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ONSET OF ITINERANT FERROMAGNETISM IN COBALT-NICKEL HEUSLER-TYPE COMPOUNDS

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The magnetic properties of Co-Ni compounds with MnCu₂Al or MgAgAs-type structure (the Heusler phases) were studied. Paramagnetic, ferromagnetic moments, Curie's temperature increase with Co content. The ratio of ordered to paramagnetic moment varies with the Curie temperature following itinerant ferromagnetism models. A metal-insulator transition occurs in the TiCo_xNi_{1-x}Sn series, which causes a more rapid drop of the Curie temperature than in TiCo_xNi_{2-x}Sn solid solutions which remain metallic.

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1. Introduction

The Heusler phases are famous ternary intermetallics, of the type MM'₂X, where M and M' are transition metals. Mn, Fe and Co compounds are often ferromagnets, whereas Ni compounds are the Pauli paramagnets [1]; beyond them, Mn compounds exhibit a quasi-localized magnetism [2] due to the half-filled 3d band, but Co compounds are examples of itinerant magnetism.

We studied the magnetic properties of three series of Co and Ni Heusler phases with the general formula TiCo_xNi_y■_{2-x-y}Sn, where ■ is a vacancy in the lattice. TiCo₂Sn [1], TiCoSn [3] are metallic ferromagnets, TiNi₂Sn a metallic Pauli paramagnet, and TiNiSn a nonmagnetic semiconductor with a small gap [4]. Among these compounds, we selected three series of solid solutions: TiCo_xNi_{2-x}Sn, TiCo_x■_{2-x}Sn and TiCo_xNi_{1-x}■Sn. In the first series, there is a progressive filling of the 3d band with increasing Ni content whereas a simple dilution of Co by vacancies occurs in the second. The third series undergoes a metal-nonmetal transition.

2. Preparation and crystallography

Samples were prepared using an arc furnace, and were annealed during one month at 650°C or during one week at 800°C, with no significant changes in their properties. A single cubic phase is observed, the lattice parameter changes slightly with the composition and the values for the extremes are: TiCo₂Sn —

6.067 Å, TiNi₂Sn — 6.097 Å, TiCoSn — 5.997 Å, TiNiSn — 5.921 Å. TiCoSn and TiNiSn crystallize with the MgAgAs structure, which has a vacant site. However, careful investigations reveal that small percentages of Sn and Co exist on the “vacant site” in TiCoSn. Neutron diffraction with a high resolution diffractometer shows that there is a spread in lattice parameter for the compound TiCo_{1.6}Sn, thus inhomogeneities occur in the distribution of vacancies, with a possible consequence on the spread of the Curie points.

3. Physical properties

Magnetic measurements were performed in fields up to 7 teslas between 1.5 K and 500 K. Transport properties were measured below room temperature. We followed the variations of the ferromagnetic Curie point T_C , ordered magnetic moment $M(T)$, as well as the Curie–Weiss parameter T_p and effective moment M_{eff} when a Curie–Weiss behaviour occurs at high temperatures. In the following, M is the moment per formula unit, whereas μ is the moment per Co atom (assuming it is the only magnetic species). We assume the local moment approximation to deduce the effective moment.

In the three series, a Curie–Weiss behaviour is observed for large enough Co concentrations. T_C , $M(0)$, T_p and M_{eff} decrease with decreasing Co content; the ratio $M(0)/M_{\text{eff}}$ also decreases similarly to the decrease in the Curie temperature. This is a classical result of itinerant magnetism pointed out by Rhodes and Wohlfarth [5] which is related to the amplitude of the band splitting proportional to intersite interactions.

In the series (Co _{x} Ni_{2- x}), the limit of ferromagnetism is observed to be $x_{\text{Co}} = 1.2$. T_C and T_p decrease almost linearly with x , T_p being smaller than T_C . The difference between them is largest for low Co concentrations, pointing to large spin fluctuations in the vicinity of the ordering point. The susceptibility for Ni-rich compounds turns progressively to constant paramagnetism.

In the (Co _{x} Ni_{2- x}) series, T_C and T_p decrease less rapidly with x than in the first series, indicating that Co dilution is less efficient in decreasing the local moment on Co than adding electrons in the band. Meanwhile, the ferromagnetic Curie point and ordered moment decrease more rapidly than the paramagnetic temperature and effective moment respectively, following the reduction of intersite interactions.

Another remarkable feature in the (Co _{x} Ni_{2- x}) series is the non-linear variation of saturation and effective moments with the Co content. A rapid increase occurs for $\mu(0)$, μ_{eff} and T_C between $x = 1.6$ and 1.9. This may be due either to a rapid change in the density of states at the Fermi level, or to the occurrence of two different sites in these compounds: the partly vacant site would bear a smaller magnetic moment than the full one; it may even not fulfil the Stoner criterion for low concentrations and experience induced magnetism.

The properties of these two series are described elsewhere in more details [6].

For the (Co _{x} Ni_{1- x}) series, the experimental value of the resistivity at 4 K increases from 25×10^{-6} Ohm·cm for TiCoSn to 25×10^{-3} Ohm·cm for TiNiSn, that is by three orders of magnitude. For TiNiSn, we have to deal with a heavily

doped or degenerate semiconductor. From the Hall effect, between 100 and 260 K, majority carriers are electrons. A plot of $\text{Log}(R)$ versus $1/T$ gives a minimum value of the energy gap of 450 K for TiNiSn, and 80 K for $\text{TiCo}_{0.2}\text{Ni}_{0.8}\text{Sn}$, which may not represent the complete energy gap, but the distance between the valence (or conduction) band and impurity levels.

Ferromagnetism occurs for Co concentrations larger than 0.45, which is also the limit between metallic and semiconducting behaviour. At variance with the previous series, the magnetism changes from itinerant in TiCoSn to localised for Co diluted in TiNiSn. Indeed, a Curie-Weiss behaviour may be observed for small Co concentrations at low temperatures, where the susceptibility may be written as $X = X_0 + C_M/T$, where X_0 is temperature independent. Saturation and effective moments per formula are given in Fig. 1. The Curie constant per Co ion is C_M/x ,

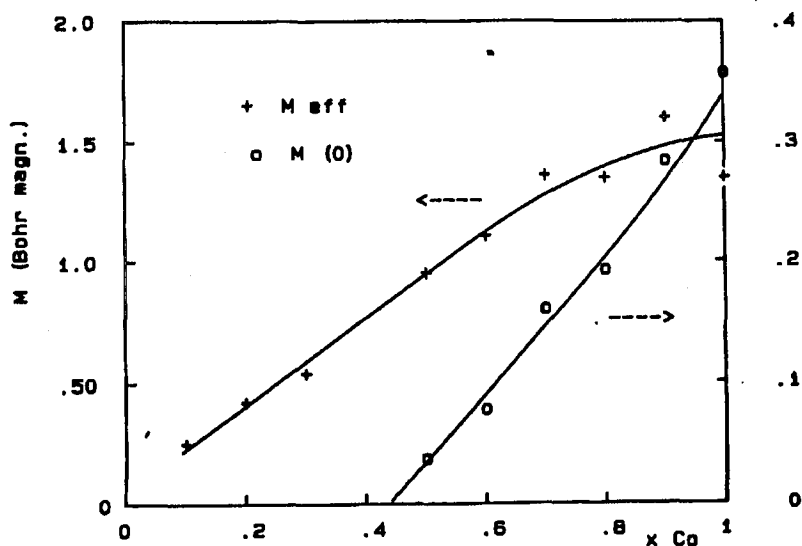


Fig. 1. Effective moment and saturation magnetization (per formula) in $\text{TiCo}_x\text{Ni}_{1-x}\text{Sn}$ series, versus Co content.

hence we obtain the effective magnetic moment of Co. Surprisingly, this moment slightly changes between TiCoSn ($1.35 \mu_B$) to $\text{TiCo}_{0.1}\text{Ni}_{0.9}\text{Sn}$ ($1.1 \mu_B$), thus Co diluted in TiNiSn keeps a local moment similar to its value for itinerant TiCoSn.

On the contrary, intersite interactions are strongly reduced by the decrease in the density of states. A good manner to visualize this feature is to plot T_C versus the saturation moment $M(0)$: for the two first series, T_C varies nearly linearly with M , whereas it varies as $M^{1.7}$ in $(\text{Co}_x\text{Ni}_{1-x})$ series (M^2 in the theory of weak ferromagnetism). Thus intersite interactions drop rapidly to zero in this last series, while the local effective moment on Co keeps a nearly constant value as the metal-nonmetal transition occurs. Conversely, T_C follows a unique law as function

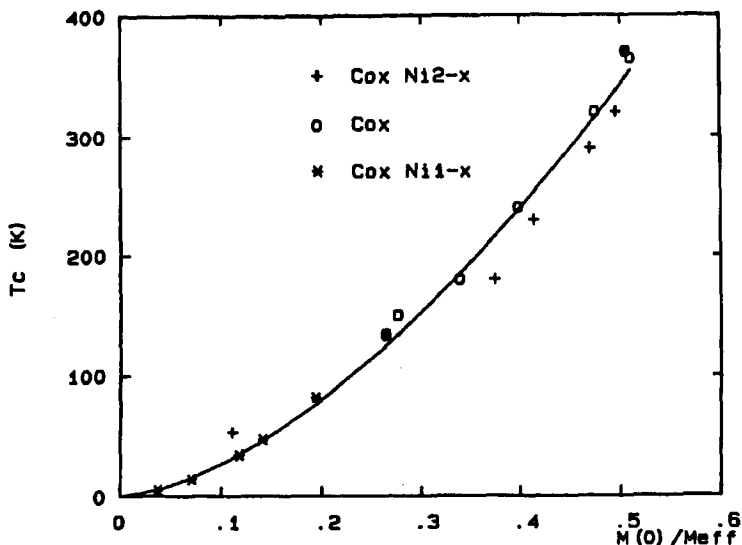


Fig. 2. Ferromagnetic Curie temperature versus the ratio $M(0)/M_{eff}$ in $TiCo_xNi_{1-x}Sn$ series.

TABLE
Magnetic properties for some selected ferromagnetic compounds.
Moments are given per cobalt atom.

Compound	T_p [K]	μ_{eff} [μ_B]	$\mu(0)$ [μ_B]	T_C [K]	$\mu_{eff}/\mu(0)$
$TiCo_2Sn$	370	1.96	0.98	370	1.98
$TiCoSn$	158	1.35	0.357	134	3.78
$TiCo_{1.4}Ni_{0.6}Sn$	115	1.42	0.166	53	8.6
$TiCo_{0.5}Ni_{0.5}Sn$	7.5	1.32	0.074	5	18

of $M(0)/M_{eff}$ for the 3 series (Fig. 2), which expresses the Rhodes-Wohlfarth law [5].

Resistivity and magnetoresistance were measured for some compounds. Among metallic systems, a negative temperature coefficient is observed at low temperatures for alloys in the vicinity of the magnetic-nonmagnetic limit ($TiCo_{1.2}Ni_{0.8}Sn$, $TiCo_{0.5}Ni_{0.5}Sn$), which may be due to spin fluctuations. The first compound, which has $T_p = +71$ K and does not order, is a 3d counterpart of heavy fermion systems. A high positive value of the magnetoresistance is observed in $TiCoSn$ at 4 K. This may be related to half-metallic conduction, a phenomenon which occurs in isomorphous $NiMnSb$ [7], and arises from a strong difference between spin-up and spin-down subbands in the ferromagnetic state.

4. Conclusion

The evolution of magnetic properties with Co concentration shows the classical features of itinerant magnetism in these compounds. The study of three series of solutions allowed to separate the influence of pure magnetic dilution, filling of the 3d band by an extra electron and that of the metal–semiconductor transition, on the building of the local moment of the Co site and on the interactions between sites.

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