Spectral migration of excitation energy among Nd^{3+} ions in fluoroarsenate glasses

Rolindes Balda[a,b,c]*, Luis Maria Lacha[a], Maria Angeles Arriandiaga[d], Joaquin Fernández[a,b,c], Jean-Luc Adam[e]

[a] *Dpto. Fisica Aplicada I, Escuela Superior de Ingenieros, Alda. Urquijo s/n 48013 Bilbao, Spain*

[b] *Centro Mixto CSIC-UPV/EHU, Donostia, Spain*

[c] *Donostia International Physics Center (DIPC), Donostia, Spain*

[d] *Dpto. Fisica Aplicada II, Facultad de Ciencias, Universidad del País Vasco, Apartado 644, Bilbao, Spain*

[e] *Laboratoire des verres & céramiques, université Rennes-1, UMR CNRS 6512, Campus de Beaulieu, 35042 Rennes cedex, France*

Abstract – In this work, we have investigated the existence of energy transfer among Nd^{3+} ions in fluoroarsenate glasses of the Na$_4$As$_2$O$_7$, BaF$_2$, YF$_3$ system with different Nd^{3+} concentrations (0.5, 2, 3, 4, and 5 mol%) by using time-resolved fluorescence line narrowing spectroscopy. The spectral features of the time resolved fluorescence line narrowing $^4F_{3/2} \rightarrow {}^4I_{9/2}$ emission spectra obtained under resonant excitation reveal the existence of spectral migration of excitation among the Nd^{3+} ions. The analysis of the time evolution of the $^4F_{3/2} \rightarrow {}^4I_{9/2}$ narrowed emission shows that the electronic mechanism responsible for the ion–ion interaction can be identified as a dipole–dipole energy transfer process. ***To cite this article: R. Balda et al., C. R. Chimie 5 (2002) 725–729*** © 2002 Académie des sciences / Éditions scientifiques et médicales Elsevier SAS

energy transfer / glasses / time-resolved laser spectroscopy / optical materials / rare earths

Résumé – Le transfert d'énergie entre ions Nd^{3+} a été étudié dans des verres de fluoroarséniates à différentes concentrations en néodyme par spectroscopie de fluorescence à résolution temporelle en rétrécissement de bande. Les résultats mettent en évidence la migration spectrale de l'excitation des ions Nd^{3+}. Le mécanisme responsable de l'interaction ion–ion a été identifié comme un processus de transfert d'énergie dipôle–dipôle. ***Pour citer cet article : R. Balda et al., C. R. Chimie 5 (2002) 725–729*** © 2002 Académie des sciences / Éditions scientifiques et médicales Elsevier SAS

transfert d'énergie / verres / spectroscopie laser à résolution temporelle / matériaux optiques / terre rare

1. Introduction

The characteristic spectroscopic feature of rare-earth ions in glass is the inhomogeneous broadening resulting from the distribution of the crystal fields at the variety of rare-earth-ion sites in the amorphous solid [1]. Several laser spectroscopic techniques, such as fluorescence line narrowing (FLN), spectral hole burning, etc., [2, 3] are required to obtain a detailed information about the local field, and ion–ion and ion–host interaction processes. When the activator ion concentration in glass becomes high enough, ions interact and ion–ion energy transfer occurs. Due to the inherent disorder of glass, ions in nearby sites may be in physically different environments with greatly varying spectroscopic properties. Therefore, in addition to causing a spatial migration of energy, the transfer may also produce spectral diffusion within the inhomogeneously broadened spectral profile [2]. The migration of the electron excitation over the inhomogeneous profile (spectral migration) determines the effectiveness of the generation (amplification) of the stimulated emission [1]. One of the kinetic methods of migration investigation consists in analysing time-resolved lumi-

* Correspondence and reprints.
  E-mail address: wupbacrr@bicc00.bi.rhu.es (R. Balda).

nescence spectra after selective excitation [1, 3–7]. The time-resolved fluorescence line narrowing (TRFLN) technique provides us with a way of measuring optical energy propagation from the initially excited subset of ions to other elements of the inhomogeneously broadened line. Previous works [1, 4, 5] on Nd-doped glasses utilised a non-resonant pumping scheme to excite the $^4F_{3/2}$ state, which is responsible for the principal Nd^{3+} fluorescence. Under the non-resonant pumping condition, the 'accidental coincidence' effect influences the originating state of the fluorescence in a complicated way and hence no direct analysis can be made of the TRFLN donor–donor dynamics in such cases [7]. The introduction of tuneable lasers for resonant excitation in the near-infrared made it possible to perform measurements on TRFLN under resonant excitation of the $^4F_{3/2}$ state of Nd^{3+} in order to study the structure of inhomogeneously-broadened bands and migration of excitation energy among Nd^{3+} ions [3, 8, 9]. It is worthwhile mentioning that TRFLN techniques have only been used in a few studies on spectral diffusion among Nd^{3+} ions in glasses [1, 3–5, 9]; among these, there are only a few works performed in a resonant pumping scheme [3, 8–11] to excite the $^4F_{3/2}$ state of Nd^{3+} ions.

This paper deals with the spectral migration of energy among Nd^{3+} ions in fluoroarsenate glasses. Recently, new glasses were discovered in the $Na_4As_2O_7$, BaF_2, YF_3 system, which are parent materials with fluorophosphates glasses of the $NaPO_3$, BaF_2, YF_3 system. As in the case of fluorophosphate glasses, large amounts of active rare-earth ions can be incorporated in replacement of yttrium. Whereas optical properties of some active ions have already been investigated in fluorophosphate glasses [12–14], the behaviour of rare-earth ions in fluoroarsenate glasses is practically unknown. In a previous work, we have characterised the optical properties of Nd^{3+} ions in these glasses [15]. In this work, we investigate the existence of energy transfer among Nd^{3+} ions in fluoroarsenate glasses of the $Na_4As_2O_7$, BaF_2, YF_3 system with different Nd^{3+} concentrations (0.5, 2, 3, 4, and 5 mol%) by using TRFLN spectroscopy and observing the emission characteristics of the system as a function of time, concentration, and excitation wavelength.

2. Experimental techniques

The fluoroarsenate glasses used in this work were prepared at the 'Laboratoire de verres et céramiques' of the University of Rennes (France). Glasses were synthesised in the ($Na_4As_2O_7$–BaF_2–YF_3) ternary system and doped with 0.5, 2, 3, 4, and 5 mol% of NdF_3.

The sample temperature was varied between 4.2 and 300 K in a continuous flow cryostat. Time-resolved resonant fluorescence line-narrowed emission measurements were obtained by exciting the samples with a Ti–sapphire laser, pumped by a pulsed frequency doubled Nd:YAG laser (9 ns pulse width), and detecting the emission with a Hamamatsu R5108 photomultiplier provided with a gating circuit designed to enable gate control from an external applied TTL level control signal. Data were processed by an EGG–PAR boxcar integrator.

3. Results and discussion

We have investigated the existence of energy transfer among Nd^{3+} ions in this glass by using TRFLN spectroscopy and observing the emission characteristics of the system as a function of time, concentration, and excitation wavelength. TRFLN spectra for the $^4F_{3/2} \rightarrow ^4I_{9/2}$ transition were performed for all concentrations at 4.2 K by using different resonant excitation wavelengths in the low energy Stark component of the $^4I_{9/2} \rightarrow ^4F_{3/2}$ absorption band at different time delays after the laser pulse. Typical results from these measurements are given in Fig. 1, which shows the normalized $^4F_{3/2} \rightarrow ^4I_{9/2}$ spectra at 4.2 K for the four concentrations 0.5, 2, 4, and 5 mol% of Nd^{3+} ions obtained at two different time delays after the laser pulse, 1 and 700 μs, by exciting at 874 nm. Two contributing components can be observed in the spectra. The one observed on the high-energy side of the line is a simple FLN line (linewidth $\approx$ 8 cm^{-1}) corresponding to the emission to the lowest component of the $^4I_{9/2}$ multiplet, which is the ground state of the ion. The position of this narrow line is essentially determined by the wavelength of the pumping radiation. The broad emission arises from the non-narrowed inhomogeneous line. As time delay increases, the relative intensity of the narrow line and the broad (non selected) emission changes, and the later becomes stronger, which indicates the existence of energy transfer between discrete regions of the inhomogeneous broadened profile. This effect increases with concentration. As can be observed, when Nd^{3+} concentration increases the broad non-selected emission becomes important. At higher concentrations, the transfer process appears at shorter time delays, but in all cases energy transfer produces a relative increase of the broad emission with respect to the narrow band.

The $^4F_{3/2} \rightarrow ^4I_{9/2}$ emission spectra performed by exciting at different wavelengths along the low energy Stark component of the $^4I_{9/2} \rightarrow ^4F_{3/2}$ absorption band show that the broad emission decreases as the excitation energy decreases, which indicates that excitation
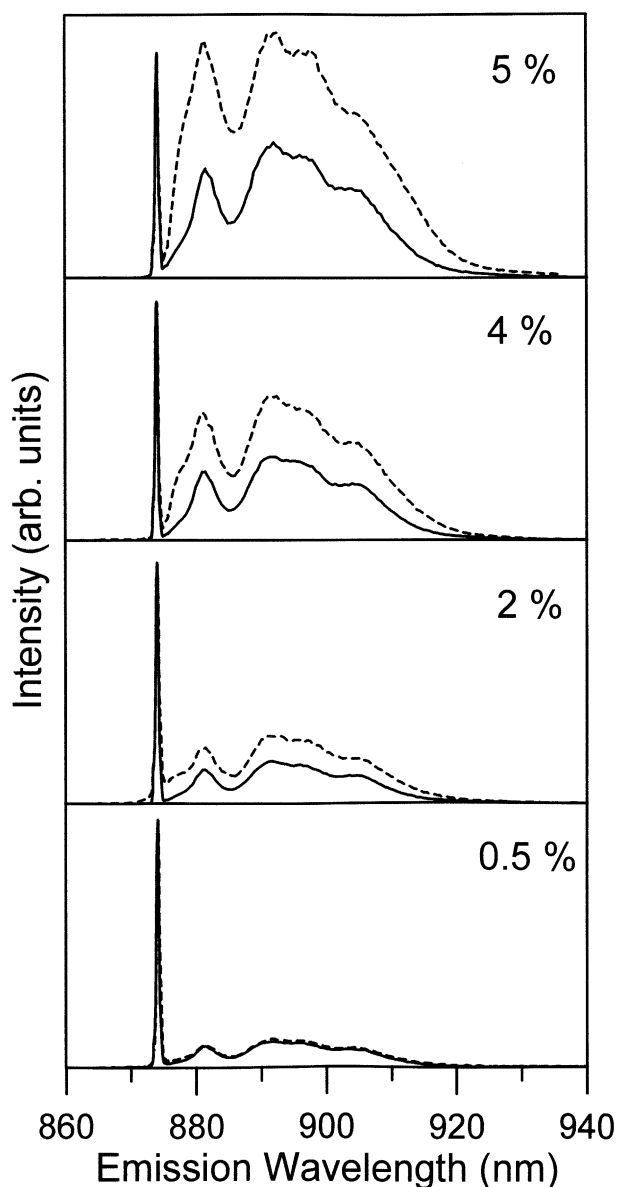
Fig. 1. Time-resolved fluorescence line-narrowed spectra of the $^4F_{3/2} \rightarrow ^4I_{9/2}$ transition obtained at 1 µs (solid line) and 700 µs (dashed line) after the laser pulse by excitation at 874 nm for the samples doped with 0.5, 2, 4, and 5 mol%. Measurements correspond to 4.2 K.

Fig. 2. Time-resolved fluorescence line-narrowed spectra of the $^4F_{3/2} \rightarrow ^4I_{9/2}$ transition obtained at 1 µs after the laser pulse by excitation at three different wavelengths for the sample doped with 2 mol%. Measurements correspond to 4.2 K.

energy can migrate mainly in one direction. As an example, Fig. 2 shows the TRFLN spectra for the sample doped with 2 mol% of Nd^{3+} obtained at three different excitation wavelengths. The same behaviour is observed in all samples.

The time evolution of laser-induced resonant line-narrowed fluorescence is produced by a combination of radiative decay and non-radiative transfer to other nearby ions. Subsequent fluorescence from the acceptors ions replicate the inhomogeneously broadened equilibrium emission profile, showing that transfer occurs not to resonant sites but to the full range of
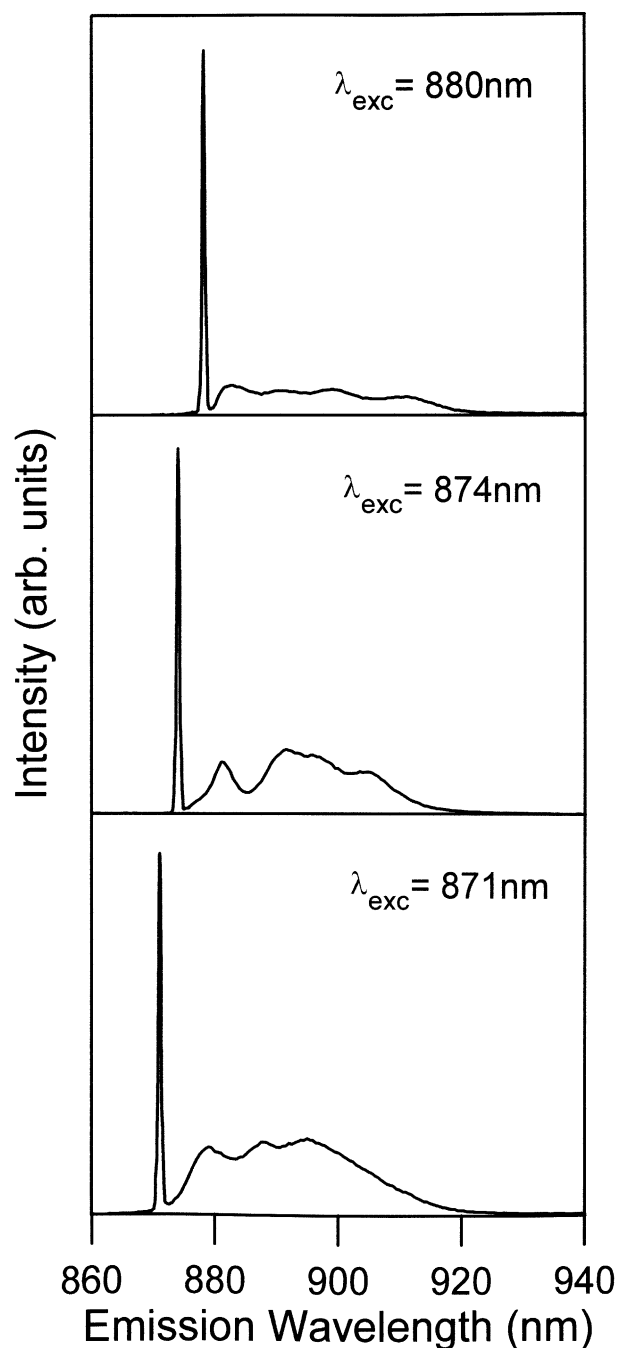
sites within the inhomogeneous profile. In this case, a quantitative measure of the transfer is provided by the ratio of the intensity in the narrow line to the total intensity of the fluorescence in the inhomogeneous band. Neglecting the dispersion in the radiative decay rate, and using the Föster formula for dipole–dipole energy transfer, one can write for the relationship between the integral intensities of the broad back-
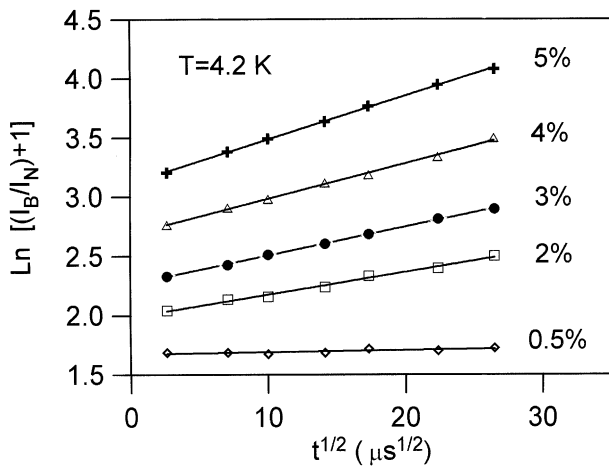
Fig. 3. Analysis of the time evolution of the TRFLN $^4F_{3/2} \rightarrow {}^4I_{9/2}$ emission by means of equation (1) for all samples. Symbols correspond to experimental data and the solid line fits equation (1). Data correspond to 4.2 K.

Fig. 4. Analysis of the time evolution of the TRFLN $^4F_{3/2} \rightarrow {}^4I_{9/2}$ emission by means of equation (1) for the sample doped with 2 mol% of Nd^{3+} for three different excitation wavelengths. Symbols correspond to experimental data and the solid line fits equation (1). Data correspond to 4.2 K.

ground emission I_B and the narrow luminescence component I_N [6]:

$$\ln\left(\frac{I_B}{I_N} + 1\right) = \gamma(E_L)\, t_{1/2} \tag{1}$$

The macroscopic parameter $\gamma(E_L)$ has the meaning of an integral characteristic, which reflects the average rate of excitation transfer from donors to the ensemble of spectrally non-equivalent acceptors [6].

This analysis deals with migration-induced changes in an individual luminescence band originating from transitions between a pair of Stark sublevels [6]. However, in the case of Nd^{3+} ions, the luminescence spectra represent a superposition of different Stark components. At low temperature, where only the lowest Stark sublevels of the ground and metastable states are populated, the spectra show a narrow resonant Stark component and some broad emission due to transitions to the other Stark components of the ground state, whereas, at higher temperatures, the spectral pattern becomes more complicated. As a consequence, though at high temperatures spectral migration can be experimentally observed, the analysis in terms of equation (1), which considers a two-level scheme, becomes more complicated.

We have analysed the TRFLN spectra of the $^4F_{3/2} \rightarrow {}^4I_{9/2}$ transition obtained at different time delays between 1 and 700 μs according to equation (1) at 4.2 K. As an example, Fig. 3 shows the results for all samples for an excitation wavelength of 874 nm. As can be observed, a linear dependence of the $\ln[(I_B/I_N) + 1]$ function on $t^{1/2}$ was found, which indicates that a dipole–dipole interaction mechanism among the Nd^{3+} ions dominates in this time regime. The values of the average transfer rate indicate that
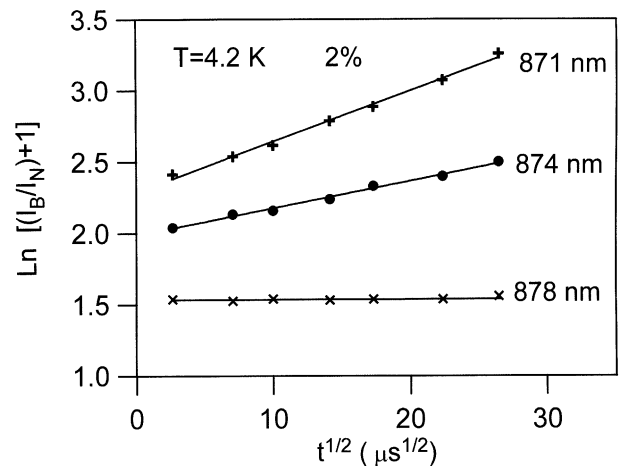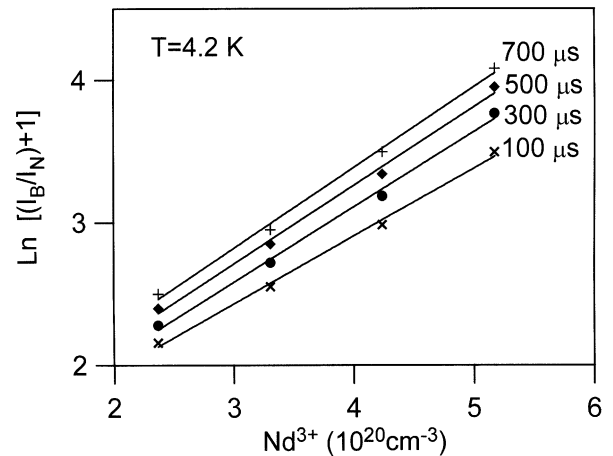

Fig. 5. Concentration dependence of the quantity $\ln[(I_B/I_N) + 1]$ for Nd^{3+} ions. Symbols correspond to experimental data and the solid line is a linear fit. Data were obtained at different time delays after the laser pulse by exciting at 874 nm.

energy transfer among Nd^{3+} ions is weak at concentrations up to 2 mol% at low temperature, and increases with increasing concentration. The γ values for this excitation wavelength were found to be 1.7, 19, 24, 30, and 37 $s^{-1/2}$ for the samples doped with 0.5, 2, 3, 4, and 5 mol% respectively. The analysis of the TRFLN spectra obtained under excitation at longer wavelengths along the low energy Stark component of the $^4I_{9/2} \rightarrow {}^4F_{3/2}$ absorption band shows that the transfer rate depends on the excitation energy. As an example, Fig. 4 shows the analysis of the TRFLN spectra for the sample doped with 2 mol% of Nd^{3+} at three different excitation energies. As can be observed the value of the average transfer rate increases from 0.2 $s^{-1/2}$ to 36 $s^{-1/2}$ when the excitation energy

increases from 11 389.5 cm^{-1} (878 nm) to 11 481.05 cm^{-1} (871). This rise in the energy migration rate is due to the increasing number of possible acceptors.

The concentration dependence of the spectral migration rate can be obtained from the luminescence spectra of different concentration samples with the same time delay after laser excitation. The increase of the intensity of the broad band relative to that of the narrow component shows the concentration induced growth of the migration transfer rate. Fig. 5 shows the concentration dependence of $\ln[(I_B/I_N) + 1]$ obtained at 4.2 K at 100, 300, 500, and 700 µs after the laser pulse. The observed linear behaviour is again consistent with a dipole–dipole energy transfer mechanism.

4. Conclusions

Resonant time-resolved fluorescence line-narrowing spectroscopy shows the existence of energy migration between discrete regions of the inhomogeneous broadened $^4F_{3/2}$ spectral profile. The analysis of the $^4F_{3/2} \rightarrow {}^4I_{9/2}$ emission spectra obtained at low temperature as a function of time, concentration, and excitation wavelength shows that the electronic mechanism responsible for the Nd^{3+}–Nd^{3+} interaction can be interpreted in terms of a dipole-dipole energy transfer.

The average energy transfer rate found in these fluoroarsenate glasses is a 40% lower than the one found in oxide glasses [11] for the same concentration of Nd^{3+} ions.

References

[1] L.A. Riseberg, Phys. Rev. A 7 (1973) 671.

[2] M.J. Weber, in: W.M. Yen, P.M. Selzer (Eds.), Laser Spectroscopy of Solids, 49, Springer, Berlin, 1981, p. 189.

[3] S.A. Brawer, M.J. Weber, Appl. Phys. Lett. 35 (1979) 31.

[4] L.D. Merkle, R.C. Powell, E.E. Freed, J. Lumin. 24–25 (1981) 755.

[5] L.A. Riseberg, Solid State Commun. 11 (1972) 469.

[6] T.T. Basiev, V.A. Malyshev, A.K. Prhevuskii, in: A.A. Kaplyanskii, R.M. Macfarlane (Eds.), Spectroscopy of Solids Containing Rare Earth Ions, North-Holland, Amsterdam, 1987, p. 303.

[7] W.M. Yen, in: A.A. Kaplyanskii, R.M. Macfarlane (Eds.), Spectroscopy of Solids Containing Rare Earth Ions, North-Holland, Amsterdam, 1987, p. 185, pp. 185.

[8] M.M. Broer, D.L. Huber, W.M. Yen, W.K. Zwicker, Phys. Rev. Lett. 49 (1982) 394.

[9] T.T. Basiev, K. Vorońko Yu, S.B. Mirov, A.M. Prokhorov, JETP Lett. 29 (1979) 639.

[10] R. Balda, J. Fernández, M. Sanz, A. de Pablos, J.M. Fdez-Navarro, J. Mugnier, Phys. Rev. B 61 (2000) 3384.

[11] R. Balda, M. Sanz, J. Fernández, J.M. Fdez-Navarro, J. Opt. Soc. Am. B 17 (2000) 1671.

[12] N. Duhamel-Henry, J.L. Adam, B. Jacquier, C. Linares, Opt. Mater. 6 (1996) 197.

[13] R. Balda, J. Fernández, I. Sáez de Ocáriz, J.L. Adam, A. Mendioroz, E. Montoya, Opt. Mater. 13 (1999) 159.

[14] R. Balda, J. Fernández, J.L. Adam, M.A. Arriandiaga, Phys. Rev. B 54 (1996) 12076.

[15] J.-L. Adam, R. Balda, I. Melscoët, F. Smektala, L.M. Lacha, J. Fernández, J. Non-Cryst. Solids 256–257 (1999) 390.