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Anharmonicity-induced glasslike transition in a plastic crystal without α relaxation

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In the low-temperature crystal phase of $TlNO_2$ studied by dielectric spectroscopy (10 mHz to 3 GHz), the α-relaxation process does not evolve, and the molecular dynamics is controlled only by one relaxation process with Arrhenius energy of 19.8 kJ mol^{-1}. Its characteristic time is comparable to the measurement time scale at ~62 K, where its C_p, the expansivity α, and the T derivative of the mean-square atomic displacement decrease in a manner similar to that on the dynamic freezing of the α process. However, neutron powder diffraction measurements show no evidence for two-site occupancy or orientational disordering [Phys. Rev. B **57**, 11 125 (1998)]. We propose a nonconfigurational mechanism for this dynamics, namely, that when a vacancy appears at a Tl site, the anharmonicity of librations of the NO_2^- ion increases, which changes the mean dipole vector and raises C_p and α. When the vacancy diffusion does not occur during the measurement period, the anharmonic contribution vanishes and C_p and α decrease.

The dynamics of viscous liquids[1–6] and supercooled plastic crystals such as cyclohexanol[7] and 1-cyanoadamantane[8] have a characteristic bimodal distribution of relaxation times. This is usually observed in their dielectric relaxation spectra, which contains two peaks (see inset in Fig. 1). The high-frequency peak is attributed to localized diffusion (β process or the Johari-Goldstein relaxation[6]) and the low-frequency peak to the collective or correlated dynamics of the α process involving many molecules. In one view of molecular dynamics, the β process is the primitive motion which initiates the α process at particular sites in the disordered structure.[9,10] In the second, the β process is the noncooperative motion and the α process the cooperative motion of a group of atoms.[4,5,11] At high temperatures, as the liquid approaches its boiling point and the plastic crystal its melting point, only one relaxation peak of the β process with a single relaxation time is observed at GHz frequencies.[12] On supercooling, the α process becomes discernible from the β process at a certain temperature [see inset (a) in Fig. 2]. Since the rate of the α process is sensitive to temperature, according to the Vogel-Fulcher-Tamman equation, the α process becomes progressively slower on cooling and unobservable at T near T_g, the liquid-glass transition temperature,[1–6] or T_g', the glasslike transition temperature of a plastic crystal.[7,8] At T_g (or T_g' for a plastic crystal), the heat capacity, C_p and the coefficient of thermal expansion, α, change with temperature in a sigmoid-shaped manner. The rate of the β process varies according to the Arrhenius equation with a characteristic activation energy of 20–50 kJ mol^{-1}, and it persists in the glassy state and the glasslike state of a plastic crystal.[7,8]

Broadband dielectric spectroscopy of a plastic crystal, $TlNO_2$, performed here reveals a molecular-dynamics freezing, with thermodynamic features similar to those of a glass transition, but in which the characteristic features of the α process are absent. The relaxation dynamics apparently involves only the β process and no configurational contributions. In this work, we propose a mechanism of this dynamics that involves an increase in the anharmonicity of the librations of the NO_2^- ions when a vacancy appears in its vicinity. This changes the mean dipole vector, thereby contributing to electrical polarization, in addition to contributing to C_p and expansivity. Cooling decreases the vacancy population and slows its diffusion, thus slowing the dielectric relaxation. When the vacancy diffusion does not occur during the measurement period, the contributions to C_p and expansivity vanish, and a glasslike dynamic transition is observed.

$TlNO_2$ crystals were prepared by chemically reacting $90\% Ba(NO_2)_2 (10\% BaCl_2)$ and $99.99\% Tl_2CO_3$ in distilled water, and slowly evaporating the solution at 292 K. The crystals were washed with cold water in order to remove impurities and recrystallized twice. The fine powder was pressure molded into 1-mm-thick disks or tightly packed into a cylinder containing a concentric electrode for time-domain reflectometry. The dielectric equipment used for measurement at 10 mHz to 3 GHz frequencies consisted of a low-frequency bridge,[12] a computer-interfaced GenRad 1689 Digibridge, an HP impedance analyser model 4192 A, and a time-domain reflectometer.[13]

$TlNO_2$ is a mechanically soft, plastic crystal in space group $Pm\bar{3}m$ at 298 K, with no long-range order for NO_2 group orientations. An earlier study of single-crystal x-ray diffraction had proposed that $TlNO_2$ transforms to a $Cmm2$ or $Cmmm$ structure[14] at 282.4 K. However, recent neutron diffraction studies of $TlNO_2$ powder,[15] in which the relative positions of N and O atoms were resolved, have shown that the structure is in space group $P3_121$, instead of $Cmm2$ or $Cmmm$, and a long-range order of NO_2 groups is present in the low-temperature, dielectrically active,[14] $P3_121$ phase.[15] Typical dielectric loss, ε'', spectra of its low-T phase studied over the 80–279 K range is shown in Fig. 1. The spectra

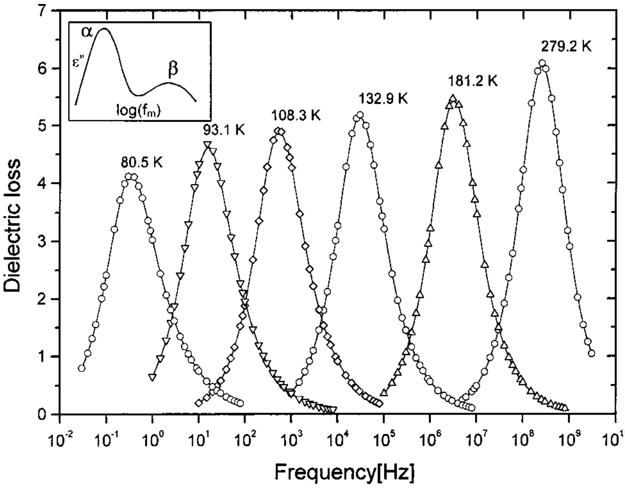

FIG. 1. Typical dielectric loss spectra of TINO$_2$ showing a single relaxation peak at all temperatures. The inset is an illustration of the generally observed bimodal relaxation in viscous liquids and glasses, and in supercooled plastic crystals.

show only one relaxation peak. A second ε'' peak was expected to appear at a *lower* frequency, as in supercooled liquids[1–6] and plastic crystals,[7,8] but no indication of a second peak was found. In view of the possibility that the ε'' peak in Fig. 1 may be due to the α process, we searched for features that could be attributed to a second relaxation process at the high-frequency side of the peak. For that purpose, ε'' of TlNO$_2$ was measured from 10 mHz to 100 MHz at 78.1 K, when the ε'' peak had shifted already to ~50 mHz or less. The ε'' showed no indication of a second relaxation process.

The frequency of the ε'' peak in the spectra is plotted against 1000/T in Fig. 2. The data available in the literature,[16] which are only over the 2.5 decade range (10^2–10^5 Hz), overlapped ours. The Arrhenius equation $f_m(T)=f_m(T\rightarrow\infty)\exp(-E/RT)$ fitted the data with $f_m(T\rightarrow\infty)=1.27$ THz and $E=19.8$ kJ mol^{-1}. (This fit should not be mistaken for the ''strong liquid'' behavior,[17] because here the α process is absent, the NO$_2{}^-$ motions are localized, and E is small.) The shape of the spectra is found to be that of a stretched exponential relaxation function, written in the time domain as $\phi=\phi_0\exp[-(t/\tau)^\beta]$, where $0<\beta<1$, as for most viscous liquids.[1] Here, as the spectra broadened, β was found to decrease from 0.98 at 279.2 K to 0.66 at 80.5 K, and the static permittivity determined from the spectra was found to decrease from 28.6 at 279.2 K to 26.4 at 80.5 K. The five features, (i) $f_m(T\rightarrow\infty)$ in the THz range, (ii) E less than 20 kJ mol^{-1}, (iii) absence of the α process, (iv) broadening of the spectra on cooling, and (v) decrease in the static permittivity on cooling, are all attributable to the reorientation of the NO$_2{}^-$ dipoles.

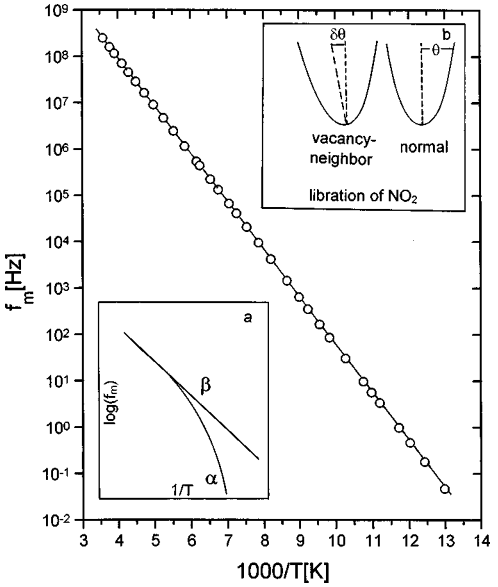

FIG. 2. The dielectric relaxation rate of TINO$_2$ is plotted against 1000/T. Inset (a) illustrates the evolution of the α-relaxation from the β-relaxation process on supercooling a liquid and a plastic crystal at $T>T_g$, and inset (b) the stretching of potential energy profile when a vacancy defect is in the vicinity of the NO$_2$ ion. θ and $\delta\theta$ are energy dependent.

Adiabatic calorimetry has shown that C_p decreases by ~ 5 J mol^{-1} K^{-1}, relatively rapidly in the 60–70 K range, as seen in Fig. 3(a), and the calorimetric relaxation time reaches ~5 ks at 62 K.[14] Extrapolation of f_m in Fig. 2 gives the dielectric relaxation time ($=1/2\pi f_m$) as ~2 ks at 62 K. In view of the extrapolations involved in both calorimetry and dielectrometry, the difference between the two relaxation times is insignificant. (Much larger differences found commonly[1] have been attributed to the fact that modes of molecular motions contributing to C_p differ from those contributing to polarization.) The close agreement between the two relaxation times near 62 K indicates that the decrease in C_p in the 60 K range is associated with the slowing of the dipolar reorientation. Furthermore, the low sensitivity of the dielectric relaxation time or of f_m to T, according to the Arrhenius equation, causes the decrease in C_p of TlNO$_2$ to spread out over a broader temperature range than for other liquids and crystals.[12]

In most glasses, the decrease in C_p on configurational freezing of the β process is difficult to observe.[18] The relatively large decreases of ~5 J mol^{-1} K^{-1} in C_p and ~3 $\times10^{-4}$ K^{-1} in the expansion coefficient α, as shown in Figs. 3(a) and 3(b), are likely to be a reflection of the gradual freezing out of other contributions, which are nonconfigurational. Figure 3(c) shows that even at the highest T, the mean-square atomic displacement, $\langle u^2\rangle$ of Tl, N, and O atoms in the NO$_2{}^-$ ion is 0.2 Å^2, which is unusually small and much less than 0.58 Å^2 observed for glassy selenium.[19] Also, at T just above 60 K, where a decrease in $(d\langle u^2\rangle/dT)$ occurs, $\langle u^2\rangle$ of 0.02 Å^2 is already low. Its extrapolation to $T\rightarrow0$ K from the data above 80 K yields negative values for $\langle u^2\rangle$ for both the N and O atoms. In this T range, $\langle u^2\rangle$ contains contributions in addition to those from the harmonic model,[15] and these amount to an additional rms displacement of 0.17 Å at 275 K.[15] The discontinuities of the slope at about 80 K seen in Figs. 3(b) and 3(c) are remarkably similar to those observed for configurational freezing on the slowing of the α process in liquids[6,19] near their vitrification.

The decrease in C_p and α over the 60–70 K range, which is due to the loss of energy and entropy on slowing of the β process (localized motions of the Johari-Goldstein process), has been interpreted in terms of a two-site model for the reorientation of the NO$_2{}^-$ ions.[14,16] But our neutron diffraction studies[15] gave no indication of two positions for O atoms, as required by a two-site model with different dipole

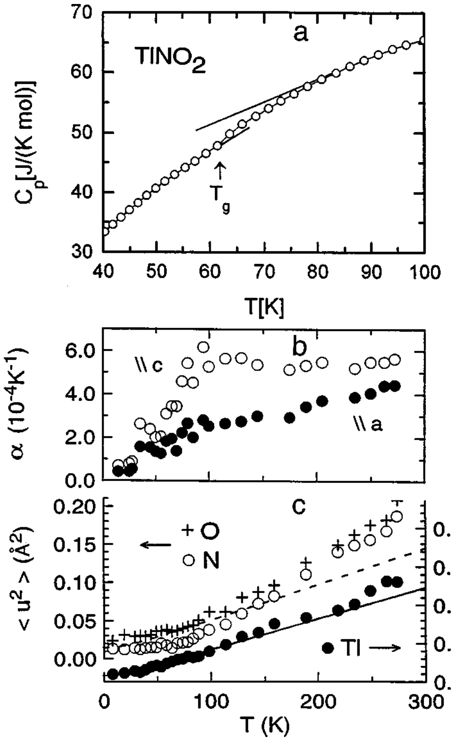

FIG. 3. (a) The heat capacity (Ref. 14), (b) the expansion coefficient along and normal to the *c* axis (Ref. 15), and (c) the atomic mean-square displacement (Ref. 15). The heat capacity shows a rapid decrease in the same 60–70 K range where the expansivity and ($d<u^2>/dT$) decrease abruptly and the dielectric relaxation rate becomes comparable to the experiment's time scale. Note the difference between the *T* scale from (a) to (b) and (c).

vectors. Rather, the reorientational motions of the NO_2^- ions could be interpreted only as librational in a single potential well. This means that the decrease in C_p and α near ~62 K is due to effects other than those associated with configurational excitations in an assumed two site-model. We consider these in terms of the loss of anharmonic contributions, while pointing out that the low value of $\langle u^2 \rangle$ in Fig. 3(b) does not necessarily suggest that such contributions are small, as $\langle u^2 \rangle$ at T_g of the *liquid* Se is also small. ~0.13 Å^2,[19] although the anharmonic contribution in Se is believed to be large.

In general, the dielectric relaxation rate is the regression rate of the random fluctuations in the direction of the dipoles. But, as the O atoms are fixed in position,[15] such fluctuations are absent. On that basis, it seems necessary to determine a novel mechanism for the dielectric polarization which may be consistent with the changes in C_p, α, and $(d\langle u^2 \rangle/dT)$ observed in the 60–70 K range. We propose that the dielectric polarization in $TlNO_2$ arises from anharmonic effects and develop a theory for the dielectric relaxation whose slowing leads to its dynamic freezing, as follows.

In a $TlNO_2$ crystal of space group $P3_121$, two processes occur: (i) confined to their lattice sites, the NO_2^- ions librate about an axis other than the C_{2v} axis, and (ii) point defects diffuse randomly through its neighboring, less sterically hindered, Tl^+ lattice sites. These defects are expected to be mainly vacancies, because their energy of formation is less than that of interstitial defects. When a randomly diffusing vacancy appears at a site neighboring the NO_2^- ion, the potential energy contour for the NO_2^- librations becomes stretched towards the defect site [inset (b) in Fig. 2]. The consequent increase in anharmonicity has two effects; (a) C_p and α increase and (b) the mean dipole vector changes. As there are six NO_2^- sites surrounding one Tl site in the $P3_121$ structure, random diffusion of a single vacancy through 10^{23} Tl sites in the (dielectric relaxation) time τ_D $(=[2\pi f_m]^{-1})$ would affect the librations of one mole of NO_2^- ions. At 100 K, the diffusivity D $(=a^2/\tau_D$, where a, the lattice distance, is ~4 Å and τ_D is 3 ms) is $0.5\times10^{-12}\,\mathrm{cm^2\,s^{-1}}$. This means that a single vacancy should take 3 ms to visit 10^{23} sites at 100 K. If D is assumed to be much less, say, $0.5\times10^{-6}\,\mathrm{cm^2\,s^{-1}}$, the number of vacancies visiting the 10^{23} sites in 3 ms would be 10^{17}, ignoring the multiple visits by a vacancy to a single site. This population of 1 vacancy to 10^6 vacancies per mole of $TlNO_2$ appears reasonable.

To substantiate the above interpretation, we also calculate the speed of the vacancy's random movement in $TlNO_2$ from the preexponential term of the Arrhenius equation that fits the dielectric relaxation rate data. This speed is given by $a2\pi f_m(T\rightarrow\infty)$, and with the above given values for a $=4.2$ Å and $f_m(T\rightarrow\infty)=1.27$ THz, it yields $3.4\times10^5\,\mathrm{cm\,s^{-1}}$. This, being of the order of the speed of sound in solids, confirms our interpretation of the anharmonic effects and dielectric relaxation in terms of the vacancy population.

Therefore, we conclude that f_m of $TlNO_2$ represents the probability of a vacancy appearing at the Tl site. This probability decreases on cooling as the population and D of vacancies decrease. At a low enough T, when this probability is low, contributions from anharmonicity vanish. This occurs gradually in the 60 K range with almost complete freezing of the vacancy diffusion at ~ 62 K, where the extrapolated f_m is 135 μHz. The magnitude of E would therefore correspond to the activation energy for the diffusion of the Tl vacancies. The distribution of relaxation times, as indicated by $\beta<1$, arises from the static distribution of relaxation rates in the $TlNO_2$ crystal similar to that discussed for viscous liquids.[20]

In the proposed mechanism, the increased anharmonicity of NO_2^- ion libration, not an exchange between two potential wells of a two site-model, produces the dipolar relaxation and a large C_p and α. Thus the mechanism of the apparent dynamic freezing in $TlNO_2$, as studied by dielectric spectroscopy, is of a novel type. Here we recall an earlier suggestion by Goldstein[21] that anharmonic effects can also cause a decrease in C_p and α in a manner similar to configurational freezing.

The contributions from anharmonicity to C_p and α and the dynamics in such crystals seem significant for three further reasons: (i) the Kauzmann situation does not develop because there is no underlying state of complete order for $TlNO_2$, (ii) the cooperativity does not develop enough to produce an α-relaxation process, and (iii) the observed Arrhenius-type relaxation dynamics and the absence of a second relaxation are remarkably similar to the two-site reorientations of molecules trapped individually in the cagelike structures of a foreign host lattice.[22,23]

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[1] See collection of papers in the special issues of J. Non-Cryst. Solids **131-133** (1991); **172-174** (1994); **235-237** (1998).

[2] R. D. Deegan and S. R. Nagel, Phys. Rev. B **52**, 5653 (1995); in *Phase Transitions and Relaxations in Systems with Competing Energy Scales*, edited by T. Riste and D. Sherrington (Kluwer Academic, Dordrecht, 1993), pp. 259–283.

[3] K. Y. Tsang and K. L. Ngai, Phys. Rev. E **54**, R3067 (1996).

[4] A. Kudlik, C. Schirwitz, T. Blochowicz, S. Benkhoff, and E. Rossler, Europhys. Lett. **40**, 649 (1997); J. Non-Cryst. Solids **235-237**, 406 (1998); J. Mol. Struct. **479**, 201 (1999).

[5] A. Hofman, F. Kremer, E. W. Fisher, and A. Schonhals, in *Disorder Effects on Relaxational Processes*, edited by R. Richert and A. Blumens (Springer-Verlag, Heidelberg, 1994), Chap. 11.

[6] See articles in Science **267**, 1924 (1995) and others.

[7] K. Adachi, H. Suga, S. Seki, S. Kubota, S. Yamaguchi, O. Yano, and I. Wada, Mol. Cryst. Liq. Cryst. **18**, 345 (1972).

[8] K. Pathmanathan and G. P. Johari, J. Phys. C **18**, 6535 (1985).

[9] J. Y. Cavaille, J. Perez, and G. P. Johari, Phys. Rev. B **39**, 2411 (1989).

[10] K. L. Ngai, in *Disorder Effects on Relaxational Processes* (Ref. 5), Chap. IV.

[11] E. W. Fisher, E. Donth, and W. Stiffen, Phys. Rev. Lett. **68**, 2344 (1992); E. Donth, *Relaxation and Thermodynamics in Polymer-Glass Transitions* (Academic-Verlag, Berlin, 1992).

[12] G. P. Johari, Ann. (N.Y.) Acad. Sci. **279**, 117 (1976); J. Chem. Phys. **58**, 1766 (1973).

[13] D. A. Wasylyshyn, G. P. Johari, E. Tombari, and G. Salvetti, J. Phys.: Condens. Matter **9**, 10 521 (1997); Chem. Phys. **293**, 313 (1997).

[14] K. Moriya, T. Matsuo, and H. Suga, J. Phys. Chem. Solids **44**, 1103 (1983).

[15] R. Feyerherm, M. F. Collins, and G. P. Johari, Phys. Rev. B **57**, 11 125 (1998).

[16] K. Moriya, T. Matsuo, and H. Suga, Chem. Lett. **1977**, 1427 (1977).

[17] R. Bohmer and C. A. Angell, in *Disorder Effects on Relaxational Processes* (Ref. 5), Chap. 2.

[18] H. Fujimori and M. Oguni, Solid State Commun. **94**, 157 (1995).

[19] U. Buchenau and R. Zorn, Europhys. Lett. **18**, 523 (1992).

[20] B. Scheiner, R. Bohmer, A. Loidl, and R. V. Chamberlain, Science **274**, 752 (1998).

[21] M. Goldstein, J. Chem. Phys. **67**, 2246 (1977).

[22] A. Huwe, F. Kremer, P. Behrens, and W. Schwieger, Phys. Rev. Lett. **82**, 2338 (1999); J. Phys.: Condens. Matter **11**, A175 (1999).

[23] G. P. Johari, in *Comprehensive Supramolecular Chemistry*, edited by J. E. D. Davies and J. A. Ripmeester (Elsevier, Oxford, 1996), Vol. 8, Sec. 3.8.2, pp. 121–174.