Fast Dynamics in CKN and CRN Investigated by Dielectric Spectroscopy

P. Lunkenheimer, A. Pimenov, and A. Loidl
Experimentalphysik V, Universität Augsburg, D-86135 Augsburg, Germany
(Received 29 October 1996)

Dielectric spectroscopy up to a frequency of 380 GHz has been performed on the molten salts $[Ca(NO_3)_2]_{0.4}[KNO_3]_{0.6}$ (CKN) and $[Ca(NO_3)_2]_{0.4}[RbNO_3]_{0.6}$ (CRN). For the first time, conclusive results for the transition region between the α-relaxational and the far-infrared response have been obtained in ionically conducting glass formers using dielectric spectroscopy. In addition to the dielectric loss, we present data for the reactive part of the dielectric constant. At high temperatures and the highest frequencies investigated, both materials exhibit a sublinear spectrum. For CRN the dielectric loss follows a power law with a frequency exponent 0.2 over three decades of frequency. [S0031-9007(97)02888-3]

PACS numbers: 64.70.Pf, 77.22.–d

Despite enormous theoretical and experimental progress [1], the glass transition in viscous liquids still is an unresolved problem. In recent theoretical approaches the fast dynamics in glass forming liquids came into the focus of interest: Here various scenarios have been proposed to describe or predict the dynamic susceptibility at high frequencies. Among them are the coupling model [2] with its prediction of a fast process at high frequencies, and the avoided critical point theory [3] which also predicts a fast process. Based on the universal scaling of the α relaxation [4], Nagel and co-workers proposed a divergence of the static susceptibility [5] which essentially implies a constant loss behavior at high frequencies and low temperatures as has early been predicted by Wong and Angell [6]. Maybe the most controversially discussed theoretical approach of the glass transition is the mode coupling theory (MCT) which explains the glass transition in terms of a dynamic phase transition at a critical temperature T_c significantly above the glass temperature [7].

So far the high-frequency behavior (10^{10}–10^{13} Hz) of glasses has been investigated mainly by neutron and light scattering techniques (see, e.g., [8–11]). Only recently were we able to extend the frequency range of dielectric experiments on glass forming liquids up to some 100 GHz [12] using backward wave oscillators as coherent sources of electromagnetic radiation [13]. These experiments, which have been performed on glycerol, revealed the existence of a relatively broad minimum in the frequency dependence of the dielectric loss, $\varepsilon''(\nu)$, at frequencies above 100 GHz. Its functional form and temperature dependence cannot be explained by a simple crossover from the structural (α) relaxation to the far-infrared (FIR) response but is indicative of additional fast processes prevailing in this glass former. Glycerol is a relatively strong [14], hydrogen-bonded glass former. In dipolar systems such as glycerol, the dielectric susceptibility couples mainly to the reorientational motions of the molecules, and its coupling to the density fluctuations, considered by most theoretical approaches, is not well understood. Indeed, the high-frequency dielectric results in glycerol revealed clear deviations from the neutron and light scattering data [12]. It seemed interesting to extend these high-frequency dielectric experiments to molten salts which are characterized by mobile ions. Here a strong coupling of the ionic motion, tested by dielectric spectroscopy, and the density fluctuations can be intuitively expected. In addition, the investigation of more fragile glass formers is highly desirable as it can be assumed that in these glass formers the additional vibrational excitations giving rise to the so-called Boson peak are less pronounced [15].

To study fast processes in fragile glass formers we have investigated the high-frequency dielectric response of the ionic conductors $[Ca(NO_3)_2]_{0.4}$ $[KNO_3]_{0.6}$ (CKN) (see, e.g., [16,17]) and $[Ca(NO_3)_2]_{0.4}$ $[RBNO_3]_{0.6}$ (CRN) [18]. The ionic mixture CRN ($T_g \approx 333$ K) was one of the first glass formers on which the high-frequency behavior had been examined using neutron [9] and light scattering techniques [10]. In addition, we investigated another nitrate mixture that also can easily be vitrified: CRN ($T_g \approx 333$ K). In a recent study up to 300 MHz [18], dielectric properties similar to that of CKN have been found. We investigated the complex dielectric permittivity $\varepsilon^* = \varepsilon' - i\varepsilon''$ for frequencies $10^{-3} \leq \nu \leq 3.8 \times 10^{11}$ Hz. Results from our group on ε'' of CKN up to 40 GHz have already been published elsewhere [19]. However, the upper limit of the frequency range available to us at that time prevented a clear statement about the behavior at frequencies above the ε'' minimum. In this Letter we present data in an extended frequency range up to 380 GHz. In addition, we also show the real part, ε', which, in contrast to the scattering experiments, is directly accessible in dielectric spectroscopy. These new results provide a conclusive picture of the high-frequency behavior of the susceptibility which is a prerequisite for the unambiguous comparison with theoretical predictions.

The measurements presented in this Letter have been performed using various techniques. For the radio-frequency experiments a reflectometric technique was employed [20]. The microwave data were taken in reflection

and in transmission using waveguides. Above 60 GHz a quasioptical technique was used with an experimental arrangement similar to a Mach-Zehnder interferometer [13]. To cover the complete frequency range, a single $\varepsilon''(\nu)$ curve at a given temperature is superimposed, using results from different experimental setups. For the measurements at $\nu < 40$ GHz there are some uncertainties of the absolute values originating from an ill-defined geometry of the samples or parasitic elements. Therefore it was necessary to shift the $\log_{10}\varepsilon''$ values of the measurements at the lower frequencies with respect to the high-frequency results in order to construct a smooth $\varepsilon''(\nu)$ curve. It is important to note that $\varepsilon''(\nu, T)$ from each experimental setup is shifted by one gauge factor only, which depends neither on frequency nor on temperature. The high-frequency results provide a good estimate of the absolute values of ε' and ε''.

Figure 1 shows $\varepsilon''(\nu)$ for CKN in a double-logarithmic plot. $\varepsilon''(\nu)$ reveals a minimum similar to that observed with neutron [9] and light scattering techniques [10]. Indeed, when scaled appropriately, χ'' obtained from the scattering experiments agrees well with our results for ε''. Our data also agree reasonably well with the most recent data by the group of Funke [17] which, however, are too incomplete to enable an unambiguous evaluation of the susceptibility minimum. The $\varepsilon''(\nu)$ minimum is relatively broad and, most important, exhibits a high-frequency wing which increases significantly less than $\varepsilon'' \sim \nu$ (indicated by the dotted line). At 342 K, $\varepsilon''(\nu)$ seems to become constant for $\nu < 1$ GHz. This could be due to the appearance of a constant loss region which has been predicted by Wong and Angell [6]. However, at these low values of ε'' the uncertainty of the data is rather high, and further measurements with better resolution have to be performed at low temperatures. Figure 2 shows the real and imaginary parts of the dielectric constant for frequencies $\nu \geq 10$ GHz. $\varepsilon'(\nu)$ decreases significantly in the frequency range where the minimum appears in $\varepsilon''(\nu)$. It is not possible to obtain $\varepsilon'(\nu)$ simply by a Kramers-Kronig transformation of $\varepsilon''(\nu)$ for which a larger frequency range, especially at high frequencies, would be necessary. Therefore the $\varepsilon'(\nu)$ data provide valuable additional information about the high-frequency dynamics in CKN. Figure 3 shows $\varepsilon''(\nu)$ for CRN. The data resemble that obtained for CKN with a relatively broad minimum and a power law exponent at its high-frequency wing which is clearly smaller than unity (dotted line).

We want to emphasize that the observed $\varepsilon''(\nu)$ minimum cannot be described by a simple crossover from the α-relaxation response to the FIR absorption bands. In this case the increase of $\varepsilon''(\nu)$ towards the FIR bands can be assumed to follow a power law with an exponent equal to or larger than unity, a behavior that has been found commonly in glasses [21]. However, similar to our results in glycerol [12], the $\varepsilon''(\nu)$ minima observed in CKN and CRN are too broad to be described by the simple ansatz $\varepsilon'' = c_1\nu^{-b} + c_2\nu$. In glycerol it was possible to fit the data by introducing an additional constant loss factor, i.e., using $\varepsilon'' = c_1\nu^{-b} + c_2\nu + c_3$ [12]. In the present data (Figs. 1–3), the minimum is located at significantly lower frequencies when compared to glycerol and, even taking into account a temperature-dependent constant loss, cannot account for $\varepsilon''(\nu)$ at the high-frequency wing of the

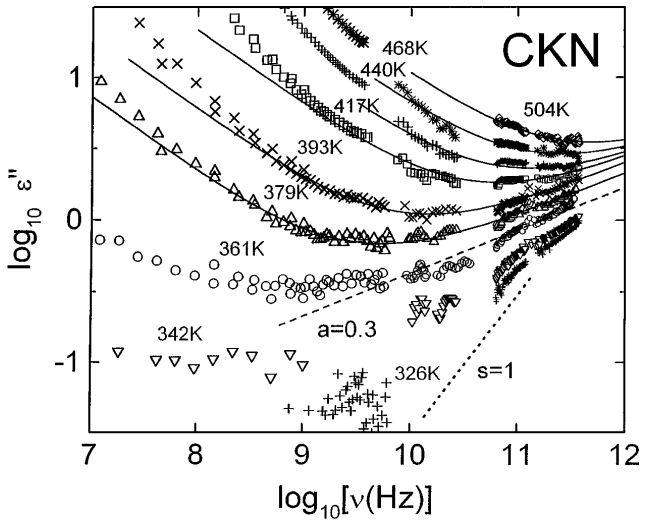

FIG. 1. Frequency dependence of the dielectric loss of CKN for various temperatures (double-logarithmic plot). The solid lines represent fits using Eq. (1) with $a = 0.3$ and $b = 0.54$.

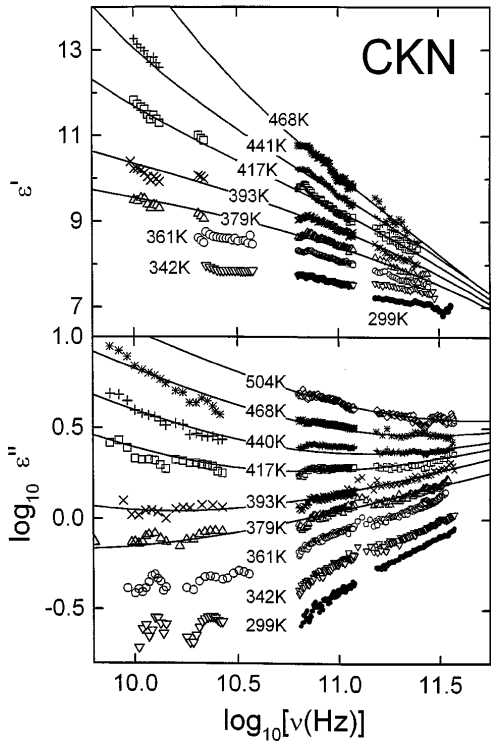

FIG. 2. Temperature dependence of the real (upper panel) and imaginary part (lower panel) of the permittivity of CKN for various temperatures. The lines in the lower panel are the same as in Fig. 1. The lines in the upper panel are fits with Eq. (2), with f_ε as the only free parameter. The other parameters have been taken from the fits of $\varepsilon''(\nu)$.

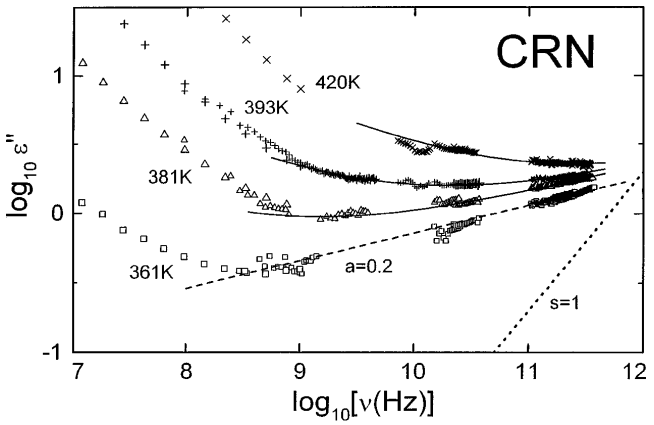

FIG. 3. Same as Fig. 1 but for CRN and with $a = 0.2$, $b = 0.35$.

minimum. This becomes most evident in the data on CRN (Fig. 3), where, at $T = 361$ K, $\varepsilon''(\nu)$ follows a power law with a frequency exponent $a = 0.2$ (dashed line) over three decades of frequency. The difference between the experimental results and the dotted line with $s = 1$ gives an estimate of the additional high-frequency processes in CRN in the GHz range. This behavior puts serious constraints on any theory describing the high-frequency response of viscous liquids. To our knowledge, at present the MCT is the only theory that can take account of such a sublinear power law increase of $\varepsilon''(\nu)$ at frequencies above the minimum [7]. At the critical temperature T_c, MCT predicts a critical spectrum with $\varepsilon'' \sim \nu^a$, $a < 0.4$.

Guided by these findings, in the following we try to compare our results with the scaling predictions of the simplest version of MCT [7]. Above T_c, the high- and low-frequency wings close to the minimum of $\varepsilon''(\nu)$ are described by power laws with exponents a and b, respectively. We fitted $\varepsilon''(\nu)$ [7] and $\varepsilon'(\nu)$ [22] using the interpolation formulas:

$$\varepsilon''(\nu) = \varepsilon''_{\min}[a(\nu/\nu_{\min})^{-b} + b(\nu/\nu_{\min})^{a}]/(a + b), \tag{1}$$

$$\varepsilon'(\nu) = f_\varepsilon + \varepsilon''_{\min}[a\cot(b\pi/2)(\nu/\nu_{\min})^{-b} - b\cot(a\pi/2)(\nu/\nu_{\min})^{a}]/(a + b). \tag{2}$$

$\nu_{\min}$ and $\varepsilon''_{\min}$ denote position and amplitude of the minimum, respectively. The parameters a and b are temperature independent and constrained by the exponent parameter $\lambda = \Gamma^2(1 - a)/\Gamma(1 - 2a) = \Gamma^2(1 + b)/\Gamma(1 + 2b)$, where Γ denotes the gamma function. The only additional parameter for the description of $\varepsilon'(\nu)$ is the constant f_ε. We found a consistent description of the ε'' minima using $a = 0.3$, $b = 0.54$, $\lambda = 0.76$ for CKN at $T \geq 379$ K and $a = 0.2$, $b = 0.35$, $\lambda = 0.91$ for CRN at $T \geq 381$ K (solid lines in Figs. 1–3). At low frequencies, data and fits deviate. This may be ascribed to additional conductivity contributions which lead to a divergence of ε'' for decreasing frequencies. It is interesting that, for high values of λ and temperatures near T_c, MCT predicts a $\nu^{-0.5}$ behavior instead of ν^{-b} for the low-frequency wing of the minimum [23] which, indeed, is consistent with the data of Fig. 3. The parameters for CKN agree reasonably well with those obtained by Li *et al.* [10] ($a = 0.273$, $b = 0.458$, $\lambda = 0.811$) from fits of Eq. (1) to their light scattering results. The lines in the upper frame of Fig. 2 are fits using Eq. (2) with a, b, $\nu_{\min}$, and $\varepsilon''_{\min}$ fixed at the values obtained from the fits of $\varepsilon''(\nu)$ (lower panel) and only f_ε as a free parameter. The agreement of fits and data is very good. f_ε is nearly temperature independent, varying between 10.5 and 11.5.

The critical temperature T_c should manifest itself in the temperature dependence of the $\varepsilon''(\nu)$ minimum. For $T > T_c$, MCT predicts the following relations: $\nu_{\min} \propto (T - T_c)^{1/2a}$ and $\varepsilon''_{\min} \propto (T - T_c)^{0.5}$. In addition, MCT also predicts critical behavior for the time scale of the α response, i.e., the peak frequency $\nu_{\max} \propto (T - T_c)^{\gamma}$, with $\gamma = 1/2a + 1/2b$. Since the dielectric loss maxima are obscured by the dc-conduction process, we take $\nu_{\max}$ from the fits to the imaginary part of the dielectric modulus, $M'' = \mathrm{Im}(1/\varepsilon^*)$, published elsewhere [18,19]. We are aware of the ongoing controversy about the use of the dielectric modulus formalism [24]. But we think that at least in CKN this procedure is justified by the fact that the relaxation times evaluated from $M''(\nu)$ at high temperatures closely follow those obtained from mechanical experiments [19]. Figure 4 shows the results for $\varepsilon''_{\min}$, $\nu_{\min}$, and $\nu_{\max}$ for CKN (closed symbols) and CRN (open symbols). Here representations have been chosen that lead to straight lines that extrapolate to T_c if the above critical temperature dependences are obeyed. Indeed, for CKN all three data sets can consistently be described with a critical temperature $T_c \approx 375$ K, as indicated by the solid lines. This compares well to $T_c = 378$ K, as obtained by Li *et al.* from light scattering experiments [10]. For temperatures near T_c the data deviate from the predicted behavior. Within MCT this can be ascribed to a smearing out of the critical behavior near T_c due to hopping processes which are considered in extended versions of MCT only [7]. For CRN the situation is worse. The dashed lines in Fig. 4 correspond to a T_c of 365 K for all three quantities which, however, leads to clear deviations between theory and experiment. However, one has to note that for λ near unity the simple scaling relations mentioned above are expected to fail [22]. The above critical temperature dependences of $\varepsilon''_{\min}$, $\nu_{\min}$, and $\nu_{\max}$ should be observed only for temperatures not too far above T_c. Depending on the data points used for the scaling, much lower values for T_c can be obtained, and the significance of the representations of Fig. 4 should not be overemphasized.

Another prediction of MCT concerns the temperature dependence of the dielectric strength, which should exhibit a square root singularity at T_c: $f = f_c + h[(T - T_c)/T_c]^{0.5}$ at $T < T_c$, and $f = f_c$ at $T > T_c$ [7]. As we have shown earlier [19] the dielectric strength of CKN obtained from the modulus representation is consistent

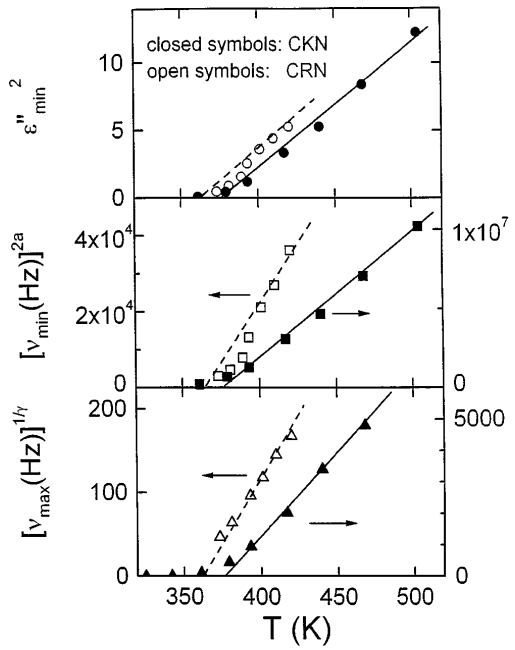

FIG. 4. Temperature dependence of height and position of the dielectric loss minimum and of the α-peak position of CKN (closed symbols) and CRN (open symbols). Representations have been chosen that result in straight lines according to the predictions of the MCT. The solid lines are consistent with a critical temperature of $T_c = 375$ K for CKN, the dashed lines with $T_c = 365$ K for CRN.

with this prediction with a T_c of 362 K, which is somewhat smaller than the T_c determined from Fig. 4. For CRN the scatter of the $f(T)$ data is too high to make a clear statement. According to MCT the functional form of the α-relaxation peak should be temperature independent for $T > T_c$ [7]. Indeed, for CKN and CRN the stretching parameter β which determines the width of the α peak becomes approximately constant for temperatures $T > 360$ K [18,19]. Finally, MCT predicts a critical spectrum at T_c and a significant change in the behavior of $\varepsilon''(\nu)$ at T_c: For $T < T_c$, $\varepsilon''(\nu)$ should exhibit a so-called "knee" at a frequency ν_k, i.e., a change of power law from $\varepsilon'' \sim \nu^a$ at $\nu > \nu_k$ to $\varepsilon'' \sim \nu$ at $\nu < \nu_k$. Indications of a critical spectrum can be detected in CRN at 361 K (Fig. 3) which is close to T_c as determined from Fig. 4. In CKN, the minimum near T_c becomes very broad, and, at lower temperatures, indications of constant loss behavior can be detected. But again we have to stress that these data are at the edge of the resolution of the experimental setup. For $T \lesssim 361$ K in CKN, the frequency exponent above the minimum becomes larger than $a = 0.3$ (Fig. 1). This observation is most significant at the two lowest temperatures for frequencies $\nu > 150$ GHz, where the data are reliable.

In conclusion, we have presented high-frequency dielectric results on two ionically conducting glass formers which reveal a clear minimum in $\varepsilon''(\nu)$ at microwave frequencies. For the first time, we show $\varepsilon'(\nu)$ in the relevant frequency range. The most important result is the finding that at frequencies above ν_{min} the dielectric loss exhibits a sublinear increase. For CRN we find a spectrum that follows $\varepsilon'' \sim \nu^{0.2}$ over three decades of frequency. A preliminary analysis in terms of the MCT [7] shows that the frequency dependences of $\varepsilon''(\nu)$ and $\varepsilon'(\nu)$ are consistent with the predictions of MCT. However, there are some discrepancies concerning the critical behavior in CRN and concerning the determination of the critical temperatures. The data show unambiguously that there are nontrivial additional processes contributing to the susceptibility at high frequencies which should be taken into account by any theoretical approach of the glass transition.

We gratefully acknowledge stimulating discussions with C. A. Angell, R. Böhmer, W. Götze, K. L. Ngai, W. Petry, L. Sjögren, and A. P. Sokolov. We are grateful to L. Sjögren for making Eq. (2) available to us.

[1] See, e.g., special issue, *Relaxations in Complex Systems,* edited by K. L. Ngai, E. Riande, and G. B. Wright [J. Non-Cryst. Solids **172-174** (1994)].
[2] K. L. Ngai *et al.,* J. Chem. Phys. **86**, 4768 (1987).
[3] D. Kivelson *et al.,* Physica (Amsterdam) **219A**, 27 (1995).
[4] P. K. Dixon *et al.,* Phys. Rev. Lett. **65**, 1108 (1990).
[5] N. Menon and S. R. Nagel, Phys. Rev. Lett. **74**, 1230 (1995).
[6] J. Wong and C. A. Angell, in *Glass* (Marcel Dekker, New York, 1974), p. 750.
[7] W. Götze, Z. Phys. B **60**, 195 (1985); for a review, see W. Götze and L. Sjögren, Rep. Prog. Phys. **55**, 241 (1992).
[8] For a review of neutron scattering results, see W. Petry and J. Wuttke, Transp. Theory Stat. Phys. **24**, 1075 (1995).
[9] W. Knaak *et al.,* Europhys. Lett. **7**, 529 (1988).
[10] G. Li *et al.,* Phys. Rev. A **45**, 3867 (1992).
[11] J. Wuttke *et al.,* Phys. Rev. Lett. **72**, 3052 (1994); Phys. Rev. E **52**, 4026 (1995).
[12] P. Lunkenheimer *et al.,* Phys. Rev. Lett. **77**, 318 (1996).
[13] A. A. Volkov *et al.,* Infrared Phys. **25**, 369 (1985); A. A. Volkov *et al.,* Infrared Phys. **29**, 747 (1989).
[14] C. A. Angell, J. Chem. Phys. Solids **49**, 863 (1988).
[15] A. P. Sokolov *et al.,* Phys. Rev. E **52**, 5105 (1995).
[16] F. S. Howell *et al.,* J. Phys. Chem. **78**, 639 (1974); C. A. Angell, Chem. Rev. **90**, 523 (1990).
[17] K. L. Ngai *et al.,* in *Proceedings of the Workshop on Non-Equilibrium Phenomena in Supercooled Fluids, Glasses, and Amorphous Materials, Pisa, Italy, 1995* (World Scientific, Singapore, 1996), p. 1.
[18] A. Pimenov *et al.* (to be published).
[19] A. Pimenov *et al.,* Phys. Rev. E **54**, 676 (1996).
[20] R. Böhmer *et al.,* J. Appl. Phys. **65**, 901 (1989).
[21] U. Strom *et al.,* Solid State Commun. **15**, 1871 (1974); U. Strom and P. C. Taylor, Phys. Rev. B **16**, 5512 (1977); C. Liu and C. A. Angell, J. Chem. Phys. **93**, 7378 (1990).
[22] L. Sjögren (private communication).
[23] M. Fuchs *et al.,* J. Phys. Condens. Matter **4**, 7709 (1992).
[24] See, e.g., S. R. Elliott, J. Non-Cryst. Solids **170**, 97 (1994); C. T. Moynihan, J. Non-Cryst. Solids **172-174**, 1395 (1994).