J Supercond Nov Magn (2009) 22: 529–533
DOI 10.1007/s10948-009-0474-9

ORIGINAL PAPER

A Model for Liquid-Striped Liquid Phase Separation in Liquids of Anisotropic Polarons

D. Innocenti · A. Ricci · N. Poccia · G. Campi · M. Fratini · Antonio Bianconi

Received: 27 March 2009 / Accepted: 31 March 2009 / Published online: 9 April 2009

Abstract The phase separation between a striped polaron liquid at the particular density and a high density polaron liquid is described by a modified Van der Waals scheme. The striped polaron liquid represents the pseudo gap matter or Wigner-like polaron phase at 1/8 doping in cuprate superconductors. The model includes the tendency of pseudo-Jahn-Teller polarons to form anisotropic directional bonds at a preferential volume with the formation of different "liquid phases". The model gives the coexistence of a first low density polaron striped liquid and a second high density liquid that appears in cuprate superconductors for doping larger than 1/8. We discuss how the strength of anisotropic bonds controls the variation the phase separation scenarios for complex systems in the presence of a quantum critical point where the phase separation vanishes.

Keywords Phase separation · Critical point · Spinodal lines · Phase diagrams · Van der Waals · Anisotropic interactions · Polaron liquids

1 Introduction

The Van der Waals scheme is the simplest scheme to describe the spinodal phase separation in a complex system such as polaron liquids. It has been used to study the phase separation in a polaron liquid by Emin [1, 2]. We propose to extend the Van der Waals scheme to describe the complex phase separation in cuprates appearing for doping larger than 1/8 where a polaron striped metallic phase with doping larger than 1/8 coexists with a high density phase [3–6]. This phase separation has been shown to be driven by the coexistence of pseudo-Jahn-Teller polarons (PJTP), associated with the rhombic distortion of the CuO_4 square plane and its tilting in the vertical or horizontal direction or antinodal directions [7–10]. These PJTP polarons are in the intermediate coupling range between large and small polarons, having an area of about 8 Cu sites [11]. These PJTP coexist with itinerant particles moving in the nodal direction [12, 13].

The PJTP get self-organized below a critical temperature T^* with the formation of electronic polaron striped phases at a critical density close to 1/8 holes per Cu site, giving the so called pseudo-gap phase [14–21]. The interaction between the PJTP is clearly anisotropic because of the associated rhombic distortion; therefore they have the tendency to form linear polaron strings [22, 23]. The polaronic electron-phonon interaction depends in these heterostructures at the atomic limit [24–26] on the lattice misfit strain between the active CuO_2 layers and the spacer layers [27–31], which plays a key role also in diborides [32] and iron pnictides [33].

The phase diagram of cuprate superconductors shows that a PJTP polarons striped phase, called also a quasi 1D generalized Wigner polaron crystal, is formed at critical values of the charge density (1/8 holes per Cu site and a critical strength of the elastic field due to the misfit strain. The critical density for the formation of a electronic polaronic crystal depends on the effective volume occupied by the polaron carriers. The anisotropic interactions between the polarons produce the stripe phases. In order to give an account of the

D. Innocenti · A. Ricci · N. Poccia · M. Fratini · A. Bianconi (✉)
Department of Physics, Sapienza University of Rome,
P. Aldo Moro 2, 00185 Rome, Italy
e-mail: Antonio.bianconi@roma1.infn.it

G. Campi
Istituto di Cristallografia, CNR, Via Salaria Km 29, 300,
00016 Monterotond, Rome, Italy

new emerging complex phase diagram, where phase separation is controlled by doping and misfit strain [27–33], we have extended the model of Poole et al. [34] for supercooled water, as proposed by Campi et al. [35], to describe the 3D phase diagram including all different HTcS families.

2 The Model

We use a modified Van der Waals interaction model, analogously to the one introduced for the phase diagram of supercooled water [34, 35]. In fact, supercooled water, a prototype of complex matter, shows a phase separation driven by the tendency of water molecules to form quasi 1D arrays of hydrogen bonds. This tendency gives fluctuating clusters made of a low density liquid (LDL) that coexists with the high density liquid water (HDL). In order to describe this anomalous phase separation in water, the model of Poole et al. [35] implements the standard Van der Waals model by including a characteristic gain in energy "γ" for the formation of clusters with directional hydrogen bonds at a particular preferential volume "V_γ". The introduction of this anisotropic interaction provides a phase diagram with the coexistence of a high density liquid (HDL) and a low density liquid (LDL) when γ is larger than a threshold value.

Here we have extended the Poole model in order to describe the phase separation in the polaron liquid in cuprates. The free energy of a complex system in which a phase separation is observed, is obtained by adding the term A_γ to the Van der Waals free energy A_{VDW}, yielding a total free energy

$$A = A_{\mathrm{VDW}} + A_\gamma \tag{1}$$

where A_{VDW} and A_γ are given by

$$A_{\mathrm{VdW}} = -RT\left\{\ln\left[(V-b)/\Lambda^3\right]+1\right\} - a^2/V \tag{2}$$

$$A_\gamma = -RTf\ln\left[\Omega + \exp\left(-\frac{\gamma}{RT}\right)\right] - RT(1-f)(\Omega+1) \tag{3}$$

Here a and b are the standard Van der Waals constants. The Van der Waals constant a is associated with the isotropic inter-particle attraction and the constant b is associated to the volume occupied by a fluid particle. These parameters are used to define the critical values of the thermodynamic variables T_c, P_c and V_c and the standard parameter $\gamma_0 = a/b$ for the Van der Waals model. The value of the parameter Ω is defined as $\Omega = \exp(-S_\gamma/R)$, where S_γ is the entropy of formation for a mole of anisotropic bonds. The intermediate phase is characterized by the anisotropic inter-particle interaction γ. In this approach there are $\Omega \gg 1$ configurations all having $\gamma = 0$ and only a single configuration in which the formation of the anisotropic bonds with energy γ is allowed. The anisotropic interaction is most likely to occur when the bulk molar volume is consistent with the preferential volume V_γ. In fact, each particle has an optimal local volume for the formation of anisotropic bonds to its neighbors. Changing the particle density, when $V \neq V_\gamma$, the anisotropic interactions are only a fraction f of the total, since V is no longer consistent with the possibility that all anisotropic interactions are saturated at the optimal volume. The remaining fraction of bonds, $1-f$, occurs in an unfavorable local volume and therefore, they cannot form the anisotropic bonds of the phase. The term f is given by

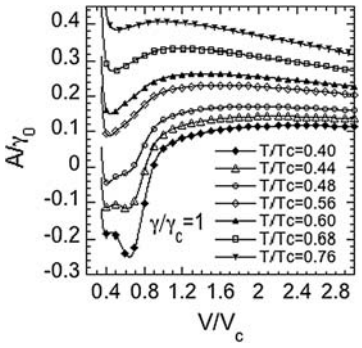

Fig. 1 The normalized free energy as a function of reduced volume V/V_c at different temperatures. In this way the novel minimum of the free energy occurs at a reduced density different from the minimum of the VdW model. This new minimum indicates the occurrence of the intermediate phase, becoming deeper when the temperature decreases, as shown in the plots for $T/T_c = 0.40$, 0.44, 0.48, 0.56, 0.60, 0.68 and 0.76

$$f = \left[-\left(\frac{V-V_\gamma}{\sigma}\right)^2\right] \tag{4}$$

where σ characterizes the width of the region of volume around V_γ over which a significant fraction of anisotropic bonds can be described by (3).

To describe the phase diagram of cuprates where we observe two phase separations, we consider a Poole model with one anisotropic interaction γ giving rise to the intermediate phase with preferential volume V_γ, which simulates the striped polaron phase in cuprates at doping 1/8.

The inclusion in the model of the optimum volume V_γ for the anisotropic bond introduces a new minimum in the free energy when V approaches V_γ. In Fig. 1 we have plotted the normalized free energy A/γ_0 as functions of the normalized volume V/V_c at the fixed normalized interaction energy $\gamma/\gamma_c = 1$. We observe in the phase diagram that the new minimum occurs only for a temperature lower than the critical value $T/T_c = 0.68$.

We observe that the effect of the A_γ term in (1), related with the strength of the anisotropic interactions, is to "split" the normal Van der Waals spinodal curve by imposing thermodynamic stability in the region of states centered at the

reduced density $b/V = 0.5$ where the intermediate phase is stable. As a result, two spinodal lines occur, each terminating at a critical point producing two phase separation regions. As the directional bond energy γ decrease with respect to the Van der Waals interaction γ_0, the phase separations generated by the strength of the directional bond decrease and the stabilizing effect of A_γ set in only at lower temperature. The critical points merge with the high density spinodal of the main Van der Waals spinodal line that is formed when γ goes to zero.

In the phase diagrams of panel (a), (b), (c) of Fig. 2 we change the γ value in order to show the effects of the strength of the anisotropic interaction on the thermodynamic behavior of the system.

In panel (a), we have used the value $\gamma/\gamma_0 = 3.0$, in fact for a value of $\gamma/\gamma_0 > \gamma_c$ we observe that there appears a second phase separation that becomes more defined when we continue to increase γ interaction.

When γ is decreasing to the critical value ($\gamma = \gamma_c$) $\gamma/\gamma_0 = 1.48$, the two spinodal lines, $(1 + 2)$ and $(2 + 3)$, are going to overlap in a point (panel (b)), and then, when γ becomes lower than the threshold γ_0, a phase separation merges with the other in a greater region of phase coexistence and the intermediate phase (2) becomes an isolated pocket of stability completely enclosed within a spinodal line as shown in panel (c). If we continue to decrease the strength of the anisotropic interaction we obtain a more isolated pocket with a lower critical temperature until the anisotropic interaction γ/γ_0 goes to zero; then we reach a quantum critical point where we obtain the standard Van der Waals phase diagram.

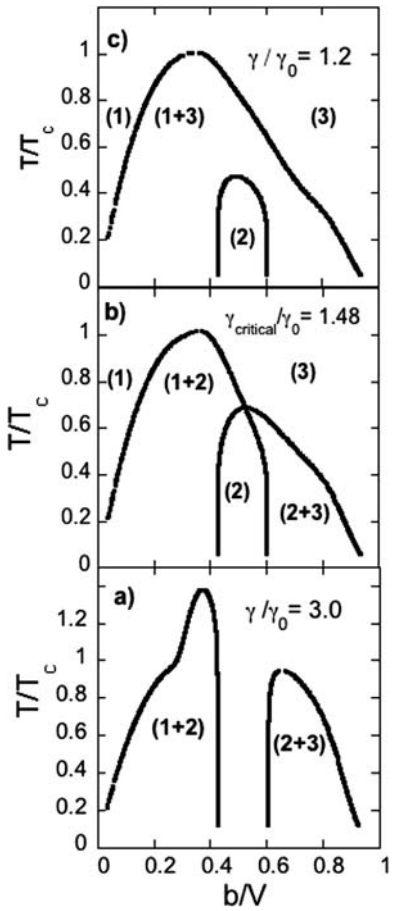

Fig. 2 The phase diagrams obtained by computing the spinodal lines from (1). We can observe the occurrence of two phase separations indicated by the two spinodal lines in panel (**a**). In panel (**b**) and (**c**) we show the effect of the decreasing strength of the directional bond

3 Interaction Energy Phase Diagram

Here we present the phase diagram at constant low temperature as a function of the directional interaction energy and the reduced density. We have used the previous phase diagrams to get the new one, in fact we calculate the value of each interaction energy normalized to γ/γ_c at a certain reduced density b/V with the temperature fixed at a fixed value.

As we have normalized all the thermodynamic variables and energies with respect to their critical values we obtain a universal phase diagram.

We obtain the result that three different phases occur, separated by three regions of phase coexistence. As the temperature increases, the phase separations generated by the strength of the directional bond decrease and the different phases are no longer well separated.

In the phase diagram of Fig. 3 we use a value of $T/T_c = 0.4$ and we observe the occurrence of three different phases, well separated by three regions of phase coexistence.

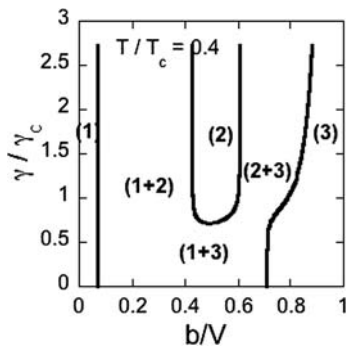

Fig. 3 The normalized energy of the directional interaction γ/γ_c as a function of the reduced density b/V at $T/T_c = 0.4$. We identify three different phases, well separated by three regions of phase coexistence with a critical minimum value of the directional interaction γ/γ_c, and below this minimum value the pure phase (2) assigned to the PJT striped polaron phase, or pseudo gap phase, is not observed

4 Conclusions

In conclusion we have presented a model for an electronic complex system that simulates the phase diagram of the polaron liquid in cuprates with the coexistence of different electronic phases at critical densities and the coexistence of different liquids described by the modified Van der Waals model.

We discuss the critical values of the anisotropic interactions for the spinodal lines and we find that this model is able to describe a generic complex system with a variable anisotropic energy interaction.

Finally we have shown the phase diagram for a complex system where the critical temperature depends on the density and the energy of the anisotropic interaction.

This approach might be useful to study complex phased separations like that in high T_c superconductors.

Acknowledgement This work was supported by European project 517039 "Controlling Mesoscopic phase separation" (COMEPHS) (2005).

References

1. Emin, D.: Phys. Rev. B **49**, 9157 (1994)
2. Emin, D.: Phys. Rev. Lett. **72**, 1052 (1994)
3. Kusmartsev, F.V., Di Castro, D., Bianconi, G., Bianconi, A.: Transformation of strings into an inhomogeneous phase of stripes and itinerant carriers. Phys. Lett. A **275**, 118 (2000). doi:10.1016/S0375-9601(00)00555-7
4. Kusmartsev, F.V., Saarela, M.: Two-component physics of cuprates and superconductor–insulator transitions. Supercond. Sci. Technol. **22**, 014008 (2009)
5. Kugel, K.I., Rakhmanov, A.L., Sboychakov, A.O., Poccia, N., Bianconi, A.: A model for the phase separation controlled by doping and the internal chemical pressure in different cuprate superconductors. Phys. Rev. B **78**, 165124 (2008). doi:10.1103/PhysRevB.78.165124
6. Kugel, K.I., Rakhmanov, A.L., Sboychakov, A.O., Kusmartsev, F.V., Poccia, N., Bianconi, A.: A two-band model for the phase separation induced by the chemical mismatch pressure in different cuprate superconductors. Supercond. Sci. Technol. **22**, 014007 (2009). doi:10.1088/0953-2048/22/1/014007
7. Bianconi, A., Flank, A.-M., Lagarde, P., Li, C., Pettiti, I., Pompa, M., Udron, D.: On the Cu 3d holes in high T_c superconductors. Is a Cu 3dz2-r2 bipolaron the superconducting pair? In: Askenazi, J., Vezzoli, G. (eds.) Electronic Structure and Mechanisms of High Temperature Superconductivity. Plenum, New York (1992). Proc. of the Miami Workshop, Miami 3–9 January 1991. ISBN:978-0-306-44117-2
8. Bianconi, A., Saini, N.L., Lanzara, A., Missori, M., Rossetti, T., Oyanagi, H., Yamaguchi, H., Oka, K., Ito, T.: Phys. Rev. Lett. **76**, 3412–3415 (1996). doi:10.1103/PhysRevLett.76.3412
9. Müller, K.A.: Essential heterogeneities in hole-doped cuprate superconductors. In: Superconductivity in Complex Systems. Book Series Structure & Bonding, vol. 114, pp. 1–11. Springer, Berlin (2005). doi:10.1007/b101015
10. Müller, K.A.: From phase separation to stripes. In: Bianconi, A., Saini, N.L. (eds.) Stripes and Related Phenomena. Selected Topics in Superconductivity, vol. 8, pp. 1–8. Kluwer–Plenum, New York (2002). doi:10.1007/b119246
11. Bianconi, A., Missori, M., Oyanagi, H., Yamaguchi, H., Ha, D.H., Nishiara, Y., Della Longa, S.: The measurement of the polaron size in the metallic phase of cuprate superconductors. Europhys. Lett. **31**, 411 (1995)
12. Müller, K.A., Zhao, G.-M., Conder, K., Keller, H.: J. Phys., Condens. Matter **10**, L291 (1998)
13. Shen, K.M., Ronning, F., Lu, D.H., Baumberger, F., Ingle, N.J.C., Lee, W.S., Meevasana, W., Kohsaka, Y., Azuma, M., Takano, M., Takagi, H., Shen, Z.X.: Science **307**, 901 (2005)
14. Missori, M., Bianconi, A., Saini, N.L., Oyanagi, H.: High critical temperature by resonant quantum confinement: evidence for polarons ordering at $T* \sim 1.5T_c$ in Bi-2212 and La-214 by EXAFS. Nuovo Cimento D **16**, 1815 (1994)
15. Bianconi, A., Missori, M.: The coupling of a Wigner charge density wave with Fermi liquid from the instability of a Wigner polaron crystal: a possible pairing mechanism in high T_c superconductors. In: Sigmund, E., Müller, K.A. (eds.) Phase Separation in Cuprate Superconductors, pp. 272–289. Springer, Berlin–Heidelberg (1994). Proc. of the Workshop held at Cottbus, Germany Sept. 4–10, 1993
16. Campi, G., Di Castro, D., Bianconi, G., Agrestini, S., Saini, N.L., Oyanagy, H., Bianconi, A.: Photo-induced phase transition to a striped polaron crystal in cuprates. Phase Transit. **75**, 927 (2002)
17. Bianconi, A., Di Castro, D., Bianconi, G., Pifferi, A., Saini, N.L., Chou, F.C., Johnston, D.C., Colapietro, M.: Coexistence of stripes and superconductivity: T_c amplification in a superlattice of superconducting stripes. Physica C **341**, 1719 (2000)
18. Di Castro, D., Colapietro, M., Bianconi, G.: Metallic stripes in oxygen doped La_2CuO_4. Int. J. Modern Phys. B **14**, 3438 (2000). doi:10.1142/S0217979200003927
19. Bianconi, A.: The instability close to the 2D generalized Wigner polaron crystal density: A possible pairing mechanism indicated by a key experiment. Physica C **235–240**, 269 (1994)
20. Bianconi, A.: On the Fermi liquid coupled with a generalized Wigner polaronic CDW giving high T_c superconductivity. Solid State Commun. **91**, 1 (1994)
21. Bianconi, A., Missori, M.: The instability of a 2D electron gas near the critical density for a Wigner polaron crystal giving the quantum state of cuprate superconductors. Solid State Commun. **91**, 287 (1994)
22. Kusmartsev, F.V.: Phys. Rev. Lett. **84**, 530 (2000). Ibidem **84**, 5026 (2000)
23. Kusmartsev, F.V.: Europhys. Lett. **54**, 786 (2001)
24. Bianconi, A.: Process of increasing the critical temperature T_c of a bulk superconductor by making metal heterostructures at the atomic limit. United State Patent No.: US6, 265, 019 B1 (2001)
25. Tokura, Y., Arima, T.: New classification method for layered copper oxide compounds and its application to design of new high T_c superconductors. Jpn. J. Appl. Phys. **29**, 2388 (1990). doi:10.1143/JJAP.29.2388
26. Bianconi, A.: On the possibility of new high T_c superconductors by producing metal heterostructures as in the cuprate perovskites. Solid State Commun. **89**, 933 (1994)
27. Fratini, M., Poccia, N., Bianconi, A.: J. Phys. Conf. Ser. **108**, 012036 (2008). doi:10.1088/1742-6596/108/1/012036
28. Bianconi, A., Saini, N.L., Agrestini, S., Di Castro, D., Bianconi, G.: Int. J. Modern Phys. B **14**, 3342 (2000). doi:10.1142/S0217979200003812
29. Agrestini, S., Saini, N.L., Bianconi, G., Bianconi, A.: The strain of CuO_2 lattice: the second variable for the phase diagram of cuprate perovskites. J. Phys. A, Math. Gen. **36**, 9133 (2003). doi:10.1088/0305-4470/36/35/302
30. Poccia, N., Fratini, M.: The misfit strain critical point in the 3D phase diagrams of cuprates. J. Supercond. Novel Magn. **22**, 1557 (2009). doi:10.1007/s10948-008-0435-8

31. Bianconi, A., Bianconi, G., Caprara, S., Di Castro, D., Oyanagi, H., Saini, N.L.: J. Phys.: Condens. Matter **12**, 10655 (2000). doi:10.1088/0953-8984/12/50/326
32. Agrestini, S., et al.: High T_c superconductivity in a critical range of micro-strain and charge density in diborides. J. Phys.: Condens. Matter **13**, 11689 (2001)
33. Caivano, R., et al.: Feshbach resonance and mesoscopic phase separation near a quantum critical point in multiband FeAs-based superconductors. Supercond. Sci. Technol. **22**, 014004 (2009). doi:10.1088/0953-2048/22/1/014004
34. Poole, P.H., Sciortino, F., Grande, T., Stanley, H.E., Angell, C.A.: Phys. Rev. Lett. **73**, 1632 (1994) and references therein
35. Campi, G., Bianconi, A.: In: Symmetry and Heterogeneity in High Temperature Superconductors. NATO Science Series II Mathematics, Physics and Chemistry, vol. 214, p. 147. Springer, Dordrecht (2006)