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Properties on request in semi-Heusler phases

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Abstract

Various transport and magnetic properties of semi-Heusler phases are described, which arise from the particular crystallographic structure and narrow band phenomena. Semiconducting-to-metal cross overs are observed by varying the electron concentration. The onset of weak itinerant ferromagnetism often arises in the metallic state. Even in NiMnSb, where the strong ferromagnetism results in a half metallic state below 80 K, the magnetism evolves from Heisenberg-like to itinerant by increasing the temperature. Giant magnetoresistance effects are observed in the semiconducting rare earth compounds NiRSb. © 1997 Elsevier Science S.A.

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1. Crystallographic structure

Semi-Heusler phases are cubic ternary compounds, with formula XYZ, where X and Y are transition metals and Z one *sp* element. They are derived from true Heusler phases X_2YZ by removing one X atom over two, leaving a vacant site. The structure holds through covalent bonding, after transfer of *s* electrons from X and Y metals to the *p* shell of Z element, which is most frequently Sn or Sb. The structure is most stable when the total number of peripheral electrons is close to 18, favouring sp^3 hybridization around Z. Due to the vacant site, the overlap between transition metal wavefunctions is much reduced, giving rise to narrower bands and to the appearance of gaps in the density of states (DOS). This structure became famous after the discovery of so-called 'half metallic character' in NiMnSb and PtMnSb [1], a feature which will be explained hereafter. The narrow band character and the presence of gaps raised our interest for such a structure, as it gives rise to a lot of very different magnetic and transport properties.

As always for Heusler phases, the properties are strongly dependent on the degree of crystallographic order. All samples were annealed after preparation during several days at temperatures ranging from 650 to 800°C. In these conditions, the X site is occupied by the smaller transition metal.

2. Semiconductor — metal transitions

A first surprise was the discovery [2,3] that adding three metals can give rise to a semiconducting compound when the valency electron concentration by formula (EC) is 18, for instance in NiTiSn, NiZrSn, NiHfSn.

More recently, some of us showed that this feature also exists for CoTiSb [4], NiRSb compounds (R = Dy,Lu) [5], and probably in CoNbSn and FeVSb, all with EC = 18.

Adding (subtracting) one electron on (from) one crystallographic site gives rise to a metal, for instance

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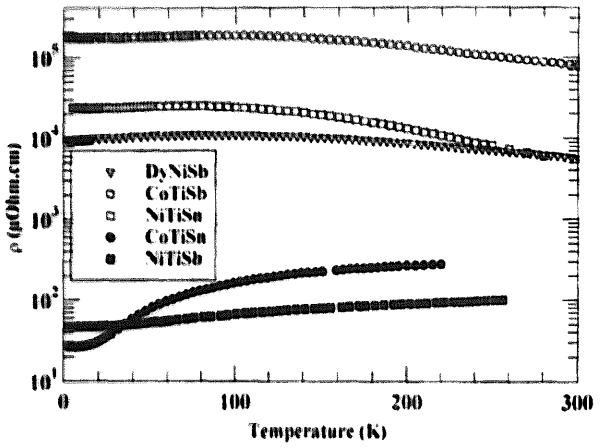

Fig. 1. Resistivity for some semi-Heusler phases.

for 17 electrons: CoTiSn (weak ferromagnet) [3], FeTiSb (Curie–Weiss paramagnet) and for EC = 19: NiTiSb (Pauli paramagnet), CoVSb (weak ferromagnet). Resistivity curves for some of these compounds are given in Fig. 1.

One first question is about the nature of the semiconductor (SC), and the origin of the gap, which may arise [6] from electron transfer, *3d* shell correlations (Mott–Hubbard insulator), or from another mechanism.

Band structure calculations using the Korringa–Kohn–Rostoker (KKR) formalism have been undertaken, mostly for Co and Ni based compounds, and the coherent potential approximation (CPA) was used to describe the electronic structure of solid solutions [7]. Fig. 2 presents the band structure of some compounds. The partial density for each atom and each electron character has been worked out. For CoTiSb, which has the largest gap (0.9 eV from band calculations), the largest contributions near the gap come from Co *3d* states below the gap and Ti *3d* states above. Thus the gap seems to arise mainly from the hybridization between *3d* metals and the separation of bonding/antibonding wavefunctions.

The transport properties of solid solutions between semiconducting and metallic phases were studied [3,4], especially for solutions between CoTiSn (ferromagnetic metal) and SC phases with one electron added on each site, leading to NiTiSn, CoNbSn, CoTiSb respectively. We shall see that it is not equivalent to fill one site or the other. Although all series end in a semiconducting phase and the overall band shape remains similar, the rigid band model cannot be applied.

2.1. $Co_{1-x}Ni_xTiSn$ series

This series exhibits a regular decrease of lattice parameter a with Ni content. There is a continuous increase in residual resistivity $\rho(0)$, from about 15 $\mu\Omega$ cm in CoTiSn to more than 25 000 in NiTiSn [3]. It is difficult to define a precise concentration for the metal–SC cross-over. First the SC phases do not present a vanishing conductivity at low temperature: we have to deal with ternary compounds with a vacant site, and it is almost impossible to keep an intrinsic regime down to low temperatures, due to the number of defects. Nevertheless we will fix the somewhat arbitrary cross-over concentration where $\rho(0)$ is close to the Mott's limit for metallic resistivity, i.e. a few 10^{-3} Ω cm, or when the derivative $d\rho/dT$ changes its sign from positive to negative, that is for x near 0.6, or a hole concentration/cell of about 0.4.

A problem arises: why do SC–metal cross-overs occur only for such large doping rate? This feature is rather common in disordered semiconductors, the chemical disorder leading to the localization of carriers, defining some mobility edge and driving variable range hopping of carriers [8]. Hence a much reduced conductivity occurs until the Fermi level is well below the edge of the band (for hole doping).

2.2. $CoTiSn_{1-x}Sb_x$ series

This series is characterized by a sudden discontinuity of the lattice parameter between $x(Sb) = 0.5$ and 0.6, where a two-phases region occurs. Sn-rich solutions with a larger volume are metallic, whereas smaller Sb-rich ones are SC [4]. Thus this transition cannot be a classical Mott's transition, where the metallic state has the smaller volume and the larger overlap between wavefunctions.

An interesting feature is that the magnetic contribution to the metallic resistivity strongly increases up to a Sb concentration of about 0.5, and then rapidly decreases for higher Sb content. This contribution, characterized by an S-like shape of the resistivity, and by an enhanced T^2 term at low temperatures, corresponds to the disappearance of the ferromagnetic order (see below), and to a strong influence of spin fluctuations.

2.3. $CoTi_{1-x}Nb_xSn$

This series seems to be metallic nearly up to CoNbSn, but the resistivity strongly increases with Nb content. Either CoNbSn is a semi-metal, or our samples are dirty semiconductors. Band calculations indicate a low gap SC for a well ordered structure, but the permutation of Co and Nb atoms on X and Y sites would lead to a semi-metal. Thus disorder may prevent a true SC behaviour in our samples. Metallic precipitates are also present, as indicated by a superconducting transition corresponding to the critical

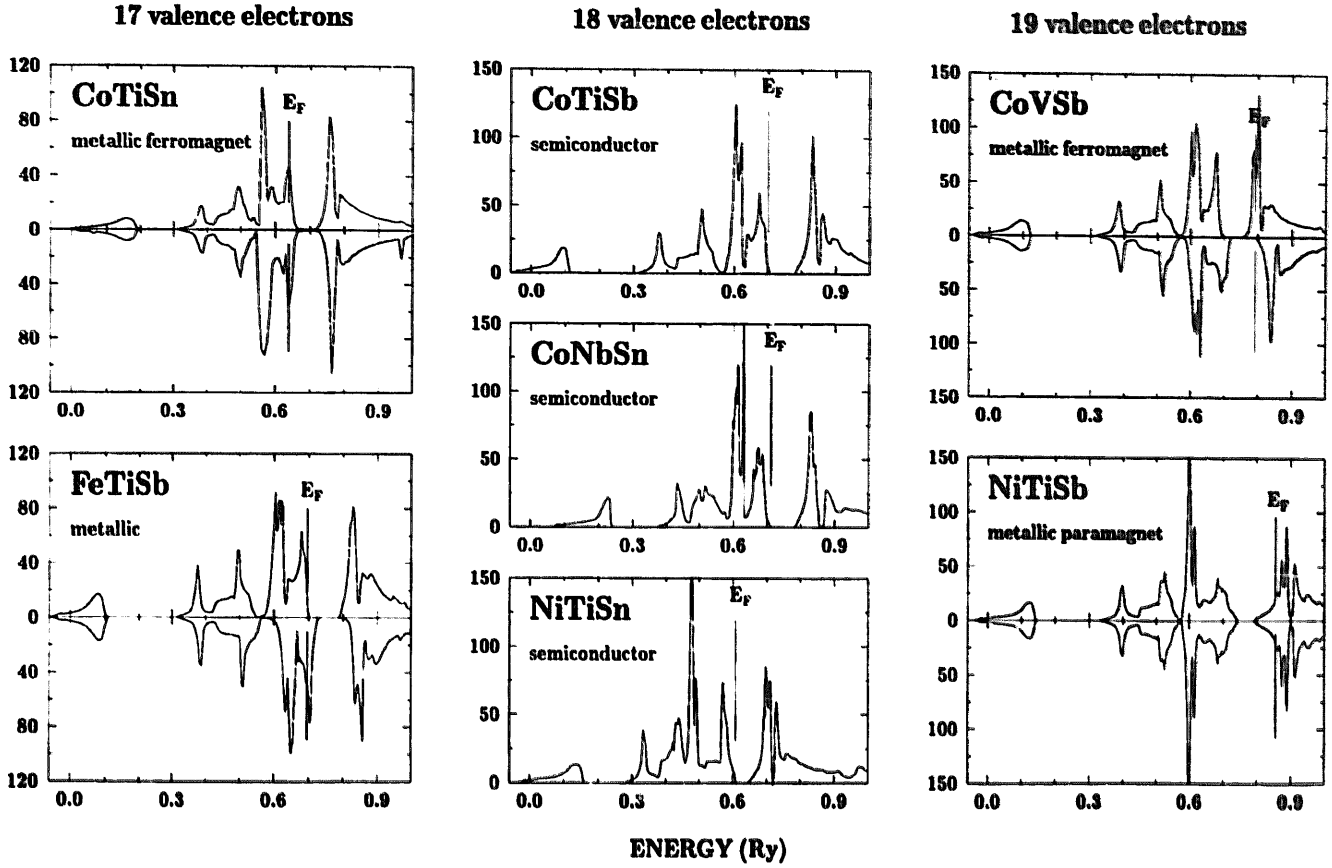

Fig. 2. Total densities of states for some semi-Heusler phases with 17, 18 and 19 peripheral electrons. Calculations indicate almost full magnetic polarisation in FeTiSb and CoVSb, not observed in magnetic measurements.

temperature of Sn, possibly due to the large difference in melting points between Nb and Sn.

3. Itinerant magnetism in the Co–Ni phases

Manganese Heusler alloys were, for a long time, given as examples of localized magnetism in *3d* metals, but the localized character of magnetism (Heisenberg-like hamiltonian) nevertheless comes from itinerant electrons and from the exclusion of minority spins from the Mn shell [9].

Conversely, weak itinerant ferromagnetism occurs for CoTiSn, Co–Ni compounds, and CoVSb. The effective paramagnetic and ordered moments are given in Table 1. CoVSb is very close to the magnetic instability, and its properties strongly depend on annealing conditions: the spontaneous moment $M(0)$ at 0 K may vary from 0.04 to 0.18 μ_B, and the Curie point from 11 to 58 K [10a,10b].

We must first discuss the occurrence of constant paramagnetism or Curie–Weiss behaviour depending on compounds, this being related to the shape of

Table 1
Lattice parameter (300 K), Curie, Néel and Curie–Weiss temperatures, ordered and paramagnetic moments for some semi-Heusler phases

Phase	a (Å)	T_c, T_N (K)	$M(0)$ (μ_B)	θp (K)	M_{eff} (μ_B)	$10^4 \chi$ (emu mol^{-1})
CoTiSn	5.997	$T_c = 135$	0.357	158	1.35	—
CoTiSb	5.884	—	—	—	—	1.7
CoNbSn	5.947	—	—	—	—	0.53
NiTiSn	5.947	—	—	—	—	1.3
CoVSb	5.791	$T_c = 11$–58	0.04–0.18	15–75	0.9–1.26	—
NiTiSb	5.872	—	—	—	—	1.4
NiTbSb	6.310	$T_N = 5.5$	5.6	−17	9.7	—
NiDySb	6.305	3.5	—	−8	10.9	—
NiHoSb	6.286	2.5	—	−7.5	10.7	—
NiMnSb	5.930	$T_c = 730$	4.02	~ 900	4.5–2.9	—

DOS near the Fermi level E_F. All semiconducting or semimetallic compounds, except rare earth ones, exhibit a temperature independent paramagnetism. For CoTiSn, CoVSb, FeTiSb, E_F is close to a peak in DOS, which results in a Curie–Weiss behaviour and ferromagnetic order for the two first phases. For CoVSb and FeTiSb, band calculations indicate almost full magnetic decoupling of the bands and do not agree with experiments. Metallic NiTiSb has a weaker DOS near E_F, as the Ni shell is nearly full and the Ti shell without large correlations; the Stoner criterion is not fulfilled and Pauli paramagnetism results.

For solid solutions, the susceptibility has an intermediate behaviour:

$$\chi = \alpha C/(T - \theta) + \chi o$$

where the Curie-like contribution comes from rather localized *3d* electrons with a peak in the DOS near E_F, and the Pauli-like term arises from other electrons.

3.1. $Co_{1-x}Ni_xTiSn$ series

The Curie–Weiss term is present for all Co concentrations, thus Co atoms bear an effective moment μ_{eff} even when diluted in semiconducting NiTiSn [3]. The localization happens without a great change in the effective moment M_{eff} (1.1 μ_B per diluted Co atom compared to 1.35 μ_B in pure CoTiSn). The ground state turns from paramagnetic to ferromagnetic for a Co concentration of 0.45, corresponding approximately to the point where the resistivity regime changes from semiconducting to metallic. The critical temperature (T_c) varies as $M(0)^{1.7}$ in the series, close to the case of localized systems. The spontaneous magnetization $M(0)$ is given as a function of concentration in Fig. 3, its variations well agree with the results of CPA band calculations.

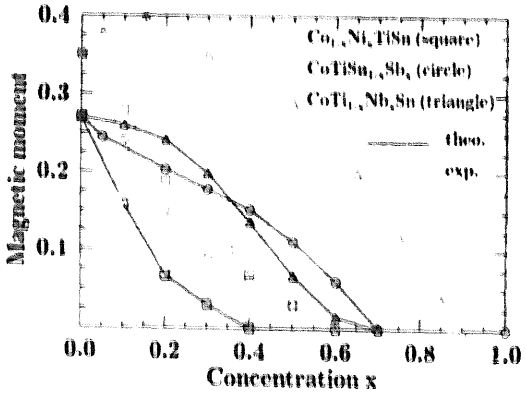

Fig. 3. Total ordered magnetic moment versus composition, obtained by magnetic measurements (dotted lines) and band calculations (continuous lines) in solid solutions between CoTiSn ($x = 0$) and semiconducting phases ($x = 1$).

For Co-rich compounds, the square of the magnetization varies linearly with the square of temperature up to the Curie point, which is classical for itinerant ferromagnets. However, close to the magnetic instability concentration, $M(T)^2$ varies as $(T/T_c)^{4/3}$, due to the fluctuations of the order parameter [11].

3.2. $CoTiSn_{1-x}Sb_x$ series

In this case, the ferromagnetic ground state turns to paramagnetism near $x(Sb) = 0.5$, close to the crystallographic phase transition. On the metallic side, T_c varies as $M(0)$, which is related to this cross-over from ferromagnetic to Pauli behaviour, as it was observed in $Co_{2-x}Ni_xTiSn$ series. For a larger Sb content (semiconducting side), the Curie–Weiss behaviour changes to enhanced paramagnetism, which means that a non magnetic ground state occurs near the CoTiSb composition. This is surprizing for a configuration close to $3d^8$ as shown by band calculations, close to that for CoTiSn; it should result from the interplay of crystal field, spin-orbit coupling and hybridization effects.

3.3. $CoTi_{1-x}Nb_xSn$

In this series, θp, T_c, M_{eff}, $M(0)$ all begin to increase with Nb content, due to the fact that the partial density of states and the correlations begin to increase on the Ti–Nb site, and drop to zero close to CoNbSn.

Despite these different magnetic behaviours, all series follow the same universal Rhodes–Wohlfarth law $T_c = f(M_{eff}/M(0))$. Some peculiar features appear in these systems. First ferromagnetism is stabilized due to a less than half filled (or less than half empty) band. Most properties are characteristic of itinerant magnetism, but some others are related to the narrow band situation. Among the properties of the first kind are the weakness of ordered and effective paramagnetic moments, the large $M_{eff}/M(0)$ ratio. Conversely, there is little effect of pressure on the Curie temperature for CoTiSn: there is one hole in one band, thus no change in the band occupation number under pressure.

It is surprizing that, for about the same number of Co *3d* electrons, 100% Co is not magnetic in CoTiSb, but has a Curie–Weiss moment when diluted in NiTiSn. CoTiSb is an ordered SC compound with a non magnetic ground state, but in the second case Co levels fall in the gap of NiTiSn and holes are localized on Co atoms. The rather weak value of the effective magnetic moment (about 1.1 μ_B) can arise from a low spin state due to crystal field (including hybridization effects) and spin-orbit coupling, as for CoTiSb itself.

Finally we shall see that NiRSb (R = Tb,Dy,Ho) are antiferromagnets, thus there is a strong difference between interactions in the *3d* metallic phases, where *3d* electrons participate to magnetism and conduction, and *4f* semiconducting phases, where interactions come from a superexchange mechanism.

4. Stronger and stronger: the strongest ferromagnets are... half metals

De Groot and Buschow [1] introduced the concept of half metal to describe the properties of NiMnSb and PtMnSb: due to the ferromagnetic splitting, the Fermi level for the majority spin band (metallic) falls in a gap of the minority spin (down spin) band, thus the density $n\downarrow$ (E_F) vanishes.

The main consequences are an integer value of the magnetization (apart from the weak polarisation of internal shells), for instance 4.0 μ_B in the two above compounds, and a full polarization of electrons at the Fermi level, which can be used in some spin sensitive electronic devices and gives a giant Kerr effect for PtMnSb. Various experiments have been performed in order to prove this half metallic character, like positron annihilation [12] and photoemission experiments [13].

Polarized neutron diffraction experiments have been recently performed on a NiMnSb single crystal [14], and give results in line with band calculations [15], i.e. a magnetic moment of 3.8 μ_B on Mn, and a positive polarisation of 0.2 μ_B on Ni. At 15 K, the magnetization density remains positive throughout the cell (which is related to, but not a proof of half metallic character). At 260 K, the total magnetization slightly decreases (3.8 μ_B), and regions of negative polarisation appear around the atoms. Is it related to the loss of half metallic character?

Indeed, with increasing temperature, the splitting between the two subbands decreases, and the half metallic character should disappear when the Fermi level reaches the bottom of the conduction band for down-spin.

Thermal variations of magnetization and resistivity have been investigated on single crystals (Fig. 4) [16a,16b]. At low temperatures ($T < 70$ K), $M(T)$ varies as $T^{3/2}$ (like in Heisenberg magnets), and $\rho(T)$ varies as T^2 (general case for ferromagnets or narrow band metals), which can be well explained by transverse spin wave excitations. For $T > 100$ K, $M^2(T)$ varies as T^2 (case of itinerant magnets), $\rho(T)$ varies as $T^{1.35}$ and has a larger extrapolated residual value than for the low temperature regime. This suggests the onset of a new type of excitations and the opening of a new scattering channel, linked to the amplitude fluctuations of the moment which are typical of itinerant magnetism. Thus this cross-over from Heisenberg-like to itinerant-like behaviour near 80 K can be attributed to the loss of the half metallic character.

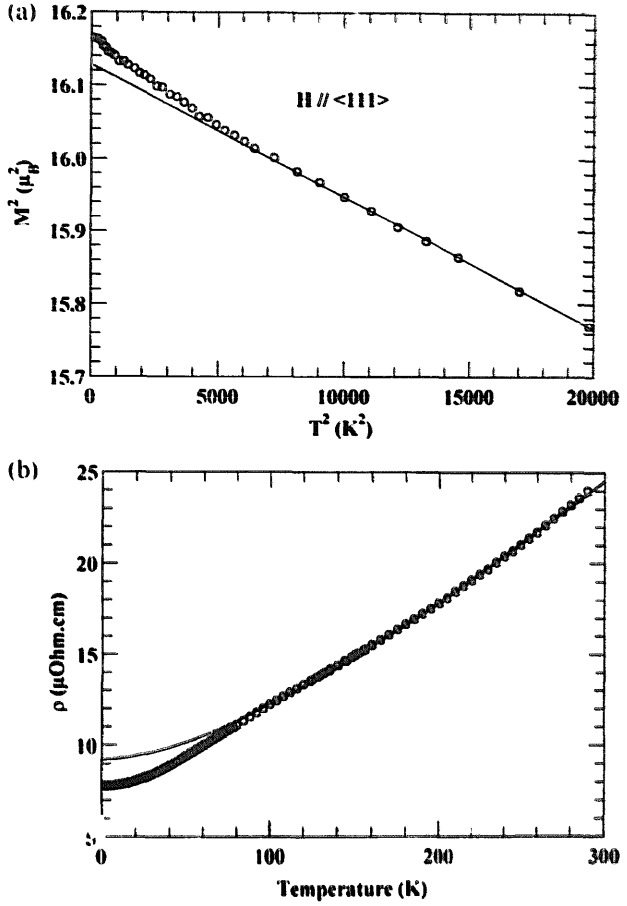

Fig. 4. Temperature dependence of: (a) square of spontaneous magnetization along a ⟨111⟩ axis; (b) resistivity for NiMnSb.

Is this behaviour reflected in the spectrum of magnetic excitations? Neutron inelastic scattering has also been untertaken on NiMSb [16a,16b]. Besides phonon branches, a single spin wave branch can be followed through the Brillouin zone up to 100 meV (Fig. 5).The initial gap (≤ 1 meV), hardly visible on the figure, is related to a weak magnetocrystalline anisotropy. The analysis of the dispersion relation gives the magnetic interactions between *3d* Mn shells: interactions J_1, J_2 with first and second neighbours dominate, but some interactions occur between more distant neighbours via Ni atoms.

But this is not all. Diffuse magnetic excitations exist and give a plateau of scattered intensity near the boundary of the Brillouin zone above 60 meV energy transfer [16a,16b]. Near this boundary, spin wave excitations are damped and nearly disappear. This feature recalls the individual Stoner-like excitations which have been observed in Ni or Fe (but at higher energies). The interpretation of such excitations is that they correspond to individual electronic excitations from the up-spin to the down-spin band, which are

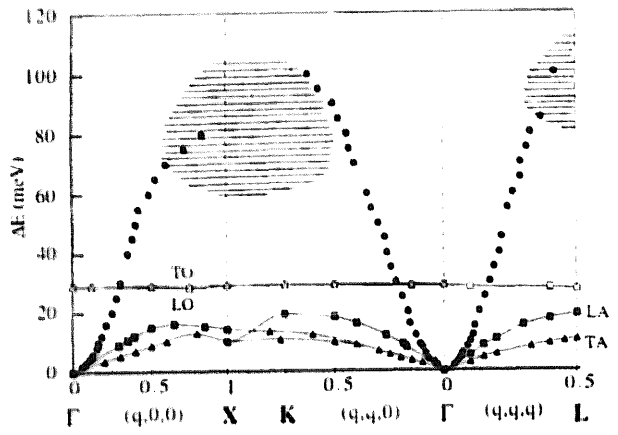

Fig. 5. Dispersion curve for phonons and magnons in NiMnSb at 300 K. Shaded area corresponds to regions where some additional diffuse intensity, or anomalies on the magnon curve were observed.

prohibited at low temperature and low energies due to the gap between the Fermi energy and the bottom of the conduction band for down-spin.

5. Magnetic semiconductors and giant magnetoresistance

Many magnetic semiconductors have been discovered having this semi-Heusler structure. May some of them present large magnetoresistance effects? A recipe is to take a narrow gap semiconductor with some internal magnetic shell, like for instance EuO, (Eu,Gd)Se, (La,Sr) MnO_3,..... but in our case, the magnetic ground state of *3d* metals disappears when we reach the SC phase and only a rather weak negative magnetoresistance is observed near the SC–metal cross-over.

The situation is different in rare earth compounds [5,17]. Particularly, NiRSb compounds with R = Tb, Dy, Ho are semiconductors [5,18]. They remain paramagnetic down to 6 K or below, and finally order antiferromagnetically with a propagation vector $Q = (1/2,1/2,1/2)$ [18]. This behaviour differs from that of ferromagnetic *3d* compounds, because we now have a true localized magnetism, semiconducting behaviour and superexchange interactions.

The magnetoresistance of NiDySb is given in Fig. 6; it is not a surprise to find a high value, reaching 35% at 4 K under 50 kOe. According to De Gennes and Friedel [19], the magnetoresistance is related to the correlation function $\langle Si.Sj\rangle_{H,T}$ between spins, or more simply, to the square of the magnetization in the paramagnetic range:

$$\rho(H,T) = \rho(0,T)\cdot\left[1 - \alpha\cdot(M(H,T)/M_0)^2\right].$$

Let us assume, neglecting crystal field effects, that the magnetization is given by

$$M(H,T) = M_0\cdot B_J(M_0\cdot H/k_B(T-\theta)),$$

where B_J is the Brillouin function, and θ the Curie–Weiss temperature. The continuous curves in Fig. 6 are fits: different isotherms may be fitted assuming a moment of 8.3 μ_B, slightly less than the free ion value, $\theta = -15$ K not far from the Curie–Weiss temperature (−8 K) deduced from susceptibility measurements, and α of the order of 0.6. This picture must be completed by the description of the zero field resistivity, which arise from the dirty semiconductor's physics. The question is whether the origin of giant magnetoresistance is only the reduction of the spin-disorder scattering, or can it arise also through the decoupling of spin-up and down subbands, which may reduce the semiconducting gap. In this case, it seems that the magnetic induction has little effect on the band structure of the SC. This is different from the case of ferromagnetic manganites (La,Ca)MnO_3, where magnetic electrons participate to the conduction and a SC to metal transition occurs at T_c.

6. Conclusion

Very different types of behaviour were observed in these semi-Heusler phases, from semiconductor to metal, from constant paramagnetism to Curie–Weiss behaviour, from weak ferromagnet to strong half metallic ferromagnet. Efforts are now done to bridge the gap between weak and strong ferromagnets, and to discover superconducting compounds in these series.

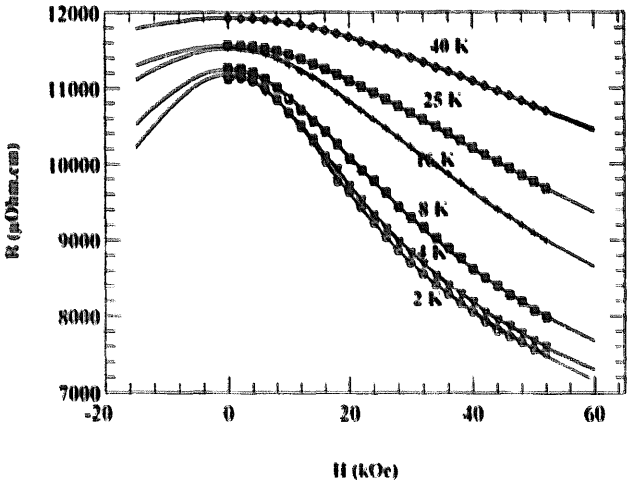

Fig. 6. Magnetoresistance in NiDySb. Continuous lines are fits using parameters given in the text.

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