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Small-signal dielectric relaxation in the disordered perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$

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Abstract. Decay-current and conventional dielectric measurements have been performed on single-crystal samples of the disordered perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN). Low-frequency dielectric data of Colla and co-workers on the same system are critically reanalysed and compared to our results.

In contrast to previously proposed spin-glass or master-plot approaches, we suggest a phenomenological description in terms of α- and β-relaxations: a relatively high-frequency β-process takes over when the characteristic α-relaxation time becomes extremely long. The continuous slowing down of polar motion distinguishes PMN from related compounds such as $Pb(Zn_{1/3}Nb_{2/3})O_3$, for which, in contrast to PMN, there is evidence of a structural phase transition.

1. Introduction

The dielectric constant of simple oxide perovskites with the general formula ABO_3 is determined by the Lyddane–Sachs–Teller mechanism, and is therefore independent of frequency up to the RF range. Introduction of isovalent substitutional impurities (e.g. Li for K in $KTaO_3$) results in mixed crystals that may show low-frequency dielectric relaxation associated with reorientations of the impurity-induced defect. The stochiometric complex perovskites $AB_pB'_{1-p}O_3$, where B and B′ have different nominal charges, and p is a rational fraction ($\frac{1}{2}$ or $\frac{1}{3}$; in some cases $\frac{1}{4}$) were primarily discovered and studied in depth by Smolenskii's group in the sixties (for a review see Smolenskii *et al* 1984). Possible applications have revived the interest in these systems in recent years. For some compositions, the B and B′ ions can be made to sit on ordered sublattices, but disorder (although perhaps not real randomness) is more frequently the case. $PbMg_{1/3}Nb_{2/3}O_3$ (PMN) is always disordered and shows a marked temperature and frequency variation of the complex dielectric susceptibility. In the Hz–MHz range, $\chi'(\omega, T)$ peaks around 270 K. Structural studies, however, fail to show a phase transition down to very low temperatures (de Mathan *et al* 1991), and thus cast doubt on the interpretation of the $\chi'(T)$-maximum as a 'diffuse' (Smolenskii 1970) or a martensitic-like (Schmidt *et al* 1981) phase transition.

This lack of long-range polar order, together with the $\chi(\omega, T)$ behaviour, has led to analogies with the behaviour of spin glasses; the most extensive treatment of this has been performed by Viehland *et al* (1991). Phenomenologically, spin glasses are paramagnetic systems that show dispersion in their AC susceptibility at frequencies very much lower than typical spin-lattice relaxation rates for uncoupled spins. It has become common to consider

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mainly $\chi'(\omega, T)$ (see however Hüser *et al* 1983) and to determine a characteristic frequency $\omega_c(T)$ from the condition $\partial\chi'(\omega_c)/\partial T = 0$. These data are then inverted to obtain $T_c(\omega)$, a frequency-dependent transition temperature.

Another possible approach starts with the observation (Johari 1987) that the phenomenology of primary (or α) and secondary (or β) dielectric relaxation seems to be common to several classes of disordered system (ionic glasses, liquid glass formers, amorphous polymers). The dielectric α-relaxation is detected primarily above the glass temperature, and the β-relaxation primarily below it. Quite generally, the characteristic α-relaxation time is markedly non-Arrhenius as a function of temperature, and the β-relaxation time distribution is much wider than the α-distribution (for a more elaborate discussion, see Johari 1987). It has been pointed out, at least for the van der Waals glass *o*-terphenyl (Wu and Nagel 1992), that the high-frequency secondary relaxation observed above the glass temperature using scattering techniques (Kiebel *et al* 1992), and also called β-relaxation in mode-coupling theory, may lack a common origin with the conventional dielectric β-relaxation in the sense of Johari and Goldstein (1971). The low-temperature dielectric behaviour of the orientational glass (Höchli *et al* 1990) $(KBr)_{1-x}(KCN)_x$ has also been described as β-relaxation (Ernst *et al* 1988); the corresponding α-relaxation has so far only been studied by elastic experiments (Volkmann *et al* 1986).

The lack of evidence of a structural transition in PMN (in contrast to what has been observed in the related compound PZN, $PbZn_{1/3}Nb_{2/3}O_3$, by Yokimozo *et al* (1970)), some unresolved questions (see section 4) regarding the treatments by Viehland *et al* (1991) and by Colla *et al* (1992) and the recent interest in wide-range low-frequency dielectric studies of α-and β-relaxation in structurally amorphous systems, such as gels and glasses (Schönhals *et al* 1993, Ren and Sorensen 1993, Wu and Nagel 1992) has led us to attempt a phenomenological description of the dielectric behaviour of PMN in terms of α- and β-relaxation, hoping to find an additional example of the generality of these phenomena.

2. Theoretical details

Equations (1)–(7) below were derived long ago, primarily to analyse the viscoelastic behaviour of polymers. Several of them seem to have been rediscovered recently. We merely present them to establish notation and refer only to the older literature.

The response of any linear and time-shift-invariant system to a small external (mechanical, electrical, magnetic) stimulus can be completely specified by just one of six characteristic functions: (i) the step-response function $b(t)$; (ii) the impulse-response function $h(t)$; (iii) the real susceptibility $\chi'(\omega)$; (iv) the imaginary susceptibility $\chi''(\omega)$; (v) the (linear) distribution of relaxation times $g(\tau)$; and (vi) the logarithmic distribution $G(\ln\tau)$ of relaxation times. A response function must be known for all positive times, a susceptibility for all positive frequencies, and a distribution for all positive correlation times. Mathematically, all representations are equivalent. In practice, numerical transformation of experimental data can lead to unphysical results due to cut-offs and noise.

Experiments measure $\chi'(\omega)$, $\chi''(\omega)$ and/or $b(t)$ over a necessarily finite interval of frequency or time: this usually means that transformation into $G(\ln\tau)$ or $g(\tau)$ cannot be done with absolute confidence, and that the data can be fitted by several (but certainly not all) of the conventional empirical expressions. Even when a distribution of relaxation times is used to describe the data, this does not necessarily mean that the sample contains a number of independent elements that relax in parallel over a distribution of individual barriers: hierarchical (sequential) relaxation of coupled elements may exhibit the same macroscopic

behaviour. We will regard a description in terms of $G(\ln\tau)$ more as a convention than as physically the most relevant. In our opinion, the cause/effect relationship is most clearly expressed by the step-response function.

The logarithmic distribution $G(\ln\tau)$ of relaxation times can be extracted from experimental data on $\chi'(\omega)$, $\chi''(\omega)$, or $h(t)$ by (Schwarzl and Staverman 1953, Böttcher and Bordewijk 1978)

$$G(\ln\omega^{-1}) \simeq [\omega/\chi'(0,T)](-\partial\chi'/\partial\omega + \tfrac{1}{4}\omega^2\partial^3\chi'/\partial\omega^3 + \cdots) \tag{1a}$$

$$G(\ln\omega^{-1}) \simeq [2/\pi\chi'(0,T)](\chi'' - \omega^2\partial^2\chi''/\partial\omega^2 + \cdots) \tag{1b}$$

$$G(\ln t) \simeq th(t) + \cdots. \tag{1c}$$

When the variation of χ with ω is slow, one needs only the first term on the right-hand side of (1*a*, *b*). Higher-order approximations for (1*c*) have been devised, but are not of immediate concern here.

A second way to relate $h(t)$, $\chi'(\omega)$, and $\chi''(\omega)$ is based on some general features of the Cole–Cole plot. The case of interest to us is that where the angles of intersection of the plot with the real axis are both less than $\pi/2$. (This excludes, among others, Wagner's Gaussian distribution function and the Kohlrausch–Williams–Watts stretched-exponential response function). Let the low-frequency angle be $m\pi/2$, the high-frequency angle $(1-n)\pi/2$, and let ω_p be the frequency of the maximum in $\chi''(\omega)$; the terms $m(T)$, $n(T)$, and $\omega_p(T)$ can be temperature dependent. For this type of Cole–Cole plot it has been shown that (Bordewijk and van Gemert 1957, Hill 1981)

$$\omega \gg \omega_p : \chi''(\omega) = \chi'(\omega)\cot(n\pi/2) \tag{2a}$$

$$(\omega/\chi'')\partial\chi''/\partial\omega = -(1-n) \tag{2b}$$

$$0 < n < 1 \tag{2c}$$

$$\omega \ll \omega_p : \chi''(\omega) = (\chi'(0) - \chi'(\omega))\tan(m\pi/2) \tag{3a}$$

$$(\omega/\chi'')\partial\chi''/\partial\omega = m \tag{3b}$$

$$0 < m < 1. \tag{3c}$$

If furthermore the slope of the log–log plot of $\chi''(\omega)$ at constant temperature, or equivalently the function

$$s(\omega,T) = 1 + (\omega/\chi'')\partial\chi''/\partial\omega \qquad 0 < s < 2 \tag{4}$$

varies slowly with frequency, then the relation between h and χ'' can be evaluated in the Hamon (1952) approximation:

$$\chi'(0,T)h(\omega^{-1},T) = \omega\chi''(\omega,T)/\Gamma(1-s)\cos(s\pi/2) \tag{5}$$

with

$$(t/h)\partial h/\partial t \simeq -s(t^{-1},T). \tag{6}$$

A third method to relate h, χ', and χ'' is to postulate a mathematical expression for any one of the six characteristic functions. Among the expressions that are compatible with (2) and (3), the Havriliak–Negami (HN) function (Havriliak and Negami 1967) is probably the

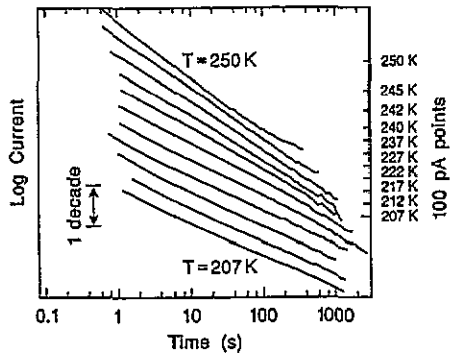

Figure 1. A log–log plot of depolarization current at 11 temperatures between 207 and 250 K. The curves have been shifted for clarity, and the position of the 100 pA point on the logarithmic vertical scale is indicated on the right-hand vertical axis.

most widely used. When written in complex form, $\chi^* - 1 = (1 + (j\omega\tau_c)^{(n-1)/m}$, it is easily recognized to yield the simple Debye relaxation in the special case where $m = 1, n = 0$. For general values, $0 < m \leqslant 1$ and $0 < 1 - n \leqslant m$, we can write

$$\chi'(\omega, T) = \chi'(0, T)\cos(\psi)[1 + x^{2m} + 2x^m \cos(m\pi/2)]^{(n-1)/2m} \tag{7a}$$

$$\chi''(\omega, T) = \chi'(\omega, T)\tan(\psi) \tag{7b}$$

$$G(\ln\tau) = \pi^{-1} y^{1-n} \sin((1-n)\theta/m)[1 + y^{2m} + 2y^m \cos(m\pi)]^{(n-1)/2m} \tag{7c}$$

where

$$x = \omega\tau_c(T)$$

$$\psi = [(1-n)/m]\tan^{-1}(x^m \sin(m\pi/2)/[1 + x^m \cos(m\pi/2)])$$

$$y = \tau/\tau_c(T)$$

$$\theta = \tan^{-1}(\sin(m\pi)/[y^m + \cos(m\pi)])$$

and $\tau_c(T)$ is related to $\omega_p(T)$ by an implicit equation involving n and m. For given m and n, the HN function yields wider loss peaks than other expressions such as those proposed by Jonscher (1983) or by Dissado and Hill (1979).

3. Experimental results

3.1. Data for PMN

We have performed measurements on a ⟨111⟩ oriented PMN single crystal with the dimensions $2.4 \times 4.6 \times 0.15$ mm^3 cut from a boule grown by A Titov at St Petersburg Optical Institute. Depolarization currents were measured between 207 and 250 K with a fast-response (40 ms) Keithley 642 electrometer and a Hewlett–Packard hp 6634A power supply (fall time = 40 μs). Each curve was obtained by first charging the zero-field-cooled sample at constant voltage and constant temperature, and then measuring the depolarization current for a time not exceeding one third of the charging time. Thus our results effectively cover a time interval from 1 s to 1000 s (figure 1), corresponding, according to equation (5), to a frequency window $\omega/2\pi = 1.6 \times 10^{-4}$–0.16 Hz.

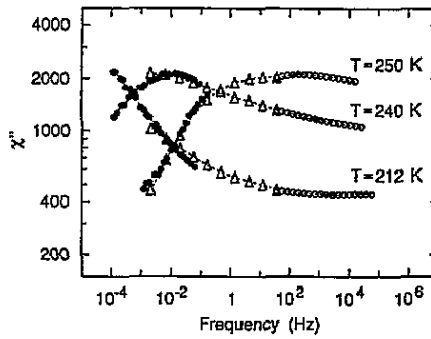

Figure 2. The value of $\chi''(\omega)$ in PMN at approximately 250 K, 240 K, and 212 K. Triangles are data from Colla *et al* (1992). Filled circles are our depolarization data, transformed in the Hamon approximation, and scaled at 10 MHz. Open circles are our conventional dielectric results scaled at 100 Hz.

Dielectric experiments were performed on the same sample, using a GR1616 capacitance bridge at frequencies ranging from 100 Hz to 100 kHz. Colla and colleagues (1992) have made available their detailed results for a ⟨100⟩ crystal in the 188–266 K and 3 mHz–100 Hz range. In the overlapping frequency ranges, the qualitative agreement between their data and ours is good (although one would expect quantitative differences from one crystal to another) (see figure 2).

3.2. *The case of* PZN

In order to better appreciate the particularities of PMN's behaviour, we now wish to summarize published results for the related compound PZN. Yokimozo *et al* (1970) have reported $\chi'(\omega, T)$ and $\tan(\delta(\omega, T))$ values for single-crystal samples at frequencies of $\omega/2\pi = 120$ Hz, 10 kHz and 1 MHz from room temperature to 500 K. They find that χ' is frequency dependent only around the peaks that occur at approximately 400 K, while $\tan(\delta)$ is frequency dependent over the entire temperature interval. This important qualitative difference from the data for PMN enabled Dissado and Hill (1983) to perform a master-plot analysis over the temperature range 323–498 K. Near 400 K, $\chi'(0, T)$ has a maximum and ω_p a minimum (see figure 3). This is typical of regular ferroelectric phase transitions, although these PZN data do not show regular critical behaviour. From x-ray results, Yokimozo *et al* (1970) find a rhombohedral structure at room temperature, and a cubic one at 570 K. The master plot (Dissado and Hill 1983) obeys (2) and (3) with $n = 0.88$ and $m = 0.41$ in both phases.

4. Discussion

4.1. *Previous treatments*

Vakrushev, Colla and colleagues (Colla *et al* 1992) have analysed their dielectric data (190 K $< T <$ 260 K, 3 mHz $< \omega/2\pi <$ 100 Hz) for a ⟨100⟩ PMN crystal using time/temperature scaling, also called the 'master-plot hypothesis'. In this method, it is supposed that one can write $\chi''(\omega, T) = \chi'(0, T)F(x)$, with $x = \omega\tau_c(T)$, and where the unknown function $F(x)$ depends on frequency or temperature only through the product $\omega\tau_c(T)$. The data analysis uses a graphical method to determine $F(x)$, so it is not necessary

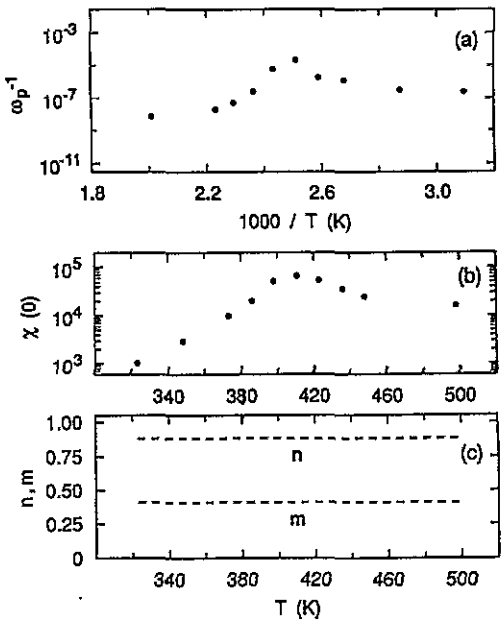

Figure 3. Parameters of the master plot by Dissado and Hill (1983) of dielectric data for PZN from Yokimozo *et al* (1970).

to have an explicit mathematical expression for it. The $\chi''(\omega, T)$ data for all frequencies and temperatures are represented by the graph of $F(x)$, and by the temperature variations of $\chi'(0, T)$ and $\omega_p(T)$, which represents the variation of the scaling variable $\tau_c(T)$. $F(x)$ thus obtained by Colla *et al* has a width at half height over seven decades, as compared to 1.14 decades for a simple Debye relaxation, or to typical values of three decades for undercooled glass-forming liquids. The graph of $\chi'(0, T)$ has not been presented but the analysis implies that it diminishes with decreasing temperature below 230 K, leading to a maximum in $\chi'(0, T)$ somewhat above this temperature. Between 235 K and 255 K, $\omega_p(T)$ (the frequency of the maximum in χ'' at constant temperature) follows an Arrhenius law. The parameters of this fit indicate that the slowing down of motion cannot be interpreted as a thermally activated single-particle phenomenon. From 255 to 260 K, Vogel–Fulcher curvature has been found. Below 250 K, there were indications of a change in shape of the function F (the inflection point near $\omega/\omega_p = 10$ in figure 3 of Colla *et al* 1992). For this temperature range, the present analysis of the original data will show that the scaling hypothesis does not hold. In fact, the observed behaviour is seen to result from a superposition of two relaxation branches. Therefore, the parameters describing the relaxation in this temperature range cannot be found from a master-plot analysis.

Nadolinskaya *et al* (1987) have obtained dielectric data on single-crystal PMN from 10^{-1} to 10^4 Hz, and between 83 and 383 K. Here we consider only the temperature interval from 225 to 262 K. In the overlapping frequency range, their data and those of Colla *et al* (1992) are qualitatively similar. However, their high-frequency data are unlike ours (and unlike those of Ye and Schmid 1993) in that they can fit a Cole–Cole equation with a high-frequency limit ϵ_∞ considerably different from zero, of the order of one third of the extrapolated zero-frequency dielectric constant. The reason for the existence of this high-frequency limit is unclear.

In their 'spin-glass' model Cross, Viehland and colleagues (Viehland *et al* 1991) show

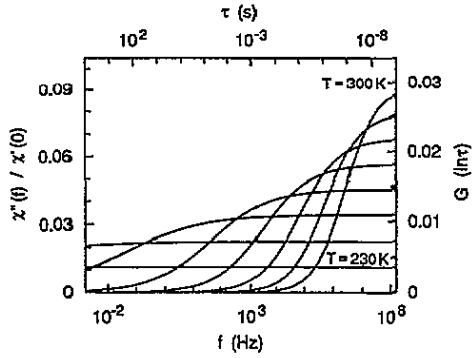

Figure 4. Bottom and left-hand scales: the value of $\chi''(f)/\chi'(0)$ in the high-temperature phase of the spin-glass model for PMN, according to (8) and (A2*a*). Note that the experimental curves for χ'' (figure 2) are not qualitatively reproduced. Top and right-hand scales: the logarithmic distribution of relaxation times, calculated from (1*b*), (8), and (A2*a*). The parameter of the curves is the temperature in steps of 10 K from 230 K to 300 K.

that their χ''-data for 10^2 Hz $< \omega/2\pi < 10^7$ Hz can be fitted to the expression

$$\chi''(\omega, T) = [c/(c + (\omega\tau_0)^{-\alpha(T)})]\phi(T) \tag{8}$$

with $c = \exp(T_c/T_d)$, $\alpha(T) = (T - T_f)/T_d$, $\tau_0 = 10^{-12}$ s, and the temperatures approximately given by $T_c = 880$ K, $T_d = 98$ K and $T_f = 220$ K; $\phi(T) = a\exp(bT)$, where a and b are positive constants that have not been specified. This means that $\chi''(\omega)$ is nearly frequency independent for $T \leqslant T_f$, whereas for $T > T_f$ it increases monotonically with frequency (see figure 4). As it stands, however, (8) is not Kramers–Konig compatible. Rigorously speaking, it does not describe a physically possible system, and therefore its parameters may lack physical significance. In the appendix we propose a simple additional hypothesis that permits a Kramers–Konig transform of (8) to be obtained; unfortunately, this leads to predicted behaviour of $\chi'(0, T)$ that does not agree with experiment. This suggests that minor modifications of (8) are not sufficient to obtain a correct description of both $\chi'(\omega, T)$ and $\chi''(\omega, T)$. The difference seems to arise from the lack of a well defined peak in the $\chi''(\omega)$ curves predicted by (8).

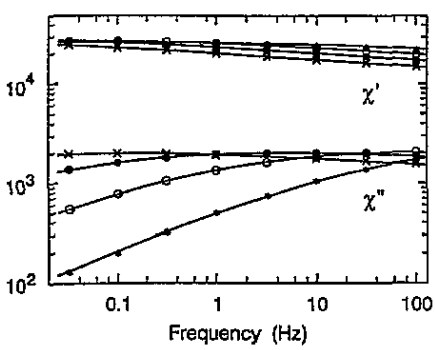

Figure 5. A fit of $\chi''(\omega)$ and $\chi'(\omega)$ for PMN measured by Colla *et al* (1992) to the HN function (7): ×, 244.5 K; ●, 248.5 K; ○, 252.5 K; *, 256.5 K.

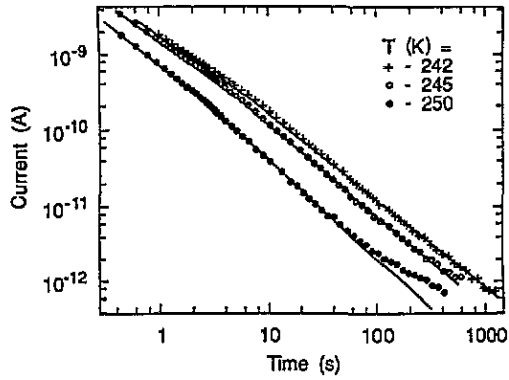

Figure 6. The depolarization current measured in PMN and the Hamon approximation, (5) and (7*b*), using n and m values derived from fits as in figure 5. The vertical scale has been adjusted. +, 242 K; O, 245 K; ●, 250 K.

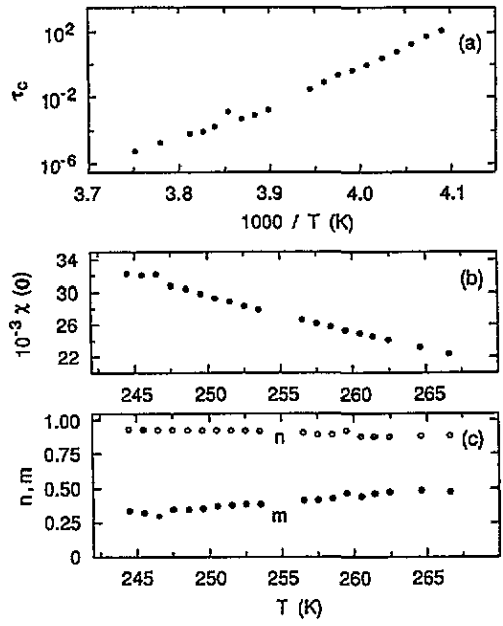

Figure 7. Parameters of the fit of dielectric data for PMN from Colla *et al* (1992) using the HN function for $\chi(\omega)$ (7*a*, *b*). Compare with figure 3.

4.2. α- and β-relaxation

Between 244 and 267 K, the dielectric relaxation is well described by the HN equations (see figures 5 and 6). Even in this fairly narrow temperature range, the master-plot approach is not strictly valid, since we find that the coefficients are temperature dependent (see figure 7). Qualitatively, this temperature dependence is seen as a 'valley' near 247 K on the peak in the family of experimental $\chi''(\omega)$ plots in figure 1(b) of Colla *et al* (1992). The variation of $\tau_c(T)$ is shown in an Arrhenius plot in figure 7(a). Approximation of these data by

a straight line results in unphysical values of the parameters, suggesting that this does not represent simple activated hopping. Using the approach explained in the introduction, we interpret the $\tau_c(T)$ behaviour as the progressive vanishing of the α-relaxation from the experimental frequency window, rather than as slowing down upon approaching a structural phase transition. For the sake of argument, we have drawn in figure 8 the equation $\tau_c(T) = \tau_0 \exp(T_a/(T - T_f))$ with $\tau_0 = 10^{-12}$ s, $T_f = 222$ K, $T_a = 720$ K (comparable to the values cited below (8)). The dashed-dotted line is the high-temperature asymptote.

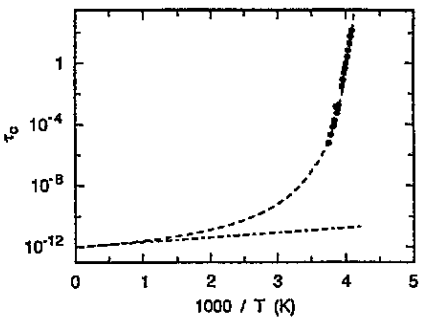

Figure 8. The data of figure 7(a) replotted on a different scale. The parameters of the lines are given in the text.

Below 230 K, the slope in a log–log plot of $\chi''(\omega)$ diminishes continuously with increasing frequency (see the 212 K curve in figure 2). Above 100 Hz, $\chi''(\omega)$ is non-zero and nearly frequency independent, whereas $\chi'(\omega)$ is clearly dispersive (note that this is contrary to what has been reported for PZN). Such behaviour does not conform to (2) and (3), and we are not aware of any empirical expression that describes such results. Qualitatively however, this resembles the behaviour of dielectric relaxation in glass formers, when the β-relaxation peak becomes visible in the high-frequency range at or below the glass temperature.

In that case, the increase towards low frequencies seen in the 212 K curve of figure 2 could be ascribed to remnants of the α-relaxation, whereas the plateau towards high frequencies would be due to an extremely large loss peak of the β-relaxation. Since the data only show a plateau rather than a resolved peak, this supposed β-relaxation unfortunately cannot be quantified. For the sake of argument, suppose it is described by a very large Fröhlich distribution (Böttcher and Bordewijk 1978). Then, compared to the α-relaxation, the average correlation time $(\tau_{min}\tau_{max})^{1/2}$ is certainly much shorter and the width of the peak much larger. On the basis of the data at hand, however, it is not possible to evaluate the value of the β-relaxation strength or its temperature dependence.

In the narrow T-interval for which the HN equations describe the $\chi''(\omega, T)$ data well, the static susceptibility $\chi'(0, T)$ grows continuously with decreasing temperature. Contrary to previous interpretations, which implicitly assume the existence of a temperature maximum in $\chi'(0, T)$, the present analysis shows that there is no evidence for such behaviour from the available data. Instead of the behaviour described in the preceding sentence, it seems that this static quantity becomes experimentally inaccessible due to the strong slowing down of motion.

5. Conclusion

From the above treatment of our decay-current and dielectric data as well as of the experimental results of Colla *et al* it transpires that the high- and low-frequency dielectric

behaviours of PMN cannot be modelled by a single process, but rather correspond to α- and β-relaxation as in glass formers. It is interesting to note that at least one model for dielectric relaxation in glass-forming polymers starts from a mean-field theory for ferroelectrics (Brereton and Davies 1977).

As observed in the studies by Colla and by Viehland, the characteristic relaxation time in the high-temperature region as a function of temperature does not follow an Arrhenius plot. A similar result has been found in PZN. However, the relaxation in this related material has been interpreted as slowing down at a phase transition (although perhaps not really *critical* slowing down). Below the phase transition, the relaxation time of this branch is again reduced and it reappears in the experimental frequency window. In PMN however, as the present study shows, the α-relaxation continuously slows down. When the typical α-relaxation time becomes extremely long, a β-type process seems to take over. On the basis of data now available, this supposed β-relaxation cannot yet be characterized, otherwise than by saying that it is extremely broad.

In thermal-depolarization ('electret') experiments (Sommer *et al* 1993), some isothermal depolarization has been found around 200 K, but virtually none at 150 K. It seems likely that the isothermal depolarization is related to the β-process, whereas the thermal depolarization is governed by the α-process. From such experiments, the boundary between 'glassy' and paraelectric behaviour has been set at 206 K (Sommer *et al* 1993) or 213 K (Ye and Schmid 1993). From the α-relaxation time in dielectric experiments (figure 8), we estimate the boundary to be at 222 ± 10 K. The difference could be due to the time-scale sensitivity of the glass temperature.

In PZN, some predominant polar motion slow down occurs, and this ultimately results in a phase transformation from cubic to rhombohedral symmetry. The slowing down seems rather sluggish, different from the power-law behaviour expected in the critical regime. This may be an indication of the 'diffuseness' of the phase transition. In contrast, the motion in PMN has so few of the characteristics of a normal mode that it just continues to slow down until it simply disappears.

Acknowledgments

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Appendix. Kramers–Kronig relations in the spin-glass model

Admitting that $\chi''(\omega)$ can be fitted satisfactorily over a certain frequency range by (8), it follows from (1*a*, *b*) that $\omega\partial\chi'/\partial\omega$ will be fitted satisfactorily as well. However,

$$\chi'(\omega) = \chi'(0) + \int_0^{\omega} (\partial\chi'/\partial\omega')\,\mathrm{d}\omega' \tag{A1}$$

and a correct fit of $\chi'(\omega)$ itself over that frequency range requires a correct value of $\chi''(\omega)$ for all frequencies.

As it stands, (8) cannot satisfy the Kramers–Kronig relations between $\chi'(\omega)$ and $\chi''(\omega)$. The simplest way to solve this problem is to impose cut-off frequencies: $\chi''(\omega, T)$ is given by (8) for $\tau_{\max}^{-1} \leqslant \omega \leqslant \tau_{\min}^{-1}$, and is equal to zero outside this interval. The static susceptibility becomes

$$\chi'(0, T) = (2/\pi)[\phi(T)/\alpha(T)] \ln([1 + c(\tau_0/\tau_{\min})^{\alpha(T)}]/[1 + c(\tau_0/\tau_{\max})^{\alpha(T)}]). \tag{A2a}$$

From this we conclude that at temperatures below T_f, i.e. when $\alpha(T) < 0$, it is necessary that $\tau_{\max} < \infty$, and that above T_f, $\tau_{\min} > 0$. For cut-off frequencies such that $\tau_{\max} \gg \tau_0$, and from (A1) and (1*a*, *b*), we have

$$\chi'(0, T) - \chi'(\omega, T) \simeq \chi'(0, T) \ln(1 + c(\omega\tau_0)^{\alpha(T)}) / \ln(1 + c(\tau_0/\tau_{\min})^{\alpha(T)}). \tag{A2b}$$

For a given frequency ω, the right-hand side of (A2*b*) is very close to zero as long as $c(\omega\tau_0)^{\alpha} \ll 1$, and is equal to $\chi'(0, T)$ for $T = T_f$. Therefore upon decreasing the temperature, the curve $\chi'(\omega, T)$ breaks away from the curve $\chi'(0, T)$ towards zero when T drops below the temperature T_m given by

$$\tau_0 \exp(T_c/(T_m - T_f)) = \omega^{-1}. \tag{A3}$$

Note that this result depends on $\chi'(\omega, T) \leqslant \chi'(0, T)$, but not on the shape of the $\chi'(0, T)$ curve itself, and that no check of the shape of $\chi'(\omega, T)$ is implied in the criterion of (A3).

The static susceptibility, $\chi'(0, T)$, in (A2) can be related to the experimental ($\omega > 0$) data via approximations for $T \leqslant T_f$ and for $T > T_m$:

$$T \leqslant T_f \qquad \chi'(0, T) \simeq (2/\pi)\chi''(\omega, T) \ln(\tau_{\max}/\tau_{\min}) \tag{A4a}$$

$$T > T_m \qquad \chi'(0, T) \simeq \chi'(\omega, T) \tag{A4b}$$

(with $\omega/2\pi$ in the frequency range 10^2–10^6 Hz). If the temperature dependence of $\ln(\tau_{\max}/\tau_{\min})$ is weak compared to that of χ', comparison with experimental data shows that (A4) predicts that $\chi'(0, T)$ goes through a maximum somewhere between T_f and T_m, since $\chi''(\omega, T)$ is an increasing and $\chi'(\omega, T)$ a decreasing function of temperature for the respective values of T and ω. However, (A2*a*) indicates that in this region, to a good approximation,

$$\chi'(0, T) \simeq (2/\pi)[T_c/(T - T_f)]\phi(T) \tag{A4c}$$

and with the proposed form $\phi(T) = a \exp(bT)$, there is an inflection point (rather than a maximum) in $T = T_f + b^{-1}$. Therefore the Kramers–Kronig transform of (8) does not describe $\chi'(\omega, T)$ for $T > T_m$ even qualitatively.

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