

Modeling the Effect of Chemical Substitution and High Pressure on the Electronic Instabilities of the Ternary Intermetallics $CeMIn_5$ ($M = Co, Rh, Ir$)

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Dedicated to Professor Gérard Demazau on the occasion of his 65th birthday

The phase diagram of the ternary intermetallics $CeMIn_5$ ($M = Co, Rh, In$) presents new forms of competition and coexistence between magnetic and superconducting phases. We briefly review the experiments that have outlined the temperature-pressure phase diagram of these materials, emphasizing the phenomenon of reversible tuning. Expanding a recently proposed model for the coexistence of antiferromagnetism and superconductivity, we study the role of electronic doping on the ordering temperatures of these phases.

Key words: $CeMIn_5$, Magnetism, Superconductivity, Pressure

Introduction

In the last decades, the study of rare earth-transition metal intermetallics has clarified the connection between magnetic moments and strange metallic behavior, the so-called heavy-electron phenomenology [1]. More recently, in these materials new relations between magnetism and superconductivity have been uncovered [2]. Specifically, one of the properties in the family of cerium-based ternary intermetallics $CeMIn_5$ (with $M = Rh, Co, Ir$) is the ability to display, simultaneously, competition and coexistence between antiferromagnetic (AFM) and superconducting (SC) phases [3, 4].

In comparison with other systems displaying these two ground states, like the cuprate perovskites, the magnetic phase diagrams for general Ce-based intermetallic compounds are richer, and the phases are more complex [5]. The antiferromagnetic phases of the compounds $CeMIn_5$ have Néel-like magnetic structures within the planes, but different modulation vectors (some of them incommensurate) have been found in the direction perpendicular to the planes. Unlike the cuprate perovskites, some of these antiferromagnetic phases are metallic, and actually have higher conductivity than the high-temperature paramagnetic phases. Furthermore, antiferromagnetism can *coexist* at the mi-

croscopic level with non-conventional superconductivity. Adding complexity to this panorama, at least two different kinds of superconducting phases have been identified in one compound of the series ($M = Ir$) [6].

The $CeMIn_5$ compounds are highly tunable systems. Their structural properties have allowed well-controlled and very homogeneous chemical substitution studies for all the three elements present in the chemical formula, together with high-pressure investigations. Therefore, it has been possible to study their phase diagrams exhaustively.

However, the conceptual understanding of these new relations between SC and AFM lags behind this accumulative experimental success. Mostly, this is due to the lack of a model of reference which could articulate the different parts of the phase diagram. In this paper we elaborate along this line, considering how metallic antiferromagnetism appears in a model of equivalent and itinerant electrons and facilitates the coexistence with a superconducting phase. Within this model, we address here the role of electronic doping in the temperature-pressure phase diagram.

Furthermore, we introduce the crystal and electronic structure of these materials, and we briefly review the recent experimental information about the combined effect on the phase diagram of a) chemical substitution and b) high pressure. We explain how to extend

the model we used to study the pressure-temperature phase diagram of $CeRhIn_5$ [7] to include the effect of chemical doping, studying its influence on the ordering temperatures.

Crystal and Electronic Structure

The three isostructural $CeMIn_5$ compounds have the tetragonal crystal structure of $HoCoGa_5$, with two independent In sites. The stacking of the four different square-planar layers forming a unit cell follows the sequence $CeIn(1)-In(2)_2-M-In(2)_2$ along the crystallographic c axis. Ce and M occupy the vertices of each square in the first and third layer, respectively, alternating along the c direction. The In(1) site lies in the center of a square formed by four Ce atoms. In(2) occupies the $(\pm\frac{a}{2}, \pm\frac{a}{2}, \frac{c}{2}(1 \pm \delta))$ positions with $a = b = 4.656 \text{ \AA}$, $c = 7.501 \text{ \AA}$, with $\delta = 0.3$ for $M = Rh$ [8]. This anisotropy in the crystal structure manifests itself in the low-energy electronic structure. De Haas van-Alphen measurements of the Fermi surface show a large quasi-bi-dimensional cylinder-like sheet with small three-dimensional pocket-like sheets [9]. Additional insight is obtained with Density Functional Theory (DFT) calculations [7, 9, 10] which show weak hybridization between the d electrons in the Co(Rh) layer and the f electrons of Ce in the CeIn(1) layer. As a consequence, the computed band structure of $CeRhIn_5$ looks very similar to that of the Co compound. Furthermore, the density of states projected for the different atoms shows predominant Ce $4f$ character. A comparison of angle-resolved photoemission and the results of band structure calculations for $CeCoIn_5$ [11] shows good agreement and confirms that the bands crossing the Fermi level have Ce itinerant f -electron character with band widths of the order of 1 eV. This value is unusually large for heavy-fermion compounds. The results suggest a large Kondo compensation in these materials, and therefore electronic instability may arise in the coherent metallic component which dominates the electronic properties at such low temperatures in a two-fluid sense [12].

In addition, two saddle points connected by the antiferromagnetic Q vector have been observed at energies very close to the Fermi energy (E_F). In accordance with previous results [9], our DFT calculations [7] show a peak in the DOS close to the Fermi level. Furthermore, due to the quasi-2D character of the material, a saddle point is observed along $(\pi/a, 0, q_z)$ dispersing along c^* and crossing the Fermi level. Experimentally, the en-

hancement of the cyclotron [13] and the specific heat masses [14] are compatible with the existence of a van Hove singularity close to the Fermi level. On the theoretical side, it is well known that the presence of a saddle-point at low energies in the dispersion relation ($\epsilon(k)$) promotes antiferromagnetic and superconducting instabilities [15, 16].

Effect of Chemical Substitution and Pressure

The ordering temperatures in all members of the family of the title compounds are of the order of few Kelvins. Therefore, one expects that only those electrons with energies very close to the Fermi energy can contribute to the magnetic ordering and the superconducting condensate. The central question we would like to address now is: Is there a way to prove the influence of a characteristic feature of the electronic structure on the properties of the ordered phases? In principle, there are two possibilities to provide an answer. The application of pressure in a metallic quasi-bi-dimensional system shifts the energy level of a van Hove singularity. Likewise, alloying can produce electronic doping and therefore shifts the Fermi level. The temperature-pressure phase diagram of $CeRhIn_5$ has been consistently determined with a variety of experimental techniques including low-temperature calorimetry [3, 4], resistivity [17], nuclear quadrupole resonance [18], and ac -susceptibility [19]. Concerning the effect of chemical substitution, the most useful information has been provided by $CeCo(In_{1-x}Cd_x)_5$ [20], and $CeCo(In_{1-x}Sn_x)_5$ [21]. Crystals with different values of x can be grown using a conventional indium-flux technique and changing the concentrations of Cd and Sn in the flux. There is a preferential site for the substitution. Extended X-ray Absorption Fine Structure (EXAFS) analysis [22] for four different concentrations of Sn have shown that tin occupies preferentially the In(1) site which belongs to the Ce plane. Therefore, the main effect is subtracting an electron from the CeIn(1) planes, which seems to be governing the low-energy electronic structure and its electronic instabilities. The phase diagram was determined by Pham *et al.* analyzing the specific heat anomalies. The experimental results for $CeCo(In_{1-x}Cd_x)_5$ (adapted from Ref. [20]) are presented in the lower panel of Fig. 2. It is important to note that the results are given in terms of the nominal concentration of Cd in the flux. Microprobe analysis performed by the same authors [20] have revealed that

the Cd concentration in these crystals is approximately 10 % of that in the flux from which they were grown.

A very remarkable phenomenon in this family of compounds is the so-called reversibility of pressure effects by electronic tuning. The phenomenon is nicely illustrated in Fig. 3 of ref. [20]. Taking the phase diagram of $CeRhIn_5$ given by $T_N(P) T_{SC}(P)$ as a reference and plotting the ordering temperatures of $CeCo(In_{1-x}Cd_x)_5$ for $x = 0.10, 0.15$ with a rigid shift of the pressure axis, for each compound a universal, compound-independent phase diagram is obtained. More precisely, plotting in a single T - P diagram $T_N(P)$ and $T_{SC}(P)$ for $CeRhIn_5$, $T_N(P + 0.7 \text{ GPa})$, $T_{SC}(P + 0.7 \text{ GPa})$ for $CeCo(In_{1-x}Cd_x)_5$ with $x = 0.10$ and $T_N(P + 0.9 \text{ GPa})$, $T_{SC}(P + 0.9 \text{ GPa})$ for $x = 0.15$ results in identical phase borders. The result strongly suggests i) a unified mechanism for the ordering for the Co and Rh compounds, and ii) that such a mechanism has its origin in a Fermi surface instability that can be tuned by either electronic doping or pressure.

We would like to emphasize that the main effect of substituting Cd for In is not the conventional chemical “negative pressure” effect. The difference in ionic volume does not justify this interpretation for such small concentrations of Cd, and in any case should produce the inverse effect. Actually, what can be considered as a negative pressure substitution (*i. e.* ascending in the series of isovalent $M = Co, Rh, Ir$ with much larger ionic volume differences), does not reverse so neatly the effect of pressure. Besides, to achieve a similar change in the ordering temperatures requires a more extensive Co-Rh substitution [23].

These results can be also contrasted with chemical substitutions in other elements present in the chemical formula. For example, 3 % of Sn substituting In completely suppresses the superconductivity [21] while 10 % of La substituting Ce reduces the critical temperature only by a factor of two [24].

Theoretical Study

To study the relevance of the electronic structure in the phase diagram we consider a model with the following ingredients: 1) Electrons contributing to the SC and the AFM are treated in equal footing and considered equivalent and itinerant, 2) the interaction terms that we know can trigger the SC and AFM instabilities are written, and 3) within a mean-field framework, it is probed what kind of dispersion relation is more prone to develop coexistence.

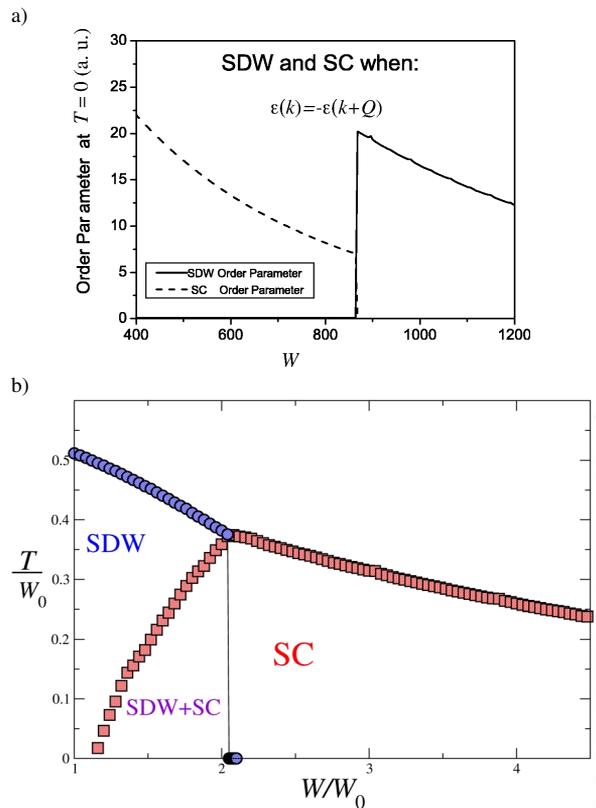


Fig. 1. a) Order parameter for a nested dispersion relation, $\epsilon_k = -\epsilon_{k+Q}$. Ordered instabilities are favored, but coexistence is impossible since both phases open a gap and compete for the same spectral density. b) Phase diagram with a relation $\epsilon_k = \epsilon_{k+Q}$. Here the AFM phase does not open a gap, and both order parameters clearly coexist, even at finite temperatures. Simultaneously, there is a competition between the phases: as T_{rmSC} increases, T_N decreases. This phase diagram is in good agreement with experimental ones (see [7] for details).

The starting point is therefore the following model [7, 25]:

$$\begin{aligned}
 H = & \sum_{k\sigma} \epsilon(k) c_{k\sigma}^\dagger c_{k\sigma} \\
 & + \sum_{kq} V_{kq} c_{(k+q)\uparrow}^\dagger c_{(-k-q)\downarrow}^\dagger c_{-k\downarrow} c_{k\uparrow} \\
 & + \frac{U}{2} \sum_{kk'} c_{k\sigma}^\dagger c_{k'-\sigma}^\dagger c_{k\sigma} c_{k'-\sigma}
 \end{aligned}$$

H_V favors SC with an order parameter symmetry related to the effectively attractive V_{kq} , but the presence of the Hubbard repulsion U forbids SC at arbitrarily low values of V_{kq} and in turn favors the SDW. What kind of quasiparticle $\epsilon(k)$ favors the co-

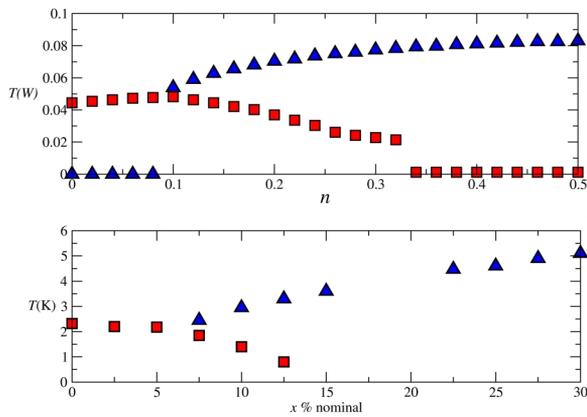


Fig. 2. Phase diagram as a function of electronic doping (upper panel) for $U = 0.76 W$, $V = 1.035 W$ computed using the model presented in the text. T_N is represented with triangles and T_{SC} with squares. Lower panel: experimental phase diagram of $CeCo(In_{1-x}Cd_x)_5$ as a function of the nominal proportion of Cd (adapted from Ref. [20]).

existence of both phases for the same electrons depends on the nature of the AFM phase. In a quasi-two-dimensional system, there are essentially two possibilities: a) Gapped SDW instabilities associated with nesting; b) gapless SDW [25, 26] which is associated with the presence of extended saddle points connected by the antiferromagnetic Q vector. Case a) implies a large spectral gap along the nested sections of the Fermi surface and therefore a metal-insulator transition at temperatures close to T_N . Therefore, SC and AFM compete but they do not coexist (see Fig. 1a), and case b), which implies $\varepsilon(k+Q) = \varepsilon(k)$, produces a coexisting phase diagram either at finite or zero temperature as shown in Fig. 1b.

To compare the theoretical phase diagrams with experimental ones we computed the pressure dependence of the bandwidth W and the Hubbard coupling U using a first-principles calculation in a planar benchmark system. We found that W increases linearly, and U is nearly constant in the relevant range of pressures. We assumed a V independent of pressure. In this model the total number of itinerant electrons is controlled by a single parameter: the chemical potential μ considered as an additive constant in the dispersion relation $\varepsilon(k)$. Different doping values correspond to different values of μ .

Our results confirm that electronic doping has an important effect if it changes the Fermi level in the proximity of the peak of the density of states. Hole doping reverses the effect of increasing the bandwidth when

the shift of the Fermi level departs from the peak in the density of states. In the upper panel of Fig. 2 we present results for the ordering temperatures in units of W . These results are compared with the experimental phase diagram for the Cd-doped compound presented in the lower panel. There is a general qualitative agreement with the three regimes of SC, coexistence and AFM present in both phase diagrams. However, there is a disagreement in the dependence in the SC phase. In our model, T_{SC} increases with hole doping while the trend observed in the experiments is the opposite.

On the other hand, electronic doping suppresses superconductivity. The suppression effect is not homogeneous in the whole range of the parameter space, and it is especially strong for large values of W . This is the regime that we illustrate in Fig. 3. The band-width dependence of the optimal value of T_{SC} and the critical doping n_c (value of the electronic doping that quenches superconductivity) are presented in the inset of Fig. 3.

Conclusion

The phase diagram of the family of compounds $CeM(In_{1-x}Cd_x)_5$ ($M = Co, Rh, Ir$) shows competition and coexistence of antiferromagnetism and superconductivity either as the Cd content is changed or as pressure is applied. We have shown that two distinctive features of both phase diagrams, *viz.* 1) the microscopic coexistence of both phases, and 2) the abrupt disappearance of the antiferromagnetic phase when both ordering temperatures become equal, are reproduced by a model of equivalent and itinerant electrons. We propose, within this theoretical framework, that those properties originate from a common effect in the electronic structure: a shift in the Fermi level in the proximity of a singularity in the density of states.

We would like to conclude mentioning a compound with analogous stoichiometry but different crystal structure: $CeRhGe$ shows a very similar dependence of T_N as a function of pressure [27]. The AFM disappears abruptly at a critical pressure of $P_c = 1.9$ GPa. *Ab initio* calculations show a peak in the density of states close to E_F [28] not dissimilar from the ones obtained in the $CeMIn_5$ compounds. Resistivity measurements at these pressures did not reveal the sharp drop characteristic of a superconducting transition, but they have shown a marked pseudo-gap. To our knowledge, specific-heat data confirming the existence and the nature of this pseudo-gap or the presence of a weak super-

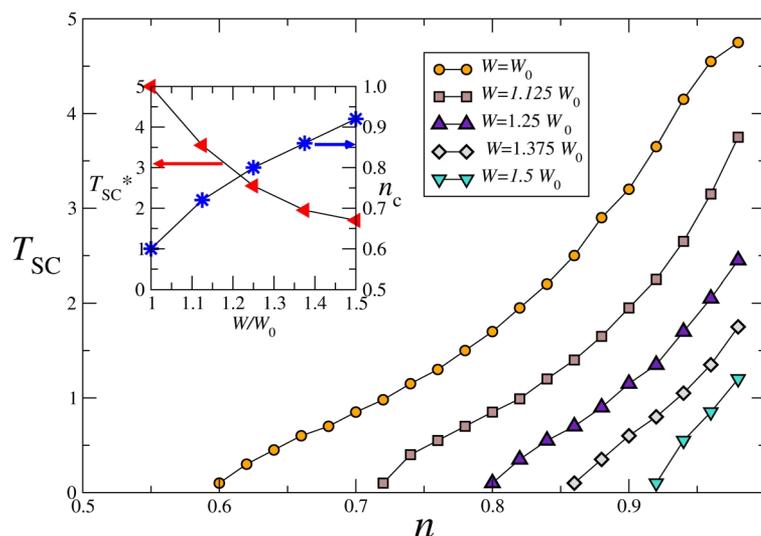


Fig. 3. Suppression of superconductivity by electronic doping for different values of the band width. $U = 0.125 W_0$ and $V = 0.2 W_0$. Inset: band-width dependence of critical doping (value of x suppressing SC) and optimal value of the critical temperature.

conducting anomaly in that range of pressures have not been published. It would be interesting to further study the band structure and phase diagram of this compound and a possible relation with the phenomena observed for CeMIn_5 .

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