MAGNETIC STUDIES OF Clb-COMPOUNDS OF TRANSITION METALS

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Résumé. — Propriétés magnétiques des séries des composés (Cu, Ni)MnSb, (Cu, Pd)MnSb et (Ni, Co)MnSb, dont la structure est du type Cl_b, ont été étudiés. Substitution de Ni ou bien Pd pour Cu dans CuMnSb, qui est antiferromagnétique, pour quelques pour cent change le magnétisme en ferromagnétisme, malgré leur effet opposée sur la constante de réseaux. Co-existence de phase de désordre fait les courbes thermomagnétiques de (Ni, Co)MnSb être complexes. Résultats expérimentaux montrent que des atomes de Mn soient les seuls porteurs de moment, et aussi que le nombre moyen d'électrons de conduction par atome joue un rôle important dans le magnétisme des composés de type Cl_b.

Abstract. — Magnetic properties of series of compounds with Cl_b type of crystal structure (Cu, Ni)MnSb (Cu, Pd)MnSb and (Ni, Co)MnSb were studied. Substitution of either Ni or Pd for Cu in antiferromagnetic CuMnSb by a few per cent changes the magnetism into ferromagnetism, in spite of their opposite effects on the lattice parameter. Co-existence of disordered phase makes the thermomagnetic curves for (Ni, Co)MnSb complex. Experimental results show that Mn atoms are the only carrier of magnetic moment and that the conduction electron concentration plays an important rôle in the magnetism of Cl_b compounds.

1. **Introduction.** — Magnetic properties of the compounds having $Cl(CaF_2)$ or Cl_b(MgAgAs) type of crystal structure, the latter being an ordered structure of the former, have been investigated by several authours. Castelliz [1, 2] reported that NiMnSb, CoMnSn and CoMnSb are ferromagnetic with Curie temperatures of 750 °K, 670 °K and 490 °K respectively. Hames [3] reported that PdMnSb is strongly magnetic at room temperature. Recent studies by Endo et al. [4] and by Forster et al. [5] revealed that CuMnSb is an antiferromagnet with Néel temperature of 55 °K, magnetic moments being aligned ferromagnetically in (111) planes with neighbouring planes oriented antiparallel. The compounds ABSb, where A stands for Fe, Co or Ni and B for Ti or V, have been reported to be of Cl_b type [6, 7], but their magnetism is not thouroughly known except our recent finding [8] that CoVSb is a Curie-Weiss paramagnet with effective magnetic moment of 1.26 μ_B per formula and assymptotic Curie temperature of 75 °K, and also that CoTiSb is a Pauli paramagnet with constant susceptibility of 5×10^{-7} cm^3/g.

In this paper we report the results of our recent magnetic studies of three series of the compounds (Cu, Ni)MnSb, (Cu, Pd)MnSb and (Ni, Co)MnSb. Possible mechanism of magnetic interaction in Cl_b-type compounds will be discussed.

2. **Experimental Result and Discussions.** — Specimens used were prepared as follows : The mixtures of the constituent metals were sealed in evacuated quartz tubes, melted at about 1 000 °C and then homogenized at 650 °C for 50 h. The purities of the starting materials were 99.99 % for copper, 99.9 % for nickel, paradium, manganese and antimony, and 99.5 % for cobalt. The specimens were examined by means of X-ray powder diffraction using CuKα radiation and also of microscopic observations. Magnetization was determined from the force excerted on the specimen placed in an inhomogeneous magnetic field up to 10 kOe at temperatures down to 77 °K. The measurements were taken down to 4.2 °K for $Cu_{1-x}Ni_xMnSb$ with $x \leqq 0.04$.

In figure 1, the lattice parameter is plotted against the composition. In the right half of the figure the

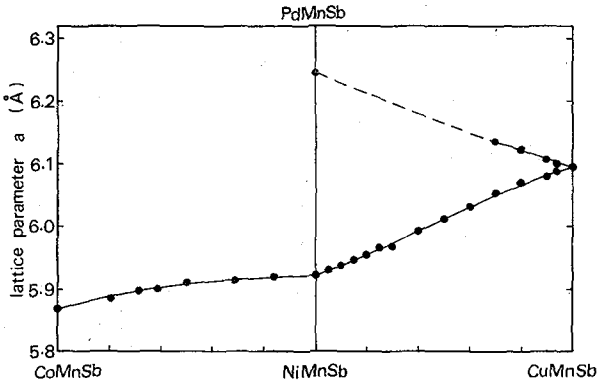

FIG. 1. — Dependence of lattice parameters of Cl_b compounds (Ni, Co)MnSb, (Cu, Ni)MnSb and (Cu, Pd)MnSb on composition.

values for both (Cu, Ni)MnSb and (Cu, Pd)MnSb are shown (**).

According to Nowotny et al. [9] Mn and Sb (or Co and Sb) are distributed at random in CoMnSb (Cl or CaF_2 structure), but the Debye diagram for our specimen indicated a partial ordering towards Cl_b structure. The degree of ordering was roughly estimated to be about a half. In (Cu, Ni)MnSb and (Cu, Pd)MnSb, the monotonic change of the lattice parameter from CuMnSb towards Ni- or PdMnSb may be taken as an evidence that, on substitution, Ni or Pd atoms properly occupy the Cu sites. The observed intensity of X-ray diffraction was consistent with the calculated one.

The magnetization vs. temperature curves for

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(**) Since actual composition of the compound CuMnSb is $Cu_{1.00}Mn_{1.00}Sb_{1.03}$, excess Sb was introduced in the dilute compounds of Ni and Pd [4, 10].

(Co, Ni)MnSb were not simple. Even the specimens for which the Debye diagrams were of single-phase pattern often demonstrated the co-existence of two ferromagnetic phases through two Curie temperatures. This peculiar results were interpreted as co-existence, in the specimen, of ordered (Cl_b) and disordered (Cl) phases with the same value of lattice parameter. Prolonged annealing at elevated temperatures tended to eliminate the lower Curie temperature but no perfect order seemed to be reached.

The results of the magnetic measurements are summarized in figure 2.

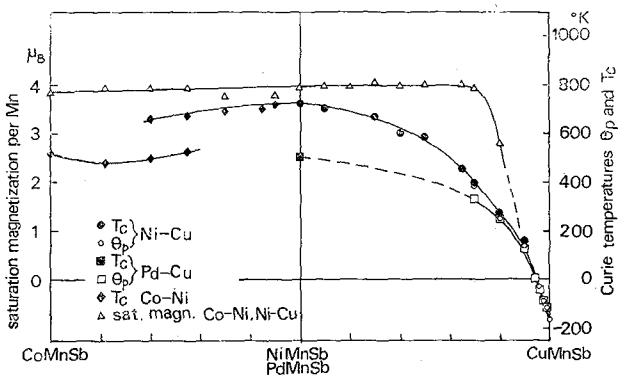

FIG. 2. — Dependences of saturation magnetization in terms of μ_B/Mn, ferromagnetic and paramagnetic Curie temperatures of (Ni, Co)MnSb, (Cu, Ni)MnSb and (Cu, Pd)MnSb on composition.

In spite of the opposite change in lattice parameter, partial replacements of Cu atoms in antiferromagnetic CuMnSb by Ni and Pd bring about a quite similar change in magnetism, reversing the sign of θ_p at about 5 to 6 % replacement, which suggests that the Mn-Mn distance is of minor importance.

The behaviour of the saturation moment in (Cu, Ni)MnSb which reaches 4 μ_B/Mn at $Cu_{0.6}Ni_{0.4}MnSb$ and stays constant thereafter may be interpreted as indicating that Mn atoms are the only carriers of magnetic moment in this series of compounds. This value stays nearly unchanged also in (Ni, Co) MnSb, apart from small decrease presumably due to the disordered nature. PdMnSb has practically the same value of saturation moment [10] as NiMnSb. In the region of composition near CuMnSb where the saturation moment is much smaller, the paramagnetic moment stays nearly constant, which may be considered to show that the decrease in saturation moment does not come from the decrease in the atomic moment of Mn, but from their incomplete alignment due to the onset of antiferromagnetic coupling among them. In contrast to the behaviour of the saturation moment, the Curie temperatures T_C and θ_p change gradually and reach the maximum value around the composition NiMnSb.

Since Pd atoms are generally in less favourable condition for the possesion of magnetic moment than Ni which in turn have no magnetic moment in (Ni, Cu)MnSb, Pd and Ni atoms may be considered to behave in the same way so far as the magnetic moment and the number of conduction electrons are concerned. Thus it may be said that it is the conduction electron concentration that plays a major rôle.

The indirect exchange interaction of Ruderman-Kittel-Kasuya-Yosida type and/or the interaction through double resonance scattering of Friedel-Caroli-Blandin type [11, 12, 13] is supposed to be important. Both of these theories lead to rather similar expressions of the interaction energy with oscillating nature, apart from the contrary dependence of the amplitude on the distance between magnetic moments when the number of conduction electrons per atom and J_{sd} are fixed.

Preference of the latter theory to the former as was discussed by Caroli and Blandin for dilute alloys of Mn in Cu and for the Heusler alloys is again the case in the Cl_b compounds, whose structure is closely related to the Heusler alloy structure : the higher Curie temperature of NiMnSb than PdMnSb is consistent with the double resonance scattering theory. Endo [10] estimated that the R-K-K-Y interaction is about 10 to 50 times smaller in the present compounds and evaluated the Caroli-Blandin expression of Curie temperature in qualitative agreement with experiment.

In conclusion, manganese atoms are the only carrier of magnetic moment in the manganese compounds of Cl_b type structure, and the conduction electron concentration is of major importance in determining the magnetic interaction among them. The interaction based on the double resonance scattering theory rather than the R-K-K-Y interaction is consistent with the experimental results.

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