Substitution effects in magnetic and superconducting materials

O. PEÑA

Laboratoire de Chimie du Solide et Inorganique Moléculaire. UMR 6511. Université de Rennes 1. 35042 Rennes cedex. FRANCE

Chemical substitutions at very low level have been proved to be a very effective tool to change important physical parameters in many kinds of materials. These modifications may be the result of, for instance, subtle variations of the position of the Fermi level with respect to the density of states, presence of additional electrons which may change the hole carrier concentration, steric effects which impose constraints in the crystallographic lattice, mixed-valence states resulting from the dismutation of chemical components, etc. We review herein three systems in which the substitution effects are at the origin of new physical states : the high- T_c superconductor bismuth cuprate of the 2212 family, the mixed-valence manganese perovskites representative of giant magneto-resistive compounds, and the Chevrel phase materials in which a structural transition may inhibit the superconducting state.

Keywords : substitution effects, phase transitions superconductivity, perovskites, giant magnetoresistance

Efectos de sustitución en materiales magnéticos y superconductores

Las sustituciones químicas a un nivel muy pequeño se han probado como una importante herramienta para cambiar los parámetros físicos en una gran variedad de materiales. Estas modificaciones pueden ser el resultado de, por ejemplo, muy ligeras variaciones de la posición del nivel de Fermi con respecto a la densidad de estados, presencia de electrones adicionales que pueden cambiar la concentración de portadores tipo huecos, efectos estéricos que imponen restricciones en la red cristalográfica, estados de valencia mixtos resultantes de la dismutación de los componentes químicos, etc. Aquí se revisan tres sistemas donde los efectos de sustitución son el origen de nuevos estados físicos: los superconductores de alta temperatura basados en cupratos de bismuto de la familia 2212, las perovskitas de manganeso de valencia mixta representantes de compuestos con magnetorresistencia gigante, y los materiales con fases de Chevrel cuya transición estructural puede inhibir el estado superconductor.

Palabras clave : Efectos de sustitución, transiciones de fase, superconductividad, perovskitas, magnetorresistencia gigante

1. INTRODUCTION.

Magnetism and superconductivity are two phenomena which have always attracted a great deal of attention of both theoreticians and experimentalists. The discovery of high-temperature superconductors HTSC and, more recently, of systems presenting giant (or even colossal) magnetoresistive properties GMR, is still another proof to this assertion. It was believed for a certain number of years that long-range magnetic order, such as ferromagnetism, could not occur simultaneously with superconductivity within the same material. Pioneers to this research, the works of Ginzburg (1) and Matthias (2) showed that a small amount of magnetic impurities could destroy a superconducting state. This effect was described by a certain number of theoretical works ; among them, those of Abrikosov and Gor'kov in the early '60s showed the importance of exchange interactions in the pairbreaking mechanisms (3). Short after, diluted magnetic alloys having weak magnetic exchange interactions allowed to study short-range spin-glass-type magnetic order in superconducting systems (4).

The discovery of two families of ternary superconducting materials, of formula $REMo_6X_8$ (RE = rare-earth, X = S, Se) and $RERh_4B_4$, brought up a completely new situation (5-7). For the

first time, two regular networks, one containing magnetic ions and the other one involving the Cooper pairs, could coexist in the same material, due to a very weak exchange interaction between the rare-earth 4f electrons and the conduction electrons. Similar results were later invoked in high- T_c cuprates $REBa_2Cu_3O_{7-\delta}$ as it seemed to be the case for RE = Gd, Dy, Ho or Er (8,9) although true ferromagnetism has not been confirmed yet.

These examples show the enormous interest developed around the problem of coexistence of long-range magnetic order and superconductivity. One way to study experimentally such a possibility is through partial substitutions in well-defined chemical systems. In this way, crystallochemistry is only slightly perturbed by these modifications, although allowing new phenomena to occur. This was our starting point to study two different classes of systems : the Chevrel-phase superconductors and the copper and manganese perovskites. In the course of our investigations we have found that substitutions may play different roles in the structure, for instance, by changing the overall electronic charge (substitutions of ions of different valence states), by modifying the electron/hole carrier concentration, by steric effects ("chemical" pressure

due to internal strains), by local fields created by a magnetic environment, etc.

We review on the following three specific examples where substitution effects are at the origin of new phenomena and where very small changes in the substituent concentration may produce very large modifications on the physical properties of the ensemble. These examples concern the interplay between magnetism and superconductivity in high- T_c bismuth cuprates, original magnetic phenomena observed in mixed-valence manganese perovskites and structural phase transformations in Chevrel phases.

2. BISMUTH CUPRATES.

It is by now well known that the superconducting temperature in HTSC materials is closely related to the hole density, this latter imposed mainly by the average valence of copper. This effect, quite remarkable in $\text{YBa}_2\text{Cu}_3\text{O}_x$ ($x = 6$, insulator ; $x = 7$, superconductor), was less obvious in the bismuth cuprates $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_y$ ($n = 1, 2$ and 3) because of the poor mobility of the oxygen in the structure. Different experimental techniques to change the total hole concentration have been reported : early experiments showed, for instance, that quenching conditions or annealing treatments influenced T_c by as much as 15 or 20 K (10,11) ; later, reversible effects on the superconducting properties after reducing-oxidizing cycles confirmed the importance of the oxygen content and showed, without any doubt, the mobility of the oxygen atoms (12,13).

Substitution of divalent calcium by trivalent rare-earths has

also been proved to be an effective method to optimize the critical temperature of the bismuth cuprate phases, specially on the $n=2$ member of the family ($\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_{8-x}$, the "2212" phase). The rare-earth occupies the Ca site and forms solid solutions $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{RE}_x^{3+}\text{Cu}_2\text{O}_{8+d}$ in the whole range $0 \leq x \leq 1$ (14). Important modifications in the hole carrier concentration take place due to the additional electrons and to the subsequent changes in the oxidation states of copper and bismuth (15,16). In this way, a significant increase of T_c occurs at low rare-earth dopings ; at intermediate substitutions ($0.3 \leq x \leq 0.5$) the critical temperature decreases very fast and it reaches zero at about $x = 0.5$. The metal-insulator transition is accompanied by a structural change from tetragonal to orthorhombic symmetry (17,18). Two regimes are well distinguished : the overdoped regime ($x \leq 0.2$) in which the hole concentration reaches 0.2 holes/Cu at optimum T_c (the Cu valence V_{Cu} is about 2.17 for $x = 0.2$) and the underdoped regime ($x > 0.2$) in which the hole concentration may reach $\sim 0.07/\text{Cu}$ ($V_{\text{Cu}} \sim 2.07$) for an insulating sample ($x \sim 0.5$) (19). Equivalent variations of T_c can be also obtained by combined effects of doping and annealing treatments (20,21).

Obviously, the variation of T_c versus the x -content of the rare-earth dopant will also depend on the formal oxidation state of the lanthanide. Figure 1 shows, for instance, the criti-

Fig. 1 : Critical temperature as a function of x for : (a) $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Ce}_x\text{Cu}_2\text{O}_y$; (b) $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{La}_x\text{Cu}_2\text{O}_y$.

Fig. 2 : Magnetic susceptibility of $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Dy}_x\text{Cu}_2\text{O}_y$ for given $x(\text{Dy})$. The inset of (b) shows the low temperature increase of the magnetization.

cal temperature of the 2212 system partially substituted by trivalent La and tetravalent (non-magnetic) Ce atoms. It is immediately seen that optima values are reached much faster in the case of $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Ce}_x\text{Cu}_2\text{O}_y$ because of two extra electrons supplied by the tetravalent atom instead of one due to La^{3+} .

Despite the obvious interest in changing the hole density, and hence the critical temperature, through such substitutions, few works have been devoted to the magnetic behaviour of the rare-earth doped 2212 systems, in particular to the interplay between magnetism and superconductivity (22,23). The dysprosium case is a remarkable example because paramagnetic (Dy^{3+} moment) and diamagnetic (superconducting) contributions can be well identified in both susceptibility and magnetization data (24). Figure 2.a. shows the Curie-Weiss behaviour of several $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Dy}_x\text{Cu}_2\text{O}_y$ samples in the paramagnetic regime. Figure 2.b. shows in particular, the low temperature data. Several important magnetic parameters can be estimated from these results : firstly, the effective moment at high temperatures $\mu_{\text{eff}}^{\text{HT}}$, which corresponds to the expected value for a Dy^{3+} free-ion (the other atoms have no, or very negligible, contributions compared to that of dysprosium) ; secondly, a diamagnetic component χ_0 at low temperatures, related to the superconducting state ; thirdly, a low-temperature effective moment $\mu_{\text{eff}}^{\text{LT}}$ calculated after subtraction of χ_0 . These data, summarized in Table I, shows a systematic decrease of the effective moment of Dy at low temperatures due to crystal field effects and a reduction of the Weiss constant Θ (-5 to -10K for HT data, and -2K to 0, at LT) (24).

Low temperature magnetization as a function of applied field H_{app} can give very important information about both paramagnetism and superconductivity. When H_{app} is below H_{c1} , the experimental slope (corrected by demagnetization factors) is directly related to the superconducting volume. On the other hand, when H_{app} is larger than H_{c2} , magnetization should saturate to a constant value σ_{sat} given by gJ in the case of lanthanides. Figure 3 shows the magnetization measured at 5 K for two samples of $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Dy}_x\text{Cu}_2\text{O}_y$. Two additive behaviours are seen : a magnetization cycle typical of a superconductor and a paramagnetic Brillouin-type curve. Even if H_{app} is well below the expected critical field H_{c2} , the magnetic moment tends to saturate towards a unique value, approximately $4.5 - 5 \mu_{\text{B}}/\text{Dy-atom}$ (Table I), well below the free-ion value of Dy^{3+} ($gJ = 10 \mu_{\text{B}}$) but in agreement with crystal-field-splitting calculations (25). On the other hand, the diamagnetic slope dM/dH of the first magnetization curve strongly depends on the dysprosium concentration and correlates well with the χ_0 diamagnetic contribution (Table I).

These results clearly show that superconductivity and magnetism are mutually excluding each other : the rare-earth substitution is responsible for the magnetic behaviour in both normal and superconducting states but, at the same time, it provides the additional electrons which trigger the metal-insulator transition at $x \sim 0.5$. In a heterogeneous model, this means that superconducting regions reduce in size while paramagnetic domains grow at their expense. Each regime will behave independent of each other, only its relative concentration (or volume) will change proportionally to the Ca/RE ratio.

3. MAGNETIC PEROVSKITES.

The discovery of giant magnetoresistance in doped manganese oxides of general formula $\text{RE}_{1-x}\text{M}_x\text{MnO}_3$ (where RE = rare earth, and M = divalent cation, in particular, an alkaline-earth element) resulted in a renewed interest on these mixed-valence perovskites over the past few years (26,27). The parent compound LaMnO_3 is an insulator composed of ferromagnetic planes of Mn^{3+} spins oriented in the basal plane, but antiferromagnetically coupled along the c-axis (28). The electron configuration of the high-spin Mn^{3+} ($S = 2$) ions is t^3e^1 , with the three electrons of the t_{2g} orbital strongly localized. The two-fold e-orbital degeneracy may be partially removed by a Jahn-Teller deformation of the MnO_6 octahedra and the extra electron becomes itinerant if holes are present (29).

Substitution of RE by a divalent ion oxidizes the MnO_3 array, creating Mn^{4+} ions ($S = 3/2$) ; by this way, doping enhances the presence of holes in the e_g band, leading to a metallic behaviour at a temperature close to the ferromagnetic Curie temperature. The antiferromagnetic phase is progressively destroyed and transforms first, into a canted structure before becoming fully ferromagnetic (30). The electron in the e_g atomic orbital, strongly hybridized with the O 2p-orbitals, is then responsible of the double-exchange $\text{Mn}^{3+}\text{-O-Mn}^{4+}$ magnetic interactions (31). The electrical and magnetic properties of these mixed-valence manganese perovskites are closely related to the ratio $\text{Mn}^{3+}/\text{Mn}^{4+}$, which depends on the degree of substitution of trivalent elements (RE^{3+}) by divalent cations. Other factors may also influence the force and nature of the magnetic interactions, for instance, the atomic size of both the RE and dopant atoms, geometrical arguments (i.e., a tolerance factor (29) which takes into account interplane distances and bond angles), the oxygen content, etc.

A large number of reports have described the structural, electrical and magnetic properties of pure and doped REMnO_3

TABLE I : HIGH TEMPERATURE ($T > T_c$) AND LOW TEMPERATURE ($T < T_c$) MAGNETIC DATA FOR THE SERIES $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Dy}_x\text{Cu}_2\text{O}_y$. THE TEMPERATURE-INDEPENDENT DIAMAGNETIC SUSCEPTIBILITY χ_0 WAS CALCULATED BELOW 10 K. dM/dH IS THE INITIAL SLOPE OF THE FIRST MAGNETIZATION CURVE. S_{SAT} IS THE EXTRAPOLATED VALUE OF THE MAGNETIZATION AT 40 kOe AND 5 K.

x (Dy)	$\mu_{\text{eff}}^{\text{HT}} (\mu_{\text{B}})$	$\mu_{\text{eff}}^{\text{LT}} (\mu_{\text{B}})$	χ_0 (emu/g)	dM/dH (emu/g)	$\sigma_{\text{sat}} (\mu_{\text{B}}/\text{Dy})$
0				-8.2×10^{-3}	-
0.1	10.0	5.6	-1.9×10^{-3}	-2.1×10^{-3}	4.5
0.2	10.3	8.1	-1.2×10^{-3}	-1.1×10^{-3}	4.5
0.3	10.7	8.0	-0.2×10^{-3}	-0.2×10^{-3}	5
0.5	9.5	7.9	-	$+0.74 \times 10^{-3}$	4.5
1.0	10.2	9.6	-	$+1.40 \times 10^{-3}$	5

perovskites ; most of these reports concern, however, light rare-earths, that is, atoms with large ionic radii and of weak- or non-magnetic nature (e.g., La, Pr, ...). These studies have generally been coupled with the parallel choice of large-sized dopants (e.g., Sr, Ba, Pb, ...). Important modifications may be expected then, when small-sized elements are incorporated in the crystal structure. In addition, cooperative effects due to the intrinsic magnetism of the rare-earth network may be an important factor which, added to the ferromagnetism of the Mn-sublattice, may modify the overall magnetic properties of the substituted perovskite.

We have thus undertaken a systematic study of the magnetic properties of mixed-valent manganese oxides based on small-sized heavy rare-earths (Er, Gd and Y), partially substituted with a small-size alkaline-earth element (Ca). Parallel reports on the synthesis, characterization and crystallochemical properties of these compounds may be found elsewhere in this issue (32,33).

Figure 4.a. shows the magnetization curve measured at 5 K for $Y_{0.7}Ca_{0.3}MnO_3$. The irreversible magnetization observed below 20 kOe and the extremely high values of M at 60 kOe are obviously connected with the presence of Mn^{4+} ions and the double-exchange $Mn^{3+}-O-Mn^{4+}$ mechanism since these effects do not appear, or at least they are not apparent, in the undoped $Y^{3+}MnO_3$ compound (inset, fig. 4.a). Figure 4.b. shows the easy saturation of the magnetic moment of a $La_{0.7}Ca_{0.3}MnO_3$ ceramic sample measured under similar conditions. It is clear that lattice size and symmetry play an important role in the observed differences between $Y_{0.7}Ca_{0.3}MnO_3$ and $La_{0.7}Ca_{0.3}MnO_3$; indeed, the smaller ionic radius of Y^{3+} is responsible of a smaller Mn-O-Mn bond angle, which in turn increases the width of the e_g band.

Figure 5 compares the susceptibility of $Y_{1-x}Ca_xMnO_3$ and $Gd_{1-x}Ca_xMnO_3$ measured under 1 kOe. In the former, the effective moment increases with x , while in the latter, this increase is compensated by a decreasing quantity of magnetic gadolinium. If one assumes that the paramagnetic regime is simply the superposition of the Mn and the RE moments, one should be able to calculate the effective moment of the Mn sublattice. Since the substitution of a trivalent RE ion by divalent Ca will provoke the conversion of a Mn^{3+} into Mn^{4+} ion, then the balance equation of the average moment gS^{av} of $RE_{1-x}Ca_xMnO_3$ will be $gS^{av} = gS(Mn^{3+}) \cdot (1-x) + gS(Mn^{4+}) \cdot x$, (i.e., $2 \geq S^{av} \geq 3/2$), and the effective moment μ_{eff} should vary between $4.90 \mu_B$ and $3.87 \mu_B$, as $\mu_{eff}^2 = \mu_{eff}^2(Mn^{3+}) \cdot (1-x) + \mu_{eff}^2(Mn^{4+}) \cdot x$. These values, however, are not respected throughout both series $RE_{1-x}Ca_xMnO_3$, being much larger than those calculated by the above equations. Even more, the effective moment of the Mn sublattice increases with the conversion of Mn^{3+} into Mn^{4+} , instead of decreasing, meaning that we are faced to the presence of magnetic clusters, and that the Mn ions are not independent entities.

The most striking behaviour comes from the ZFC/FC cycles measured for three systems $RE_{1-x}Ca_xMnO_3$, RE = Y, Gd and Er. Figure 6 shows the influence of the magnetic nature of the rare-earth sublattice on the overall magnetic behaviour of the mixed-valence manganite : while nonmagnetic Y should not contribute to the observed ferromagnetic moment, the $9 \mu_B$ of Er clearly sums up to the Mn sublattice. On the contrary, the spontaneous magnetization of the gadolinium-based sample ($gJ = 7 \mu_B/Gd$) changes sign upon cooling, reaching similar values as those obtained when reversing the magnetic field.

A few remarks should be done at this stage concerning this last result. Firstly, the reported behaviour is absolutely repro-

Fig. 3 : Magnetization of $Bi_2Sr_2Ca_{1-x}Dy_xCu_2O_y$ normalized to the Dy concentration.

Fig. 4 : Magnetization at 5 K : (a) $Y_{0.7}Ca_{0.3}MnO_3$ and $YMnO_3$; (b) $La_{0.7}Ca_{0.3}MnO_3$ (notice the different scales of the H-axis)

ductible and can be observed with the sample placed in different directions with respect to the external field. Secondly, the same phenomenon is observed for all the investigated samples of the $\text{Gd}_{1-x}\text{Ca}_x\text{MnO}_3$ series, with x ranging from 0.2 up to 0.4. Thirdly, the FC branch of the above mentioned cycle (Fig. 6.c) is a reversible state, that is, when warming the sample again, the magnetization describes exactly the last FC branch; obviously, any further cooling or heating under the same external conditions (applied magnetic field and temperature spanning) reproduces exactly the same curve. This original result is interpreted in terms of two interacting magnetic networks: a Mn-based ferromagnetic sublattice and a negatively-polarized gadolinium-based sublattice. The total magnetic moment of this latter is proportional to both the magnetic susceptibility of gadolinium and to the local field produced by the manganese sublattice. Providing a negative exchange interaction J between Mn and Gd moments, the total moment will be $M_{\text{tot}} \sim (1 - \delta\chi_{\text{Gd}}) \cdot M_{\text{Mn}}$, where M_{Mn} is the moment of the ferromagnetic lattice and χ_{Gd} is the Curie-type susceptibility of the Gd lattice. When the Curie behaviour of the Gd moment exceeds the one of the ferromagnetic sublattice (at about 40 K), the

Fig. 5 : Inverse magnetic susceptibility of : (a) $\text{Y}_{1-x}\text{Ca}_x\text{MnO}_3$; (b) $\text{Gd}_{1-x}\text{Ca}_x\text{MnO}_3$

Fig. 6 : ZFC/FC cycles measured under given fields H_{app} for : (a) $\text{Y}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$, (b) $\text{Er}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$, (c) $\text{Gd}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$

local field becomes stronger than the applied field, and the magnetic moment decreases and eventually changes sign, as observed in figure 6.c. Upon heating, the total moment is quite reversible since only the ferromagnetic Mn sublattice orders with temperature.

These results show the importance of geometrical factors (size, lattice symmetry, bond distances and angles, etc.) and of the magnetic nature of the different constituents in the partly-substituted ABO_3 perovskites. Important conclusions can be drawn from the interplay between the magnetic contributions of both A and B sublattices, a very interesting case being the one of a negatively-polarized magnetic moment, such as the Gd-case. Other interesting results have been obtained when substituting the B (Mn) sublattice with other transition-metal ions, such as Ni, where a marked threshold in the magnetic character occurs when the ratio $\text{Mn}^{3+}/\text{Mn}^{4+}$ approaches unity (33).

4. CHEVREL PHASES.

Ternary molybdenum chalcogenides $\text{M}_x^{\text{n+}}\text{Mo}_6\text{X}_8$ ($\text{X} = \text{S}, \text{Se}, \text{Te}$), known as Chevrel phases, have been studied very extensively over the last two decades (34-36). These compounds are of great interest because of their remarkable physical properties; many of them are superconductors with extremely high critical magnetic fields (for instance, $H_{c2}(0) \sim 60 - 70 \text{ T}$ and $T_c \sim 15 \text{ K}$, for PbMo_6S_8). When M is a rare-earth, the system may present coexisting phenomena of superconductivity and long-range magnetic interactions, the so-called magnetic superconductors (37,38).

Their crystal structure is based on a Mo_6 octahedral cluster surrounded by a pseudo-cubic arrangement of 8 chalcogen atoms. These Mo_6X_8 units are slightly rotated by about 25° with respect to a three-fold symmetry axis, inside a rhombohedral (or triclinic) cationic lattice. Rotation of the building blocks favours strong Mo-X and Mo-Mo bondings between units. The particular arrangement of Mo_6X_8 clusters creates 3 different pseudo-cubic cavities, which can be defined as follows: site 1, at a position (0,0,0) of the lattice, is formed by 8 chalcogen atoms belonging to 8 different Mo_6X_8 units; site 2, at (1/2,0,0), is formed by 8 chalcogen atoms belonging to 4 different clusters; site 3 is created from only 2 Mo_6X_8 units (34,38). Because of this particular crystal structure, a large number of substitutions can be made on almost any atomic site, resulting in a broad spectrum of physical phenomena (e.g., going from an insulator up to a high- T_c superconductor). Solid solutions of the type $(\text{M},\text{M}')\text{Mo}_6\text{X}_8$ or $\text{MMo}_6(\text{X},\text{X}')_8$ have been commonly studied. Also substitutions on the octahedral cluster by another transition metal can be made (e.g., $(\text{Mo},\text{Re})_6\text{S}_8$). On the following, we will mainly describe the first type of substitutions, that is, on the cationic site.

When M is of small size, the ion is delocalized at 6f positions inside the pseudo-cubic cage (site 1) of a R $\bar{3}$ crystal structure. In some cases (Cu, Fe, ...) these atoms freeze into pairs, occupying definite positions and producing a slight distortion of the Mo_6 cluster. This structural transformation (rhombohedral $\rightarrow$ triclinic) occurs at rather high temperatures (200 K - 400 K, depending on the cation).

When M is a large divalent ion ($\text{M}^{2+} = \text{Eu}^{2+}, \text{Ca}^{2+}, \text{Sr}^{2+}, \text{Ba}^{2+}, \dots$), another kind of structural transformation may take place. In this case, the half-filled band of the density of states is unstable and a partial gap opens at the Fermi surface when the temperature decreases. This metal-nonmetal phase transition is associated to a structural transformation (also rhombohedral

Fig. 7 : Resistivity measured in single crystals of $\text{Eu}_{1-x}\text{Yb}_x\text{Mo}_6\text{S}_8$: (1) $x = 0$, (2) $x = 0.36$, (3) $x = 0.39$, (4) $x = 0.67$, (5) $x = 1$

Fig. 8 : Resistivity measured in a $\text{Eu}_{0.5}\text{Ca}_{0.5}\text{Mo}_6\text{S}_8$ single crystal. Inset shows the superconducting transition

Fig. 9 : Resistance measured in a $\text{Eu}_{0.75}\text{Sn}_{0.25}\text{Mo}_6\text{S}_{7.2}\text{Se}_{0.8}$ ceramic sample at given temperatures, as a function of magnetic field (from ref. 49)

Fig. 10: Phase diagram H_{c2} versus temperature for $\text{Eu}_{0.75}\text{Sn}_{0.25}\text{Mo}_6\text{S}_{7.2}\text{Se}_{0.8}$ (from ref. 51)

→ triclinic) in which the cluster distorts but the cation remains in the 1a position at the center of the unit cell. This transformation occurs at about 45, 110, 139 and 171 K for CaMo_6S_8 , EuMo_6S_8 , SrMo_6S_8 and BaMo_6S_8 , respectively (39).

Three techniques are often used to stabilize the superconducting state and suppress the structural transitions in the $\text{M}^{2+}\text{Mo}_6\text{X}_8$ compounds : by applying an external pressure (of the order of several tens of kbars) (40,41), by introducing vacancies in the cationic lattice (thus producing an internal pressure on the Mo_6 cluster) (42,43) or by partial substitution of M^{2+} by another cation (44,45). This latter method was largely developed in the late '80s, mainly in connection with the europium-based molybdenum sulfide EuMo_6S_8 . Our goal was to search for structural parameters which are determinant to the structural instability. For this, thanks to an appropriate choice of the size, concentration and valence state of the substituent atom M we could gradually follow the phase transition in single crystals of the pseudo-ternary phases $(\text{Eu},\text{M})\text{Mo}_6\text{S}_8$ ($\text{M} = \text{Ca}, \text{Yb}, \text{Sm}$) (46,47).

Figure 7 shows the electrical resistivity measured in single crystals of $(\text{Eu},\text{Yb})\text{Mo}_6\text{S}_8$ (45). Three distinct behaviours can be noticed : firstly, EuMo_6S_8 , which shows the structural transition at $T_s = 110$ K, from a high-temperature rhombohedral phase to a semimetallic triclinic phase. Substitution of about 36-39 % Yb (curves 2 and 3) makes T_s to decrease down to 60-70 K, but a superconducting transition is also clearly noticed (inset, fig. 7). Finally, a third distinct behaviour is observed, with a monotonic metallic decrease of $\rho(T)$, a very low residual resistivity followed by a superconducting transition. The end point $\text{Yb}^{2+}\text{Mo}_6\text{S}_8$ shows a T_c of 10.1 K.

The partial substitution of europium by atoms of smaller ionic radius restrains the deformation of the Mo_6S_8 cluster (by a so-called "chemical pressure") and inhibits the transformation observed in EuMo_6S_8 in the same way as does the external pressure (EuMo_6S_8 becomes fully superconducting under 13 kbars). The main mechanism to stabilize the rhombohedral phase is related to the interatomic parameters, among them, the (Mo-S) and (S-S) intercluster distances, which strongly depend on the angle of rotation (between 25° to 28°) of the Mo_6S_8 unit with respect to the rhombohedral lattice (47). An interesting example of such mechanism is $(\text{Eu},\text{Ca})\text{Mo}_6\text{S}_8$. Neither EuMo_6S_8 nor CaMo_6S_8 are superconductors, the structural transformation being at 110 K and 45 K, respectively. However, single crystals of the solid solution may superconduct, as shown in figure 8 for a crystal of approximate composition $\text{Eu}_{0.5}\text{Ca}_{0.5}\text{Mo}_6\text{S}_8$ (48). A remnant of the structural transformation is still observed at about 65 K, followed by a net decrease of $\rho(T)$ at 5 K. A zero-resistance state is achieved at 2.2 K. Single crystal structural refinement showed that the interatomic distances (Mo-S) or (S-S), intermediate between those of either end members (EuMo_6S_8 and CaMo_6S_8), belong to a well-defined domain which is favorable to the formation of a stable rhombohedral phase, and hence, to the existence of a superconducting state (47).

The case of europium-based solid solutions of the $(\text{Eu},\text{M})\text{Mo}_6\text{S}_8$ type is extremely interesting in solid state physics. As an example, figure 9 shows the resistive behaviour of a sample of nominal composition $\text{Eu}_{0.75}\text{Sn}_{0.25}\text{Mo}_6\text{S}_{7.2}\text{Se}_{0.8}$ measured at very low temperatures as a function of the applied magnetic field (49). A triple phase transition (superconducting-to-normal, followed by a reentrant transition normal-to-superconducting, and finally back to a normal state) is observed with increasing magnetic field. A negative exchange interaction between the conduction and the 4f electrons is at the

origin of this phenomenon, known as the Jaccarino-Peter compensation effect (50). According to this model, when the exchange interaction is negative, the electron spins polarize opposite to the magnetization, and compensate the external field. At sufficiently high magnetic fields, the superconducting state will be finally destroyed. Figure 10, reproduced from ref. 51, summarizes these data: two well-defined superconducting domains appear, separated by a normal-state region at intermediate fields and temperatures. The corresponding fit, based on the Jaccarino-Peter effect and calculated from multiple pair-breaking theory, reproduces perfectly well the experimental data. Such phenomena, up to now unique in solid-state physics, is currently known as magnetic-field-induced superconductivity (MFIS).

5. CONCLUSION.

In conclusion, thanks to three examples, we have shown the importance of controlled partial substitutions. In the case of the Bi-2212 superconductor, the same electrons provided by the substituent enhance the critical temperature by about 20 K and are at the origin of the magnetic properties. In the case of manganites, the substitution of RE^{3+} by divalent earth-alkaline elements controls the $\text{Mn}^{3+}/\text{Mn}^{4+}$ ratio responsible of the double-exchange magnetic interactions. Finally, in the case of europium-based Chevrel-phase materials, the structural transformation can be monitored by internal steric mechanisms, while the electronic polarization of europium may produce fantastic effects such as the magnetic-field induced superconductivity.

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