthony and Anderson 1976),
3) from (Smith et al. 1978)

	$\lambda \cdot T^{-2}$ (W/cm·K^3)	$n_o \cdot \gamma^2$ (J/m^3)	n_o (J^{-1}·m^{-3})
KH_2PO_4	$1.0 \cdot 10^{-2}$	$4.4 \cdot 10^5$	$1.2 \cdot 10^{43}$
DLiTlT	$9.7 \cdot 10^{-3}$	$3.9 \cdot 10^5$	$1.1 \cdot 10^{43}$
TGS	$5.8 \cdot 10^{-2}$	$5.5 \cdot 10^4$	$1.5 \cdot 10^{42}$
SBN[1]	$1.0 \cdot 10^{-4}$	$1.0 \cdot 10^8$	$2.8 \cdot 10^{45}$
$SrTiO_3$[1]	$2.6 \cdot 10^{-4}$	$3.7 \cdot 10^7$	$1.0 \cdot 10^{45}$
am SiO_2[2]	$1.6 \cdot 10^{-4}$	$2.6 \cdot 10^7$	$7.1 \cdot 10^{44}$
Me-β-Alumina[3]	$4 \cdot 10^{-2}$ ... $2 \cdot 10^{-4}$	$6.4 \cdot 10^4$ ... $1.3 \cdot 10^7$	$1.7 \cdot 10^{42}$ ... $3.5 \cdot 10^{44}$

Similar to neutron-irradiated SiO_2, the results obtained for a variety of crystalline solids emphasize the suggestion that the physics of glassy behaviour cannot be characterized by any quantity criterion as given, for example, by Ackerman et al. (1981): ($\lambda \approx 10^{-4} T^2$ a.s.o.). It appears that the sizes of glassy anomalies continiously scale down to zero. So any "typical" anomaly may be masked by other effects just like the "plateau"-scattering in order-disorder-ferroelectrics. Therefore a more general definition of glassy behaviour is needed where, besides the existence of certain localized excitation spectra, the correlation of various low-temperature phenomena is the most important and characteristic feature. It is worth emphasizing a strong correlation between low-lying states and lattice dynamics of different classes of solids. So the glass transition temperature for amorphous solids plays an analogous role as the Curie-temperature

for ferroelectrics. It is of principal interest that this correlation is much stronger for ferroelectric single crystals where the disorder in domain structure is much smaller than the lattice disorder in glasses. This fact limits the simple assumptions (Raychaudhuri and Pohl 1982) in the framework of the usual tunneling model. The results suggest that the "pure" mechanism responsible for glassy phenomena is better to recognize in ordered solids. This is confirmed by recent statements that topological disorder is not sufficient for glassy behaviour (Löhneysen et al. 1981, Gardner and Anderson 1981) and that polymorphism is conducive to the creation of localized excitation spectra (Wang and Merz 1976, Mon and Ashcroft 1978). It appears that we have to look at the lattice dynamics causing phase transitions to understand the physics of low-temperature behaviour. The competition of long-range and short-range order forces that leads to a phase transition at a certain temperature T_o is essential. One can argue that fluctuations of local rearrangements between the two phases is the initial process creating low-energy excitations due to lattice responds in the neighbourhood. Then the probability of such dynamic fluctuations is determined by the long-range order, i.e. by frozen disorder. Thus, the latter plays the part of a catalyzator for the magnitude of glassy anomalies. In this picture is no need to postulate a low energy spectrum. The excitations indeed occur within the ordered regions. Consequently, glassy behaviour could not be seen in solids that have a stable phase at all temperatures and no polymorph. This is consistent with thermal conductivity and specific heat measurements on MgO (Gardner and Anderson 1981) and dielectric data for TlCl (Holste et al. 1976). In the case of β-alumina the initial excitations are thought to be the transitions of mobile ions accompanied by lattice response. However, the equilibrium disorder and, hence, the strength of anomalies can be changed due to extrinsic parameters, for instance, by cooling through T_c in the presence of an electrical field. Thus, in the limit of a single-domain sample no glassy anomalies can be observed (Villar et al. 1981, Grimm et al. 1984). For order-disorder ferroelectrics the above discussion can be specified as follows: the decisive excitations are due to the proton-(deuteron) motion in the O-H-O bonds. These can be described by a soft tunneling mode that is coupled to an optical lattice mode (Lines and Glass 1977). Below the Curie-temperature the tunneling motion of photons is nearly stopped. Now the long-range correlation in the proton system causes an asymmetric double-well potential of each O-H-O bond, and the protons will oscillate within the lower minimum. However, if the correlation is incomplete due to the disorder in the domain structure, the possibility of local fluctuations in the upper state remains finite even far below T_c. This corresponds to a dynamic rearrangement from ferroelectric to paraelectric configuration in the short-range order. Then the response of the surrounding ferroelectric matrix gives rise to additional low-energy excitations typical for glassy behaviour.

A more detailed consideration of these problems is given by (Fischer (1983) and will be published elsewhere.

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Received by Publishing Department on April 8, 1986.

Фишер З.

E8-86-213

Стеклообразное поведение сегнетоэлектрических монокристаллов типа порядок-беспорядок при низких температурах

Измерена теплопроводность монокристаллов KH_2PO_4, DLiTlT и TGS в области температур от 0,1К до 4К. Для всех образцов найдена квадратичная температурная зависимость: $\lambda = A \cdot T^2$, где $A \approx (1...6) \cdot 10^{-2}$ W/cm·K^3. Учитывая известные данные удельной теплоемкости и диэлектрических измерений, полученные результаты можно объяснить как проявление низкотемпературных аномалий, характерных для аморфных веществ. У кристаллов типа KDP обнаружена сильная связь между коэффициентом A и температурой Кюри T_c, т.е. $A \sim T_c^4$. Высказывается предположение о существовании аналогичной корреляции и для других типов кристаллов. Похожие результаты известны для аморфных веществ, где характерным параметром является температура стеклообразования T_g, обратно пропорциональная линейному вкладу в теплоемкость. Результаты указывают на то, что подробное изучение динамики решетки, отвечающей за фоновые превращения, имеет важное значение для подлинного понимания низкотемпературных аномалий сильно дефектных веществ и стекол.

Работа выполнена в Лаборатории высоких энергий ОИЯИ.

Препринт Объединенного института ядерных исследований. Дубна 1986

Fischer E.

E8-86-213

Glassy Behaviour of Order-Disorder Type Ferroelectric Single Crystals at Low Temperatures

The thermal conductivity λ of KH_2PO_4, DLiTlT and TGS single crystals was measured in the temperature range from 0.1K to 4K. For all samples λ is quadratic in temperature: $\lambda = A \cdot T^2$ with $A \approx (1...6) \cdot 10^{-2}$ W/cm·K^3 . Taking into account available specific heat data and dielectric measurements, the results can be explained by glassy behaviour. The coefficient A is found to be proportional to T_c^4(T_c is the Curie temperature) for KDP-type crystals. Analogous correlations are suggested to be true for other groups of solids. Similar results are known for amorphous solids where the important parameter is the glass transition temperature T_g and the excess specific heat is inversely proportional to T_g. This leads to the conclusion that detailed information concerning lattice dynamics causing a phase transition is essential for understanding the physics of glassy behaviour at low temperatures.

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

Preprint of the Joint Institute for Nuclear Research. Dubna 1986