ATOMIC AND MAGNETIC STRUCTURE OF THE $Ni_xCu_{1-x}MnSb$

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(Received August 1, 1972)

$Ni_xCu_{1-x}MnSb$ alloys (where x varies from 0.05 to 0.4) were studied using neutron diffraction, X-ray diffraction, and magnetometric techniques. All the compounds under investigation were found to be of atomic structure of $C1_b$ type. The complex non-collinear magnetic structure was observed in compounds of compositions $0.05 \leqslant x \leqslant 0.40$ at 77 K. $Ni_{0.4}Cu_{0.6}MnSb$ appeared to be a collinear ferromagnetic with the magnetic moment of Mn atom equal $(3.85 \pm 0.10)\ \mu_B$ at 77 K.

1. Introduction

CuMnSb is an antiferromagnetic with $T_N = 55$ K [1]. It was shown by means of X-ray and neutron diffraction [2] that its crystal structure is of $C1_b$ type, its magnetic structure being analogous to that of MnO [3]. Ferromagnetically coupled Mn atoms occupy (111) planes, whereas antiferromagnetic coupling exists between these planes. The magnetic moment as calculated from neutron measurements was $(3.9 \pm 0.1)\ \mu_B$ at 4.2 K. Castelliz [4] stated that NiMnSb was a ferromagnetic with $T_C = 750$ K. Recent investigations of NiMnSb by Szytuła *et al.* [5] showed that its crystal structure was $C1_b$ type. The magnetic moment is localized on Mn atoms only and amounts to $(3.85 \pm 0.05)\ \mu_B$ at 77 K.

Castelliz [6] and Endo *et al.* [7–9] carried out X-ray and magnetometric investigations of the $Ni_xCu_{1-x}MnSb$ system. Their results testified that the lattice constant decreased when going from CuMnSb to NiMnSb, the Curie temperature increasing at the same time. The saturation magnetization as a function of composition is of special interest. It is constant for x between 1.0 and 4.0 and amounts to about 95 emu/g, which corresponds to the approximate value 4.0 μ_B for the magnetic moment per molecule and shows the

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prominent dependence upon x in the range 0.4 to 0. In this paper the results of combined investigations (magnetometric, neutronographic, and roentgenographic) of the crystal and magnetic structure of $Ni_xCu_{1-x}MnSb$ for x varying from 0.05 to 0.40 are reported.

2. *Preparation and measurements*

The samples of $Ni_xCu_{1-x}MnSb$ were prepared by melting the mixtures of constituent metals at about 1000°C in evacuated quartz tubes. The purity was 99.9% for nickel, copper, and manganese, and 99.7% for antimony powder. The samples obtained were subsequently annealed at 650°C for 50 h. The losses in weight of the samples after this treatment did not

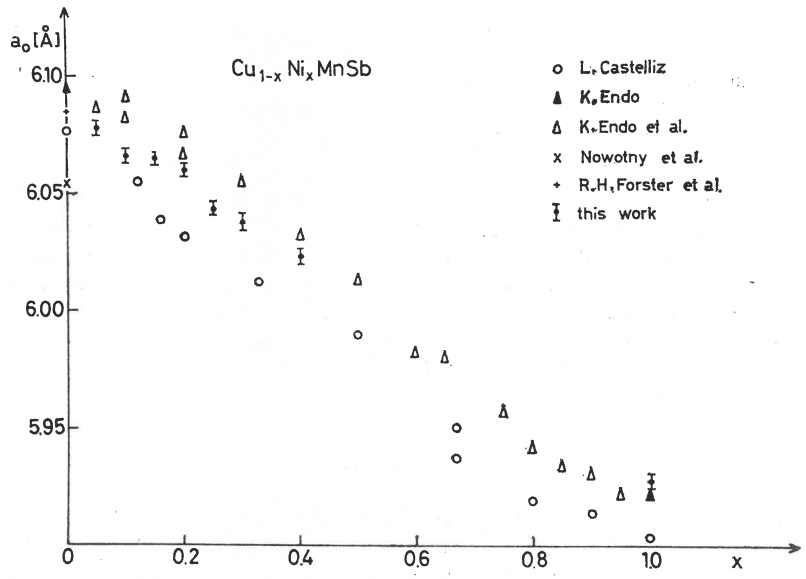

Fig. 1. The lattice parameter dependence composition in $Ni_xCu_{1-x}MnSb$

exceed 1.5%. *X*-ray analysis using Fe K_α and Cu K_α rays ascertained that only cubic phase exists, with the lattice constants presented in Fig. 1. Comparison with the results of other paper are also included in the figure.

Magnetometric measurements utilizing the modified Sucksmith method [10] were carried out in the temperature range 77 K to 1000 K. The Curie temperature and the saturation magnetization were calculated from these measurements. The results are presented in Figs 2 and 3, together with the previous ones.

Powder neutron diffraction measurements were performed at the heavy-water moderated reactor RA at Vinca. The neutron wavelength was 1.124 Å. Neutron diffractograms of $Ni_xCu_{1-x}MnSb$ were obtained at 77 K and 300 K. Some of the neutron diffraction patterns are shown in Figs 4 and 5. The effect an external magnetic field of 6 kOe, applied parallel to the scattering vector and sufficient to saturate a sample, is clearly visible (Fig. 6).

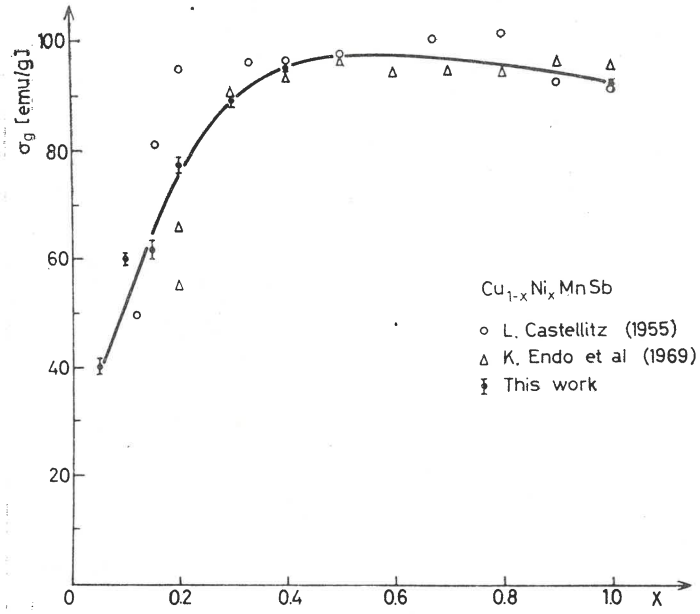

Fig. 2. Ferromagnetic and paramagnetic Curie temperature dependence in $Ni_xCu_{1-x}MnSb$ composition

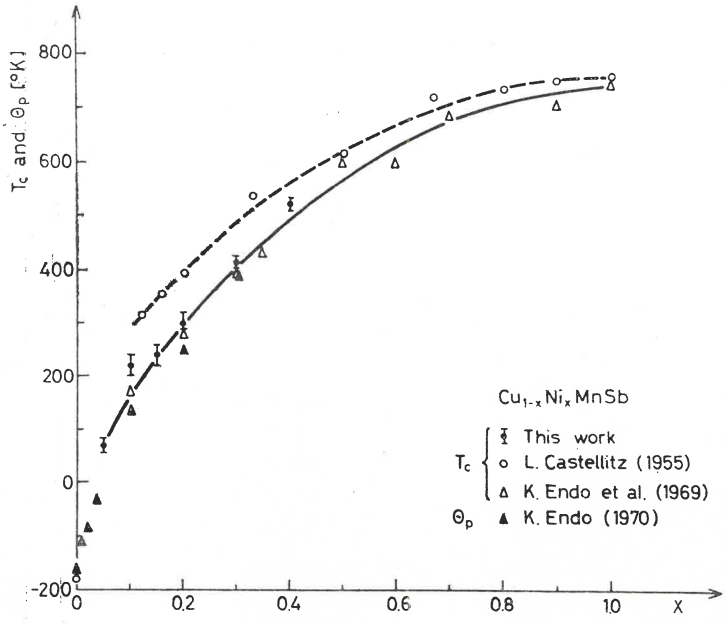

Fig. 3. Dependence of saturation magnetization in $Ni_xCu_{1-x}MnSb$ composition

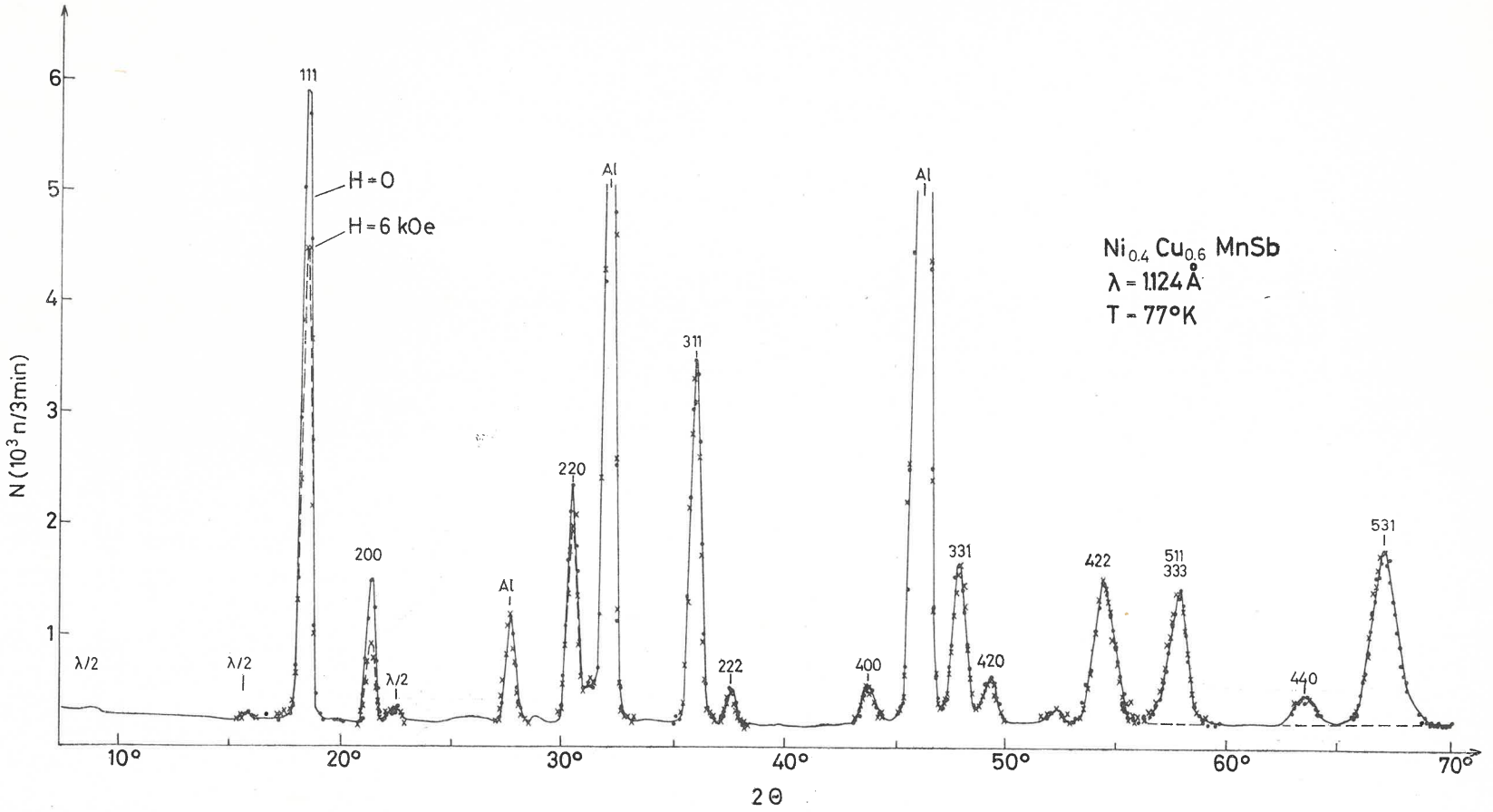

Fig. 4. A fragment of the neutron diffraction pattern in $Ni_{0.4}Cu_{0.6}MnSb$ at 77 K (× — $H = 6$ kOe, ● — $H = 0$)

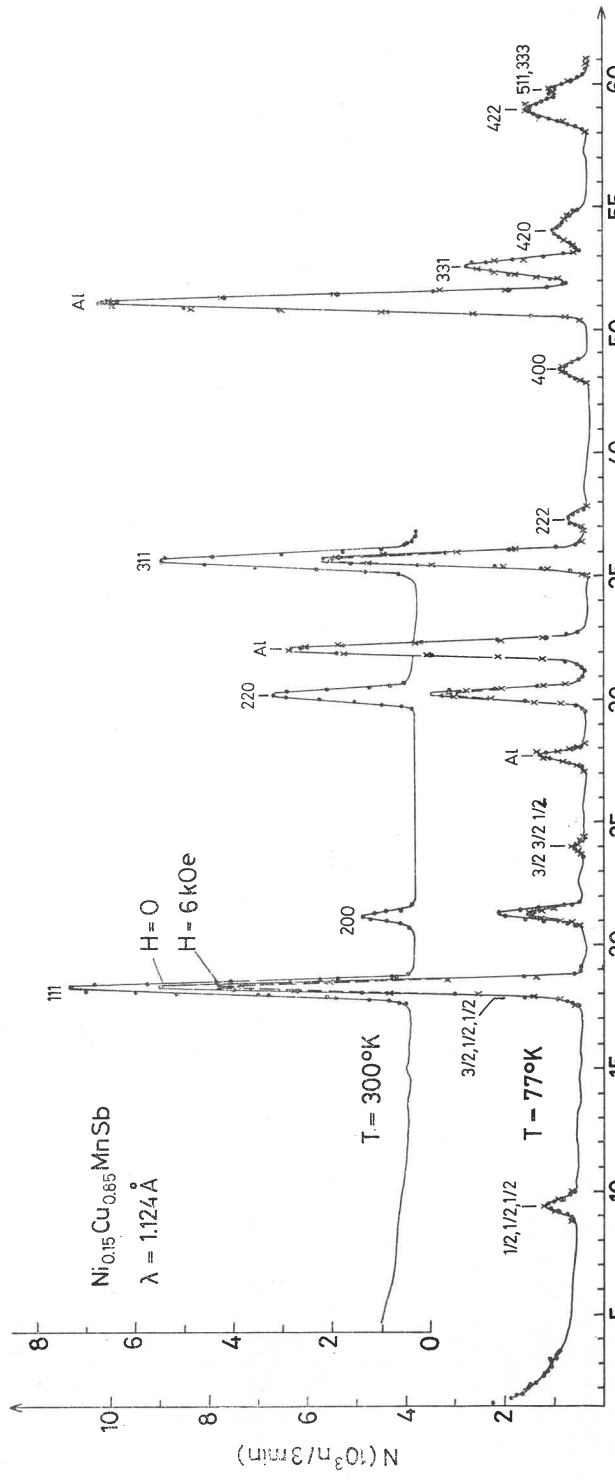

Fig. 5. A fragment of the neutron diffraction pattern in $Ni_{0.15}Cu_{0.85}MnSb$ at 300 K (×— $H = 6$ kOe, ● — $H = 0$)

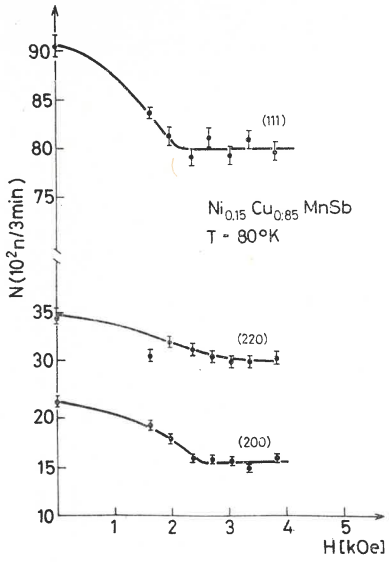

Fig. 6. Dependence of intensity of Bragg reflections (111), (220), and (200) on the magnetic field for $\bar{H} \parallel \bar{e}$ and $\bar{\varkappa} \parallel \bar{e}$

3. Determination of atomic structure

As both CuMnSb and NiMnSb have the $C1_b$ structure the compounds of mixed composition should have the same one. The intensities of several Bragg reflections were calculated for assumed $C1_b$ structure with Cu and Ni atoms occupying statistically the sublattice *A*, Mn atoms the sublattice *B*, and Sb atoms the sublattice *D*, respectively, and compared in Table I with the experimental values obtained for $x = 0.15$ and 0.4. The disagreement factors obtained for these as well as for the remaining compositions are as follows:

x	0.05	0.10	0.20	0.25	0.30
$R(\%)$	3.6	5.8	6.7	7.5	4.4

The values presented fully confirm the accordance of the experimental data obtained and the suggested model of structure of $C1_b$ type.

3. Determination of the magnetic structure

Only Bragg reflections conforming to the cubic unit cell of the lattice constant $a = (6.023 \pm 0.005)$ Å are visible in the neutronogram of the sample of $Ni_{0.4}Cu_{0.6}MnSb$, obtained in liquid nitrogen temperature. The analysis of magnetic contributions showed that the magnetic moments were localized on Mn atoms solely as had been found in the case of NiMnSb and that the ferromagnetic couplings existed between these moments. The value of a magnetic moment concluded there from is $(3.85 \pm 0.10)\ \mu_B$. The values of

TABLE I

Nuclear components of the neutron intensities from $Ni_{0.15}Cu_{0.85}MnSb$ and $Ni_{0.4}Cu_{0.6}MnSb$ at 77 K

hkl	$Ni_{0.15}Cu_{0.85}MnSb$		$Ni_{0.4}Cu_{0.6}MnSb$	
	I_{obs}	I_{cal}	I_{obs}	I_{cal}
111	3.790±210	3.790	3.932±235	3.929
200	510±45	559	617±43	611
220	1.464±94	1.630	1.747±145	1.623
311	3.192±110	3.220	3.084±245	3.355
222	233±16	260	295±45	283
400	380±23	404	467±66	424
420	440±20	436	561±44	532
422	1.056±65	1.109	1.750±110	1.735
511 333	1.884±114	1.821	2.214±196	1.993
440	414±24	377	476±28	462
531 600	2.600±140	2.662	2.960±340	2.788
442 620	697±98	570		
R(%)	3.5		5.4	

$B = 0.6 \times 10^{-16}$ cm^2

intensity, computed assuming the above value of the moment, are compared with the experimental ones in Table II.

In the case of $Ni_{0.15}Cu_{0.85}MnSb$, however, besides the reflections analogous to that mentioned above, conforming to the lattice constant $a = (6.066 \pm 0.005)$ Å and consisting

TABLE II

A comparison of the calculated and experimental values of $q^2 F_m^2(hkl)$ for $Ni_{0.4}Cu_{0.6}MnSb$ at 77 K

hkl	$[\langle q^2 \rangle F_m^2(hkl)]_{obs}$	$[\langle q^2 \rangle F_m^2(hkl)]_{cal}$
111	7.15	7.18
200	5.55	6.14
220	3.70	3.63
311	2.42	2.48
222	1.98	2.20
400	1.39	1.39
R(%)	4.4	

of both nuclear and magnetic components in 80 K (see Fig. 5), some additional Bragg reflections appear at Bragg angle $2\Theta = 9.7°$ and 24° which can be explained in terms of double-sized unit cell.

Not all magnetic reflections occurring in the neutronograms can be explained in terms of the collinear model of magnetic structure. So we had to assume that, similarly to the case of β-MnZn [11], the total magnetic moment of Mn (since it is localized only there) could be divided into two components: ferromagnetic and antiferromagnetic. Therefore the magnetic scattering of neutrons consists of the antiferromagnetic scattering, the reflections of which do not coincide with the nuclear scattering reflections, and the ferromagnetic scattering reflections overlapping the nuclear ones. The intensities of these two group of reflections are proportional to the antiferromagnetic μ_{AF} and ferromagnetic μ_F components of the magnetic moment, respectively.

The total magnetic moment per atom is expressed by

$$\bar{\mu} = (\mu_F^2 + \mu_{AF}^2)^{\frac{1}{2}}.$$

The substructure reflections $\left(\frac{h}{2}, \frac{k}{2}, \frac{l}{2}\right)$, observed for odd values of h, k, l only, indicate that the magnetic structure of the μ_{AF} component is of MnO type.

When examining polycrystalline samples of cubic crystals by means of neutron scattering, one cannot tell the orientation of the magnetic moment in relation to the crystal axes, as $\langle q_{hkl}^2 \rangle = \frac{2}{3}$ [12]. *X*-ray measurements for MnO, FeO, and NiO [13, 14] revealed that the paramagnetic — antiferromagnetic transition was connected with the change of the crystal structure symmetry from cubic to rhombohedral. Foster *et al.* [2] attributed

TABLE III

Magnetic components of the neutron intensities from $Ni_{0.15}Cu_{0.85}MnSb$ at 77 K

hkl	I_{obs}	I_{cal}
$\frac{1}{2}\frac{1}{2}\frac{1}{2}$	475.2	495.0
111	748.8	723.8
200	311.7	355.2
$\frac{3}{2}\frac{3}{2}\frac{1}{2}$	111.1	115.7
220	152.0	211.0
311	211.5	217.8
R(%)		7.9

the rhombohedral magnetic unit to the CuMnSb compound, hence $\langle q_{hkl}^2 \rangle$ would depend on the angle φ between the direction of the magnetic moment and the crystallographic direction (111) [12], which could allow the value of this angle to be found. The absence of the $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ magnetic reflections in the neutronogram of CuMnSb [2] indicates that the magnetic moments are arranged parallelly to the direction [111] [12]. The ratio of the $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and $(\frac{3}{2}, \frac{3}{2}, \frac{1}{2})$ reflection intensities shows that the component μ_{AF} is parallel to the direction [100]. In Table III the intensities of Bragg reflections are compared. The theoretical intensities are calculated assuming the following values of magnetic moments: $\mu_F = (3.0 \pm 0.1)\ \mu_B$, $\mu_{AF} = (1.9 \pm 0.1)\ \mu_B$.

The same reflections as for $x = 0.15$ appear in the neutronograms obtained at liquid nitrogen temperature for the samples of $x = 0.05$, 0.10, 0.2 and 0.3. Assuming the same model of magnetic structure as for the composition of $x = 0.15$, the values of moments μ_F and μ_{AF} and of the total moment $\bar{\mu}$ were calculated, the results obtained being listed

TABLE IV

Contributions of μ to ferromagnetic and antiferromagnetic structure of composition $Ni_xCu_{1-x}MnSb$ at 77 K

x	Magnetic moment (μ_B)			
	μ_F	μ_{AF}	$\bar{\mu}$	μ_{eff} (7)
0.05	1.7_5	0.7_5	1.9_0	5.2
0.10	2.7_5	2.1_0	3.4_6	5.0
0.15	3.0_0	1.9_0	3.5_5	
0.20	3.1_4	1.4_0	3.4_3	4.9
0.25	3.1_0	1.2_0	3.3_2	
0.30	3.5_5	1.1_0	3.7_2	5.0
0.40	3.8_5	—	3.8_5	

in Table IV. The value of a ferromagnetic component of magnetic moment per atom, calculated from the neutron measurements, agrees with the analogous value per molecule, obtained from the magnetometric method.

The neutron scattering measurements show that μ_F increases and μ_{AF} decreases as the content of nickel (x) increases. The ferromagnetic component achieves at $x = 0.04$ its maximum value, being equal to the atomic magnetic moment for NiMnSb, while the antiferromagnetic component equals zero.

Another experimental effect observed here is the slightly decreased magnetic moment in the case of samples with a small amount of nickel, both in ordered and paramagnetic states.

The results obtained for $x = 0.05$ markedly differ from the remaining ones due to the fact that the measurements were carried out here near to the Curie temperature. The author had to omit the neutron measurements of samples with smaller contents of nickel whose magnetic ordering is observed below 55 K, owing to the failure to achieve temperatures lower than 77 K.

5. *Discussion of results*

Analogously to the case of three-compound Heusler alloys the magnetic interactions between localized magnetic moments of Mn atoms in the $Ni_xCu_{1-x}MnSb$ system involve conduction electrons. The variation of concentration of conduction electrons plays a decisive part in the interaction. This is confirmed by the fact that alloys having equivalent electron concentrations exhibit analogous magnetic properties. For example, the alloys

of $C1_b$ type, CuMnSb and PdMnTe, bearing the same number of conduction electrons per atom, namely, 1.75, are both antiferromagnetic, while NiMnSb and PdMnSb each, having 1.5 conduction electrons per atom, are both ferromagnetic.

Basing our calculations on the Caroli-Blandin theory [15] and assuming that numbers of conduction electrons going from several atoms are 0 for Ni and 1 for Cu, and that μ/μ_B is -3 for Mn and 5 for Sb, we can estimate the values of temperature Θ_p for NiMnSb and CuMnSb. We take the remaining parameters of the theory from the measurements of Cu-Mn alloys with small content of Mn. The values thus obtained agree qualitatively and quantitatively with the experimental values, *e. g.* for the temperature Θ_p:

	Caroli-Blandin theory	experiment
NiMnSb	600 K	730 K
CuMnSb	−84 K	−160 K

The variation of conduction electron concentration and of lattice constant fully explain the variation of Curie temperature in the $Cu_{1-x}Ni_xMnSb$ system.

There is another problem in interpreting the values of magnetic moments in the medium range of composition. The mean magnetic moment per molecule varies from 0 to 3.8 μ_B as the content of Ni varies from $x = 0.04$ to 0.4. The above variation can be explained assuming that

i. the magnetic moment of the Mn atom varies,
ii. the system under investigation is a mixture of two phases,
iii. the mutual arrangement of Mn atoms varies.

Re *i.* It follows from the neutron investigations [2] that the magnetic moment per Mn atom is (3.9 ± 0.1) μ_B for $x = 0$ (CuMnSb). Therefore the hypothesis of a sudden change of the magnetic moment could be applied to the very narrow range of the change of composition. As it was found by means of *X*-ray and neutron investigations that the crystal structure did not undergo any change with the change of composition, the replacement of atoms within a small range of variation of composition could not lead to any essential variation of configuration of electron orbitals *d* or *s*. The replacement of a copper by a nickel could lead to a slight decrease in the magnetic moment in paramagnetic state from 5.5 μ_B for $x = 0$ to 4.9 μ_B for $x = 0.2$ and this practically excludes the first model.

Re *ii.* The transition from the antiferromagnetic to the ferromagnetic arrangement could occur also by the appearance of nuclei of ferromagnetic phase in a small part of the antiferromagnetic matrix. The scale of this phenomenon would become larger as the content of nickel increased. If this were indeed so, the $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ reflection would not have been observed in the neutronogram.

Re *iii.* The last model provides for the gradual variation of the arrangement of atomic magnetic moments, proceeding in all volume of crystal uniformly as the nickel increases. The phenomenological approach, based on the generalized Smart molecular field theory, will be applied to explain this phenomenon. We assume that the decisive effect is that of interactions with first and second neighbours, characterized by the exchange constants

J_1 and J_2. This theory was applied by Webster [16] to explain the antiferromagnetic structure of the Heusler alloy Pd_2MnIn. The structure of CuMnSb, discovered by neutron diffraction, fits the second type arrangement of fcc lattice. Taking as a basis the known values of the Néel temperature (T_N) and the paramagnetic Curie temperature (Θ_p), we can estimate the values of exchange constants J_1 and J_2, which in the case of CuMnSb are $J_1 = -2.2$ K and $J_2 = -2.3$ K respectively.

The measurements of magnetic susceptibility as a function of temperature, carried out with small contents of Ni by Endo [8], showed that the slight contributions of Ni (x from 0 to 0.04) involve no variation of Néel temperature but a strong variation of paramagnetic Curie temperature:

$x =$	0	0.01	0.02	0.04
$\Theta_p =$	−160 K	−110 K	−85 K	−30 K

Thus the constant J_2 (depending on T_N only) remains unchanged, while the constant J_1 (proportional to the sum $T_N+\Theta_p$) changes as the contents change.

$x =$	0	0.01	0.02	0.04
$J_1 =$	−2.2 K	−1.15 K	−0.62 K	+0.52 K

The relations $J_2 < 0$ and $|J_2| > |J_1|$ are fulfilled for alloys with a small admixture of nickel, and this leads to the antiferromagnetic arrangement of atomic moments. The greater the amount of nickel the greater the constant J_2, so that for $x > 0.04$ the relations $J_2 > 0$ and $J_1 > |J_2|$ are fulfilled, and this leads to the ferromagnetic arrangement of atomic magnetic moments. The collinear arrangement of atomic magnetic moments appears when the relation $J_1 \gg J_2$ is fulfilled. The latter does not happen in the medium range of composition $0.05 < x < 0.4$, hence the noncollinear structure appears, as we have just observed experimentally. The strong inequality is satisfied for $Ni_{0.4}Cu_{0.6}MnSb$ and alloys richer in nickel, therefore the collinear ferromagnetic structure is observed in them.

The author would like to express his sincere thanks to Dr Ž. Dimitrijevic and Mr J. Todorovic for their kind assistance in neutron diffraction experiment. Also, he is very grateful to Mr A. Kołodziejczyk for the magnetic measurement.

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