

**Electronic and magnetic phase diagram of  $\text{Cr}_{1-x}\text{V}_x\text{N}$** C. X. Quintela,<sup>1,2</sup> F. Rivadulla,<sup>3,2,\*</sup> and J. Rivas<sup>1</sup><sup>1</sup>*Department of Applied Physics, University of Santiago de Compostela, 15782 Santiago de Compostela, Spain*<sup>2</sup>*Center for Research in Biological Chemistry and Molecular Materials, University of Santiago de Compostela, 15782 Santiago de Compostela, Spain*<sup>3</sup>*Department of Physical Chemistry, University of Santiago de Compostela, 15782 Santiago de Compostela, Spain*

(Received 1 July 2010; revised manuscript received 5 October 2010; published 1 December 2010)

We report the structural, magnetic, and electronic phase diagram of  $\text{Cr}_{1-x}\text{V}_x\text{N}$ . Stoichiometric CrN is a narrow gap, correlation-induced, semiconductor that orders antiferromagnetically below 286 K. The changes in the chemical bond associated to the magnetic order result in a nonactivated behavior of the resistivity in the antiferromagnetic state. Introducing holes into this system produces a series of inhomogeneous magnetic/electronic states, as identified through electronic and thermal conductivity, and magnetic susceptibility. The magnetic/electronic phase diagram of  $\text{Cr}_{1-x}\text{V}_x\text{N}$  is an example of electronic complexity in a simple system from the chemical and structural point of view.

DOI: [10.1103/PhysRevB.82.245201](https://doi.org/10.1103/PhysRevB.82.245201)

PACS number(s): 75.50.Pp, 71.27.+a

**I. INTRODUCTION**

Understanding the electronic and magnetic properties of solids with strongly correlated electrons (SCEs) is one of the most challenging problems in physics. Electronic correlations are the source of a number of new phases that emerge close to the 0 K insulator-to-metal transitions in Mott systems. Up to now, most of the interest was focused on transition-metal oxides, mainly for two reasons: first, due to the optimum degree of (M:3d)-(O:2p) hybridization that can be tuned by the atomic number and oxidation state of the metal,<sup>1</sup> and second due to the discovery of high-temperature superconductivity in hole-doped cuprates.<sup>2</sup> However, other families of compounds (i.e., from group VA: N, P, and As) could also lie in this group of SCEs if the transition metal, its oxidation state and the structure are chosen wisely to control the correlations.

Transition-metal nitrides have also attracted great attention in the last few years mainly due to their technological applications.<sup>3</sup> Their strong covalent metal-nitrogen bond gives them hardness, chemical and thermal stability, and high resistance to corrosion. Besides the technological applications, the family of transition-metal nitrides also show a rich variety of interesting electronic properties, including superconductivity at 25.5 K in electron-doped layered HfN.<sup>4</sup>

An interesting case is that of CrN: the stoichiometric compound is a rocksalt paramagnet (PM) at room temperature that becomes orthorhombic and antiferromagnetic (AF) below 285 K. This magnetostructural transition was first reported by Corliss<sup>5</sup> in 1960 and theoretically associated to an exchange-striction effect by Filippetti *et al.*<sup>6</sup> Rivadulla *et al.*<sup>7</sup> proposed a charge transfer from the Cr-N to the Cr-Cr bonds, below the magnetostructural transition at  $T_N$ , consistent with the formation of itinerant electron states along the Cr-Cr direction. This scenario is in agreement with the recent report of itinerant antiferromagnetism, as claimed by Bhobe *et al.*<sup>8</sup> from photoemission experiments, making CrN one of the rare examples of itinerant AF state, such as  $\text{CaCrO}_3$ .<sup>9</sup> In addition, theoretical calculations<sup>10</sup> located CrN in the charge-transfer regime, close to the itinerant electron limit. Doping

this anomalous state to reach the itinerant electron behavior provides a unique opportunity to study how the AF transforms into a metal.

In this paper we report the electronic/magnetic phase diagram of  $\text{Cr}_{1-x}\text{V}_x\text{N}$ . We show that the low-temperature AF state of pure CrN is not a conventional semiconductor but shows electronic delocalization. Doping this system with holes produces an unexpected electronic/magnetic complexity in a simple system from the chemical and structural point of view.

**II. EXPERIMENTAL DETAILS**

Polycrystalline samples of  $\text{Cr}_{1-x}\text{V}_x\text{N}$  were synthesized by ammonolysis of  $\text{Cr}_{1-x}\text{V}_x\text{S}_2$  at 800 °C for 10 h.  $\text{Cr}_{1-x}\text{V}_x\text{S}_2$  samples were previously synthesized by mixing elemental high-purity Cr, V, and S in fused silica tubes. The tubes were evacuated, sealed and heated over a period of 24 h at 1000 °C. It is well known that electronic transport in CrN is very sensitive to stoichiometry<sup>11,12</sup> as well as to lattice strain.<sup>13–16</sup> For that reason we paid special attention to avoid N vacancies and to produce dense and well-sintered samples for transport measurements. Before the last sintering,  $\text{Cr}_{1-x}\text{V}_x\text{N}$  powder was ground and cold pressed in a tungsten carbide anvil at  $\approx 0.3$  GPa in order to achieve a high density and good intergrain connectivity. Electrical resistivity,  $\rho$ , was measured by the standard four-probe technique, thermal conductivity,  $\kappa$ , by the steady-state method, and Seebeck coefficient,  $\alpha$ , was measured applying a heat pulse on one of the ends of the sample and recording the  $\Delta V/\Delta T$  variation at each temperature. Magnetic measurements were performed in a superconducting quantum interference device (SQUID) from Quantum Design. High-pressure magnetization was measured in a SQUID using a Cu-Be cell from EasyLab.

**III. RESULTS AND DISCUSSION**

The temperature dependence of the electrical resistivity of some representative samples of  $\text{Cr}_{1-x}\text{V}_x\text{N}$  is shown in Fig. 1. The absolute value of the resistivity decreases systematically

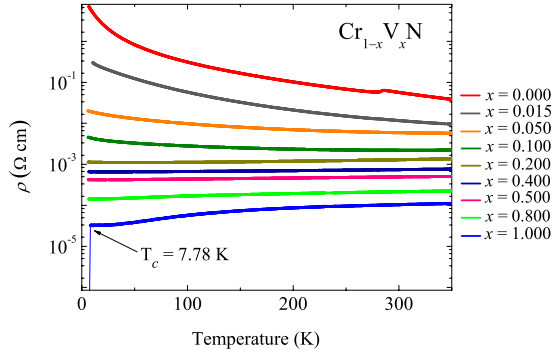


FIG. 1. (Color online) Temperature dependence of the electronic resistivity for some representative compositions of the series  $\text{Cr}_{1-x}\text{V}_x\text{N}$ . Beyond  $x \geq 0.2$  the samples present a  $d\rho/dT > 0$ , down to low temperature.

upon V doping. Negative temperature coefficient of resistivity ( $\text{TCR} = d\rho/dT$ ) is observed for samples with  $x \leq 0.1$ , whereas for  $x \geq 0.2$  the system shows a positive TCR typical of itinerant electron behavior. The end member of the series, VN, becomes a superconductor below  $T_c \approx 7.8$  K, as previously reported.<sup>17</sup>

The intrinsic mechanism of electronic transport in stoichiometric CrN is a controversial issue.<sup>8</sup> Although CrN exhibits  $\text{TCR} < 0$  in the whole temperature range, the conventional thermally activated behavior  $\rho(T) = \rho_0 \exp(E_a/k_B T)$ , is only followed in the high-temperature paramagnetic phase. As shown in Fig. 2(a), a linear fit to  $\ln \rho(T)$  versus  $1/T$  yields an activation energy  $E_a \sim 75$  meV, confirming semiconducting behavior in the high-temperature PM phase. On the other hand, the mechanism of charge transport in the low-temperature AF phase is not fully understood. As shown in Fig. 2(a) a simple mechanism of thermal activation does not

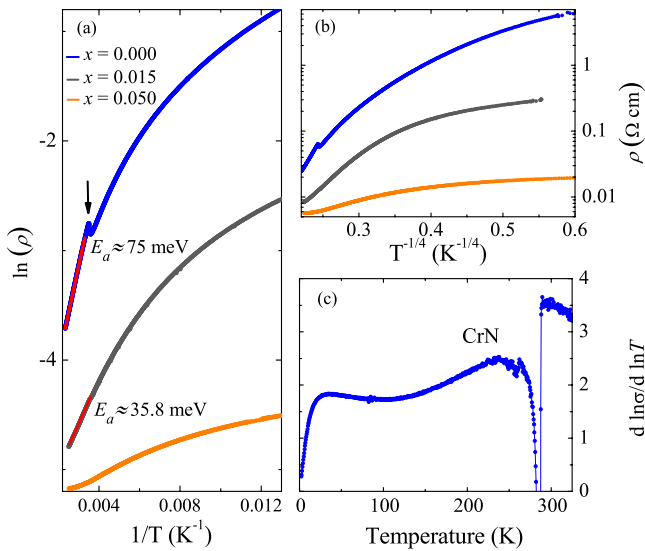


FIG. 2. (Color online) (a)  $\ln \rho(T)$  versus  $1/T$  for  $\text{Cr}_{1-x}\text{V}_x\text{N}$ ,  $x = 0.0, 0.015$ , and  $0.050$ . The red solid lines are the linear fittings to derive the activation energy. The arrow denotes the magnetostructural transition for CrN. (b)  $\ln \rho(T)$  versus  $T^{-1/4}$  to inspect the validity of Mott variable-range hopping. (c) Temperature dependence of  $d(\ln \sigma)/d(\ln T)$ .

describe  $\rho(T < T_N)$ , nor in the case of CrN nor for other members of the  $\text{Cr}_{1-x}\text{V}_x\text{N}$  series with negative TRC.

We have explored other possibilities such as Mott variable-range hopping but, as shown in Fig. 2(b), this fitting is also unsatisfactory. The attempts to fit the data to  $T^{-1/2}$  form, according to variable-range hopping in a Coulomb gap, yielded similar results.

In a system with a charge gap, irrespective of the particular form of the thermal activation mechanism, the magnitude  $d(\ln \sigma)/d \ln T$  should diverge as  $T \rightarrow 0$  given the exponential dependence of  $\rho(T)$  on temperature. The temperature dependence of  $d(\ln \sigma)/d \ln T$ , which is plotted in Fig. 2(c) for CrN, goes to zero as  $T \rightarrow 0$ . This suggests that CrN cannot be classified as a conventional thermally activated semiconductor, in spite of the negative TRC of the experimental data. Indeed, spectroscopic experiments performed by Bhojbe *et al.*<sup>8</sup> found a finite density of states at the Fermi energy proposing CrN as one of the rare examples of AF-itinerant systems.

In accordance with that result, we have previously identified a transition from localized-to-itinerant electron behavior of the  $t_{2g}$  electrons along the Cr-Cr bonds in CrN, associated to the exchange striction effect responsible for the magnetic/structural transition.<sup>7</sup> The ambient-pressure Cr-Cr distance of  $2.933(3)$  Å in the cubic phase splits into two nonequivalent distances below the orthorhombic transition: a long one of  $2.965(5)$  Å along the FM  $[1\bar{1}0]$  direction and a short one of  $2.883(5)$  Å along the AF  $[110]$  direction. The short distance is actually very close to the itinerant (molecular-orbital) electron limit for edge-shared octahedral Cr sites in oxides,<sup>1</sup> therefore the existence of molecular-orbital electrons along the Cr-Cr bonds could be the source of this semi-itinerant behavior.

From the analysis of  $\rho(T)$  for the other members of the  $\text{Cr}_{1-x}\text{V}_x\text{N}$  series, two features must be highlighted: (i) the value of the activation energy in the PM phase decreases dramatically as the concentration of vanadium increases. As shown in Fig. 2(a), for  $x = 0.015$  (1.5% vanadium) the activation energy in the PM phase is reduced by 50% in comparison with the value obtained for stoichiometric CrN, and for  $x > 0.025$  an activation energy cannot be obtained above  $T_N$ . Actually, there is a metalliclike temperature dependence of the resistivity at high temperature (see, for example, the gradual change at  $T^*$  for  $x = 0.05$  in Fig. 3). (ii) At  $x = 0.1$  there is a sudden, not gradual change in the sign of TCR at  $T_N$  from the high-temperature PM phase ( $\text{TCR} > 0$ , itinerant) to the low-temperature AF phase ( $\text{TCR} < 0$ , nonitinerant). For  $T^* < T_N$  as expected in  $x = 0.1$ , opening of a charge gap at the magnetic ordering temperature increases the activation energy, recovering semiconductinglike behavior below  $T_N$ . So, the opening of a charge gap below  $T_N$  is intrinsic to the AF ordering in CrN, consistent with *ab initio* calculations.<sup>10</sup>

The electrical-resistivity results can be contrasted with the thermoelectric power measurements, represented as function of temperature in Fig. 4. For stoichiometric CrN the thermoelectric power shows linear temperature dependence as expected for highly degenerate conductors.<sup>18</sup> This behavior is also observed for the rest of the members of the  $\text{Cr}_{1-x}\text{V}_x\text{N}$  series for temperatures above  $\approx 300$  K. The absolute value

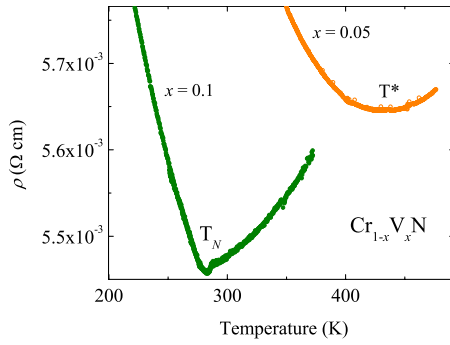


FIG. 3. (Color online) Temperature dependence of the resistivity for two member of the series  $\text{Cr}_{1-x}\text{V}_x\text{N}$  with  $x=0.05$  and  $x=0.1$ . The data for  $x=0.1$  is multiplied by 2.5 to fit both curves into the same scale. A change in the sign of  $d\rho/dT$  (signaling a semiconductor-to-metal transition) is observed at  $T_N$  for  $x=0.1$ . For  $x=0.05$  the change in slope is gradual at  $T^*$  due to an activation energy on the order of the thermal energy.

of the thermopower decreases as the concentration of vanadium increases, consistent with an increase in the concentration of charge carriers. We have not observed any discontinuity in this trend around  $x=0.2$ , where TCR goes from negative to positive at low temperatures. This supports our conclusion of an unconventional electronic state, not thermally activated neither fully itinerant, in the AF phase of pure CrN, that transforms gradually into the fully itinerant state as  $x$  increases. The values of the thermoelectric power for  $x > 0.2$  are almost linear and of a small/moderate magnitude, typical for itinerant electron systems,<sup>19</sup> in agreement with the electrical-resistivity measurements. For  $x \geq 0.8$  a change in sign from negative to positive is observed, signaling dominant hole conduction. It should be noted that, although in a simple ionic picture we could think that the change in sign should occur at around  $x=0.5$  (we are introducing a hole per vanadium), this will depend on the actual band structure, which is actually determined to a great extent by the strongly covalent Cr-N bond.<sup>6,10</sup>

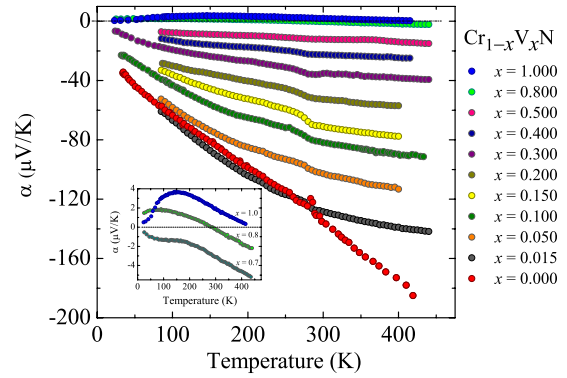


FIG. 4. (Color online) Temperature dependence of the thermoelectric power for some member of the series  $\text{Cr}_{1-x}\text{V}_x\text{N}$ . (Inset) For  $x \geq 0.8$  a change in sign from negative to positive is observed in the region 20–425 K.

The magnetic behavior is summarized in Fig. 5. The magnetic transition at  $T_N$  is driven by exchange striction and therefore produces a structural phase transition from the high-temperature PM cubic phase to the low-temperature AF orthorhombic phase.<sup>6</sup> Although the splitting of the (111) peak of the cubic phase [into the (011) and (201) peaks of the orthorhombic phase], characteristic of the phase transition, is not observed beyond  $x=0.2$  this peak still broadens below  $T_N$  for  $x=0.3$  and even for  $x=0.4$  (Fig. 6). This, along with the low sensitivity of  $T_N$  to V doping ( $T_N$  decreases only  $\approx 15$  K after introducing 40% V), the comparable pressure dependence of  $T_N$  for different  $x$  (Fig. 6, inset) and the fully itinerant behavior at  $x \geq 0.2$  observed in the electrical resistivity, points toward magnetic/electronic phase separation into hole-poor (AF) and hole-rich (FM or other types of AF order with metallic behavior) phases.

The low-doping regime ( $x \leq 0.1$ ), is rather interesting and shows a number of magnetic phases: at  $x=0.015$  [Fig. 5(b)] there is a magnetic transition at 100 K whose origin is uncertain. This survives up to  $x=0.1$ , where another FM-like transition shows up below 230 K [Fig. 5(e)]. There is an

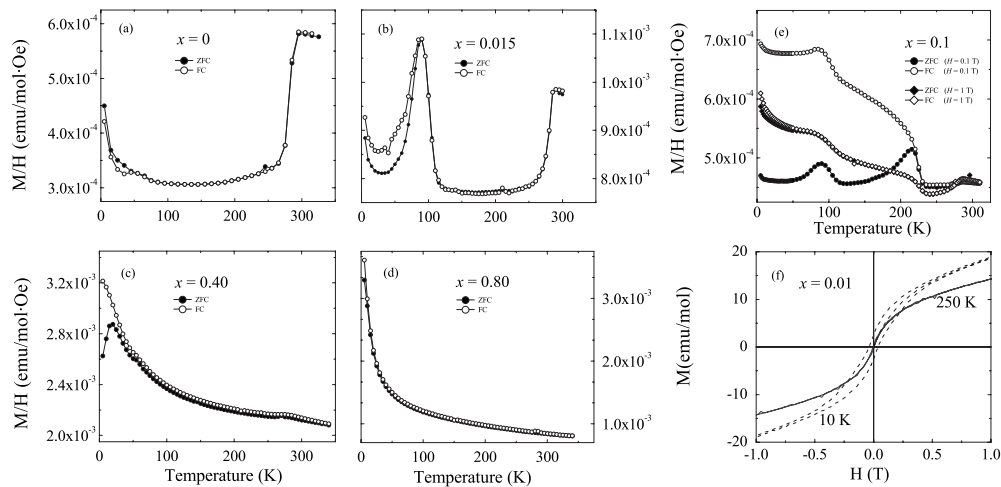


FIG. 5. [(a)–(d)] Temperature dependence of  $M/H$  (ZFC-FC curves at  $H=0.1$  T) for different members of the series  $\text{Cr}_{1-x}\text{V}_x\text{N}$ . (e) ZFC-FC temperature dependence of  $M/H$  for  $x=0.1$  at  $H=0.1$  T and  $H=1$  T. The data for  $H=0.1$  T was divided by 3 to fit in the same scale. (f) Hysteresis loops at  $T=250$  K and  $T=10$  K for the same sample.

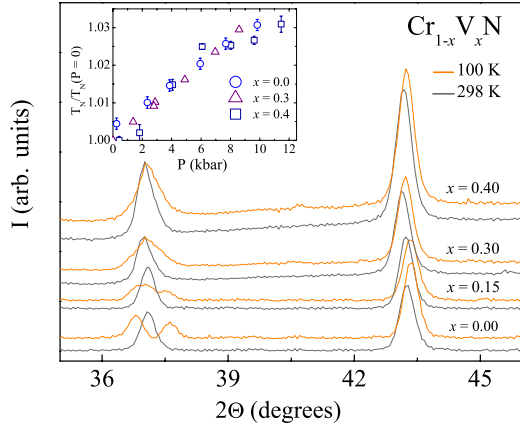


FIG. 6. (Color online) X-ray diffraction patterns of some samples of the series at two different temperatures, above  $T_N$  (298 K) and below  $T_N$  (100 K), to probe the existence of a structural phase transition. (Inset) Pressure dependence of  $T_N$  for the member of the series  $\text{Cr}_{1-x}\text{V}_x\text{N}$  with  $x=0.0$ , 0.3, and 0.4.

appreciable hysteresis in the FM region [Fig. 5(f)] and a strong temperature and field dependence of the zero-field cooled (ZFC-FC) curves, pointing again to the inhomogeneous nature of this phase. It would certainly be interesting to use more local probes to investigate whether the FM signal and the itinerant behavior come from the same phase or result from different regions of the sample.

Between  $x=0.3$  and  $x=0.6$  there is a peak in the ZFC at low temperatures and a splitting between the ZFC-FC curves, characteristic of collective relaxation behavior (cluster glass).<sup>20</sup> Again, this supports the idea of magnetic phase segregation with AF clusters in the PM itinerant phase.

Beyond  $x=0.7$  the susceptibility can be fitted to a Curie-Weiss plus a temperature independent Pauli term ( $\approx 4 \times 10^{-4}$  emu/mol Oe) in the whole temperature range. The magnetic moment increases continuously with  $x$  ( $\mu = 0.957 \mu_B$ ,  $1.01 \mu_B$ , and  $1.10 \mu_B$ , for  $x=0.7$ , 0.8, and 0.9, respectively) until VN where only a temperature-independent Pauli susceptibility was observed.

Although it is difficult to discard the possibility of paramagnetic impurities as source of local moments, the systematic increase in the magnetic moment with  $x$  goes against this interpretation. On the other hand, Curie-Weiss (CW) metallic behavior is characteristic of nearly magnetic paramagnets, in which exchange-enhanced spin fluctuations determine the magnetic properties of the system.<sup>21</sup> The proximity of these CW metals to the magnetically ordered state makes this a realistic possibility, although it needs to be further investigated.

On the other hand, given the strong spin-lattice coupling observed in CrN,<sup>6</sup> any form of magnetic phase separation as this proposed above, should be reflected in a large variation in the bond length at the boundary between the hole-rich/hole-poor regions. This bond-length fluctuation should influence the lattice dynamics and hence could be detected through measurements sensitive to the propagation of phonons. The thermal conductivity of some members of the series is presented in Fig. 7: there is a drastic change in  $\kappa$  at  $T_N$ ; the characteristic low-temperature peak of phononic

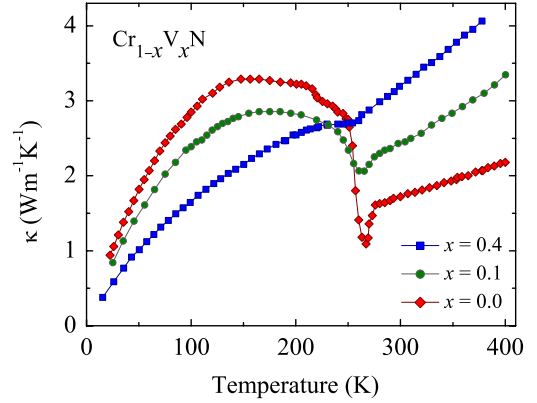


FIG. 7. (Color online) Temperature dependence of the thermal conductivity for the member of the series  $\text{Cr}_{1-x}\text{V}_x\text{N}$  with  $x=0.0$ , 0.1, and 0.4. For  $x=0.4$  the positive slope of the  $\kappa(T)$  is kept in the whole temperature range.

crystals is severely broadened, reflecting dynamic disorder. Beyond  $T_N$  the linear temperature dependence of  $\kappa$  is unusual in crystalline solids. However it has been observed in clathrate-hydrates and in some polymeric crystals, where dynamic disorder introduces a strong optic-acoustic scattering that results in a linear temperature dependence of the thermal conductivity.<sup>22</sup> The necessary energy lowering of the optical modes could be due to dynamic disorder, which in CrN must reflect the short/long Cr-Cr bonds already fluctuating at high temperature. For  $x=0.4$ , the phonon-glass behavior is kept down to the lowest temperature probed, consistent with a fluctuating multiphase scenario at low temperature.

Therefore, from the analysis of the magnetization and thermal conductivity, we can conclude that the system presents an intermediate range between CrN and the fully itin-

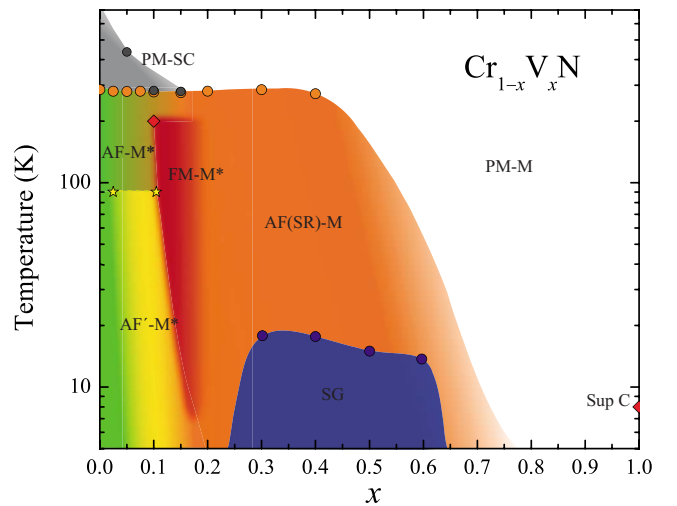


FIG. 8. (Color online) Electronic/magnetic phase diagram of  $\text{Cr}_{1-x}\text{V}_x\text{N}$ . The  $M^*$  stands for the unconventional electronic behavior in the AF phase of CrN. The low-temperature AF phase below the peak in the susceptibility is distinguished from the conventional AF phase at  $x=0$ . The paramagnetic metal (PM-M) at  $x \geq 0.4$  is strongly correlated. SupC marks the superconducting transition temperature for pure VN. The transition between different regions is not abrupt but gradual.

erant behavior of VN in which hole-rich itinerant regions are segregated from the localized-AF hole-poor regions, stabilized by bond-length fluctuations of the Cr-Cr bond. The magnetic and electronic properties of the whole series  $\text{Cr}_{1-x}\text{V}_x\text{N}$  are summarized in the phase diagram of Fig. 8.

#### IV. CONCLUSIONS

To summarize, we have reported the transport and magnetic properties of stoichiometric and hole-doped CrN and presented the magnetic and electronic phase diagram for the  $\text{Cr}_{1-x}\text{V}_x\text{N}$  series. The low-temperature AF phase at  $x=0$  is not thermally activated, neither fully itinerant, showing some similarities with other materials proposed to be itinerant AF,

such as  $\text{CaCrO}_3$ . Doping this state with holes drives the system toward itinerant electron behavior through a number of phases that coexist in a wide temperature and composition range, stabilized by bond-length fluctuations. Given the chemical and structural simplicity of this system, it could provide an interesting place to study the evolution from an antiferromagnet with a nonthermally activated charge transport, to a paramagnetic metal in a nonoxide material.

#### ACKNOWLEDGMENTS

We want to acknowledge the Ministry of Science of Spain for financial support through the project under Contract No. MAT2007-66696, and for an FPI grant (C.X.Q.).

\*Corresponding author; f.rivadulla@usc.es

- <sup>1</sup>J. B. Goodenough, *Metallic Oxides, Progress in Solid State Chemistry* (Pergamon, London, 1971).
- <sup>2</sup>J. G. Bednorz and K. A. Müller, *Z. Phys. B: Condens. Matter* **64**, 189 (1986).
- <sup>3</sup>P. F. McMillan, *Nature (London)* **1**, 19 (2002).
- <sup>4</sup>S. Yamanaka, K. Hotehama, and H. Kawaji, *Nature (London)* **392**, 580 (1998).
- <sup>5</sup>L. M. Corliss, N. Elliot, and J. M. Hastings, *Phys. Rev.* **117**, 929 (1960).
- <sup>6</sup>A. Filippetti, W. E. Pickett, and B. M. Klein, *Phys. Rev. B* **59**, 7043 (1999).
- <sup>7</sup>F. Rivadulla, M. Bañobre-Lopez, C. X. Quintela, A. Pineiro, V. Pardo, D. Baldomir, M. A. Lopez-Quintela, J. Rivas, C. A. Ramos, H. Salva, J. S. Zhou, and J. B. Goodenough, *Nature Mater.* **8**, 947 (2009).
- <sup>8</sup>P. A. Bhohe, A. Chainani, M. Taguchi, T. Takeuchi, R. Eguchi, M. Matsunami, K. Ishizaka, Y. Takata, M. Oura, Y. Senba, H. Ohashi, Y. Nishino, M. Yabashi, K. Tamasaku, T. Ishikawa, K. Takenaka, H. Takagi, and S. Shin, *Phys. Rev. Lett.* **104**, 236404 (2010).
- <sup>9</sup>A. C. Komarek, S. V. Streltsov, M. Isobe, T. Möller, M. Hoelzel, A. Senyshyn, D. Trots, M. T. Fernández-Díaz, T. Hansen, H. Gotou, T. Yagi, Y. Ueda, V. I. Anisimov, M. Grüninger, D. I. Khomskii, and M. Braden, *Phys. Rev. Lett.* **101**, 167204 (2008).
- <sup>10</sup>A. Herwadkar and W. R. L. Lambrecht, *Phys. Rev. B* **79**, 035125 (2009).
- <sup>11</sup>J. D. Browne, P. R. Liddell, R. Street, and T. Mills, *Phys. Status Solidi A* **1**, 715 (1975).
- <sup>12</sup>P. Subramanya Herle, M. S. Hegde, N. Y. Vasathacharya, and S. Philip, *J. Solid State Chem.* **134**, 120 (1997).
- <sup>13</sup>D. Gall, C. S. Shin, R. T. Haasch, I. Petrov, and J. E. Greene, *J. Appl. Phys.* **91**, 5882 (2002).
- <sup>14</sup>C. Constantin, M. B. Haider, D. Ingram, and A. R. Smith, *Appl. Phys. Lett.* **85**, 6371 (2004).
- <sup>15</sup>K. Inumaru, K. Koyama, N. Imo-oka, and S. Yamanaka, *Phys. Rev. B* **75**, 054416 (2007).
- <sup>16</sup>A. Ney, R. Rajaram, S. S. P. Parkin, T. Kammermaier, and S. Dhar, *Appl. Phys. Lett.* **89**, 112504 (2006).
- <sup>17</sup>F. I. Ajami and R. K. MacCrone, *J. Phys. Chem. Solids* **36**, 7 (1975).
- <sup>18</sup>G. J. Snyder and E. S. Toberer, *Nature Mater.* **7**, 105 (2008).
- <sup>19</sup>T. Okuda, K. Nakanishi, S. Miyasaka, and Y. Tokura, *Phys. Rev. B* **63**, 113104 (2001).
- <sup>20</sup>J. L. Dormann, D. Fiorani, and E. Tronc, *Adv. Chem. Phys.* **98**, 283 (1997).
- <sup>21</sup>T. Moriya, *Spin Fluctuations in Itinerant Electron Magnetism* (Springer-Verlag, Berlin, 1985).
- <sup>22</sup>V. Murashov and M. A. White, in *Thermal Conductivity: Theory, Properties and Applications*, edited by T. M. Tritt (Springer, New York, 2004).