Mössbauer effect study of $Cu_2MnAl_{1-x}Sn_x$ compounds

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Results of a Mössbauer effect study of a range of $Cu_2MnAl_{1-x}Sn_x$ compounds are presented
for $x = 0.05$, 0.10, 0.15, 0.25, 0.50, and 0.75. The hyperfine magnetic field at Sn nuclei is pro-
portional to a number of Sn atoms substituted for Al ones and it increases by ~ 17 kOe per Sn
atom. It does not depend, however, on tin concentration in the compound. This reflects a
well-localized character of ferromagnetism in these compounds. The coexistence of the dif-
ferent fields for a given sample cannot be explained either by the Blandin-Campbell model or by
the Jena-Geldart one. The results and their interpretation were supported by fitting the
Mössbauer spectra of the alloys studied with another independent method which gave the distri-
butions as well as the average magnetic fields. The isomer shift also depends on how many Sn
atoms have been substituted for Al ones, and it decreases on average by 0.09 mm/s per Sn
atom.

I. INTRODUCTION

Intermetallic compounds known as Heusler alloys
are formed at the stoichiometric composition X_2YZ,
where X is a transition metal, Y is normally Mn, and
Z stands for such elements as Al, Si, Ga, Ge, In, Sn,
or Sb. Although these alloys were discovered in
1898,[1] they have become a subject of more intensive
study only after the discovery of the recoilless emis-
sion of gamma radiation by Mössbauer.[2] The main
reason for the interest in these compounds lies in the
fact that they constitute rather convenient systems
for studying the origin of the hyperfine field existing
at the nuclei of atoms occupying the Z site or substi-
tuted into this site.

Investigations which have been carried out to date
have supplied much valuable information on the ori-
gin of the field. The clear picture, however, has not
yet emerged and there is lack of an adequate theoret-
ical explanation of the data available.

In the existing literature on this subject, one may
find quite a number of papers giving the systematics
of the hyperfine fields for the known and measured
Heusler alloys, e.g., Refs. 3—5. There also exist
theoretical attempts that try to describe the measured
features of these compounds, e.g., Refs. 6—8.

Due to this, we want to limit ourselves in this In-
troduction and recall only the most important facts.
One of them is that the sign and magnitude of the
hyperfine field depends (a) on the valency of the
probe atom, e.g., $H_{hf} = 93$ kOe at In in Cu_2MnIn
(valency $Z_I = 3$) and $H_{hf} = +200$ kOe at Sn in
Cu_2MnSn ($Z_1 = 4$), and (b) on the magnetic charac-
ter of the matrix itself, e.g., $H_{hf} = -35$ kOe at Sn in
Pd_2MnSn, while $H_{hf} = +200$ kOe at Sn in Cu_2MnSn.
The other established fact is that when the Z-site ele-
ment changes from Cd to Te, the field systematically
increases its value from -215 kOe at the former to
$+848$ at the latter.

At present there exist two models, which fairly well
describe this trend. They are the Blandin-Campbell
model (BC),[7] based on the RKKY (Ruderman-
Kittel-Kasuya-Yosida) spin polarization approxima-
tion and the Jena-Geldart model (JG),[8] an extension
of the model introduced by Daniel and Friedel.[9]

These two models, however, are only able to ap-
proximately predict the trend in the systematics of
the hyperfine fields mentioned above, e.g., the field
at the In site in Cu_2MnIn has the following values:
-25, -170, and -93 kOe according to the BC
model, the JG model, and the experiment, respec-
tively.[10] They fail, however, to give quantitative
agreement with the experimental data (For compari-
son of the data with the predictions of these two
models see, e.g., Ref 10). Due to this situation the
models have not been distinguished experimentally
by studying the different types of Heusler alloys.

It would be of great importance to find such exper-
imental evidence, which would permit distinguishing
between the models or stating that none of them can
properly describe the data. For this purpose, we have
carried out a Mössbauer-effect study on
$Cu_2Mn_{1-x}Sn_x$ compounds. By choosing this particu-
lar series for systemtic study, (a) the nature of the
probe atom (Sn) remains constant, while (b) the
magnetic character of the matrix is varied by substi-
tuting one of its elements Al for the probe atom Sn.

In Sec. II, we make a comparison of the results ob-
tained with the predictions of the above models.

II. EXPERIMENTAL

A. Sample preparation

The samples were prepared by melting the constituents mixed in stoichiometric quantities in an electrical furnace, in vacuum. The final mass of each sample was about 15 g and the loss during the melting process was less than 0.4%. The purity of the elements used to prepare the compounds was at least 99.9%. The process of melting was carried out in alumina crucibles.

Having melted the constituents, they were annealed at 750 °C for 24 hours. The alloys were then powdered, annealed for the next 6 hours at 750 °C or less, depending on the melting point of the particular alloy (see the table below) and finally quenched into cold water.

x	Quenching temperature / °C /
0.05	750
0.10	750
0.15	750
0.25	650
0.50	650
0.75	630

All the samples, except the one with $x = 0.75$, were found by x-ray analysis to be single phases with the $L2_1$ structure. The sample with the greatest tin content had a small addition of the $B2$ structure (6% as revealed by the present Mössbauer study).

B. Measurement of the Mössbauer spectra

The Mössbauer spectra of the samples were registered at room temperature, using a constant-acceleration Mössbauer spectrometer and a 400-channel analyzer operating in the time mode. The samples were in the form of powder and contained approximately 1 mg of ^{119}Sn isotope per cm^2. A BaSnO$_3$ source of 2 mCi activity was used to provide a monoenergetic gamma rays. Each spectrum was collected within two days with statistics of about 3 million counts per channel. The absorption was about 1%. Calibration was carried out after each spectrum had been collected. As standards, iron foil and BaSnO$_3$ powder were used.

III. RESULTS AND THEIR DISCUSSION

A. Mössbauer spectra

The Mössbauer spectra of the compounds studied are presented in Figs. 1(a) and 1(b). One may note that their shape depends on their tin content and that they can be grouped into three types, according to the shape. The first type is represented by the spectra for $x = 0.05$, 0.10, and 0.15. They are characterized by two broadened absorption peaks corresponding to rather small velocities. The alloy containing $x = 0.25$ of tin represents the second type. The characteristic feature of its spectrum is that, in addition to the two peaks observed in spectra for smaller x, one can see the additional effect of higher velocity components on the baseline. Finally, the spectra for $x = 0.50$ and 0.75 form the third type, which can be characterized by two very broad peaks, corresponding to high velocities (the spectrum for $x = 0.75$ exhibits an additional paramagnetic peak).

The common feature of all the spectra is that the peaks are not well resolved. This indicates the existence of field distributions in these compounds.

B. Fit to the spectra

The Mössbauer spectra were fitted with two different methods—I and II. In method I it was assumed that the spectra are a superposition of a number of six-line patterns having different splittings, isomer shifts as well as statistical weights. The six-line patterns have been ascribed to different tin configurations. Figure 2 shows a unit cell of Cu$_2$MnAl$_{1-x}$Sn$_x$ compound with an Sn atom in the center (Cu atoms have been omitted for clarity). As can be seen it is possible to form 13 different configurations, i.e., the maximum number of the six-line patterns contributing to a final spectrum is 13.

It was also assumed that a change of the field and the isomer shift, caused by replacing an Al atom by an Sn one, is additive, i.e., if $H(0)$ is the field at Sn nuclei having no other Sn atoms within the first coordination sphere, then the field at Sn nuclei having m Al atoms substituted by Sn ones, $H(m) = H(0) + m\Delta H$, where $\Delta H = H(1) - H(0)$. A similar relation is valid for the isomer shift. The additivity assumption seems to be a reasonable one in view of a well-localized character of ferromagnetism in the Heusler alloys.

Method II was developed by Window [11] and fitting the working spectra according to it yields the field distributions and the average magnetic fields.

C. The results

1. The magnetic fields

The Mössbauer spectra of the studied compounds have been successfully fitted with both methods described in Sec. III B. The values obtained from the
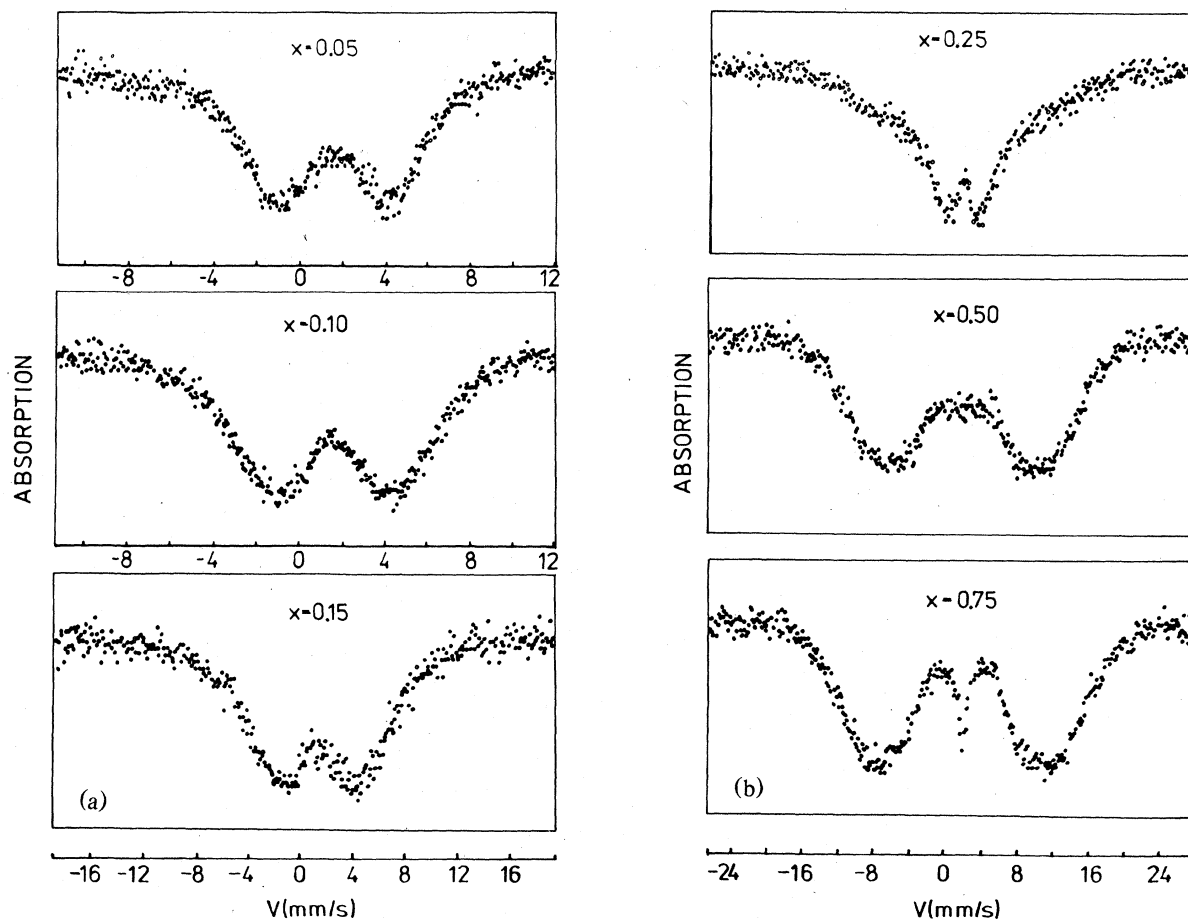
FIG. 1. (a) Room-temperature Mössbauer spectra of $Cu_2MnAl_{1-x}Sn_x$ for different tin concentration. (b) Room-temperature Mössbauer spectra of $Cu_2MnAl_{1-x}Sn_x$ for different tin concentration.

•=Mn   O=Al   ⊙=Sn
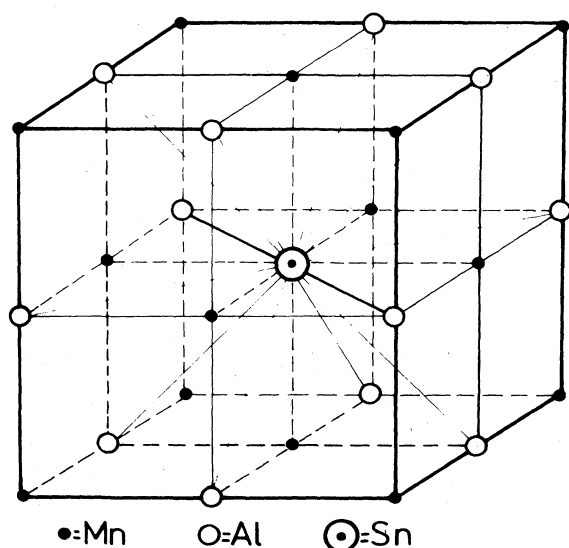
FIG. 2. Unit cell of $Cu_2MnAl_{1-x}Sn_x$ compound showing the relative configuration of the elements. Cu atoms have been omitted for clarity.

best-fit parameters are presented in Tables I and II. It can be seen that for the first three samples there are 8 different fields, while for the other three, all 13 possible configurations are present. It may be also noted that the field at the Sn nuclei depends on how many Al atoms have been substituted by Sn ones (namely, it increases by ~ 17 kOe per Sn atom). On the other hand, the field at Sn in a given configuration does not depend on tin concentration. This reflects a well-localized character of ferromagnetism in these compounds.

Taking the measured values of the fields $H(m)$, the average field $\bar{H}$ has been calculated for each of the studied samples, using the following formula:

$$\bar{H}(x) = \left[\sum P(m,x) H(m) / \sum P(m,x) \right], \qquad (1)$$

where $P(m,x)$ is the measured probability that m Al atoms have been substituted by Sn ones. X stands for tin content.

The values of the average fields obtained in this way are labeled as $\bar{H}_l$ and are displayed in Table I.

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TABLE I. Best-fit parameters describing the hyperfine magnetic fields in $Cu_2MnAl_{1-x}Sn_x$ compounds. $H(n)$ stands for the field at the Sn nuclei with n Al atoms being the nearest neighbors substituted by Sn atoms ($n = 1 \cdots 12$). $\overline{H}_I$ describes the average field obtained from method I, while $\overline{H}_{II}$ describes the average field obtained from method II. ΔH denotes a change of the field per one Sn atom and η is defined by Eq. (2). All the values of the fields are in kOe.

I	H(0)	H(1)	H(2)	H(3)	H(4)	H(5)	H(6)	H(7)	H(8)	H(9)	H(10)	H(11)	H(12)	$\overline{H}_I$	$\overline{H}_{II}$	ΔH	η
0.05	12.7	29.2	45.7	62.2	79.3	96.0	112.7	129.4	...	...	...	...	...	52.4	48.8	16.7	1.33
	±2.2	±3.1	±4.0	±5.0	±5.9	±6.8	±7.7	±8.6						±4.5	±2.5	±0.9	
0.10	19.4	35.5	51.6	67.7	83.8	99.9	116.0	132.1	...	...	...	...	...	52.7	59.7	16.1	0.27
	±4.8	±6.6	±8.4	±10.2	±12.0	±13.8	±15.6	±17.4						±8.5	±4.8	±1.8	
0.15	18.2	34.5	50.8	67.1	83.4	99.7	116.0	132.3	...	...	...	...	...	61.2	65.6	16.3	0.28
	±15.4	±16.9	±18.4	±19.9	±21.4	±22.9	±24.4	±25.9						±19.2	±4.0	±5.8	
0.25	17.5	34.6	51.7	68.8	85.9	103.0	120.1	137.2	154.3	171.4	188.5	205.6	222.7	94.0	86.5	17.2	0.26
	±3.4	±3.9	±4.5	±4.9	±5.4	±5.9	±6.4	±6.9	±7.4	±7.9	±8.4	±8.9	±9.5	±3.5	±5.3	±0.6	
0.50	7.8	25.0	42.2	59.4	76.6	93.8	111.0	128.2	145.4	162.6	179.8	197.0	214.2	137.5	140.7	17.2	0.20
	±11.3	±12.4	±13.5	±14.6	±15.7	±16.8	±17.9	±19.0	±20.1	±21.2	±22.3	±23.4	±2.45	±19.4	±2.6	±1.1	
0.75	6.3	24.6	42.9	61.2	79.5	97.8	116.1	134.4	152.7	171.0	189.3	207.6	225.9	159.5	164.9	18.3	−0.11
	±11.5	±12.5	±13.5	±14.5	±15.5	±16.5	±17.5	±18.5	±19.5	±20.5	±21.5	±22.5	±23.5	±20.4	±5.1	±1.0	

They are also illustrated as full circles in Fig. 3. To see how much the actual substitution differs from the randomness, the average field $\overline{H}_R$ has been calculated, using formula (1) with $P(m,x)$ values taken from the binomial distribution. The result of this calculation is shown in Fig. 3 as a full line. One can readily see that up to $x = 0.50$ the measured average field is greater than the one expected in the case of randomness. The biggest difference is for $x = 0.05$, when

the parameter η, defined as follows:

$$\eta = \frac{\overline{H}_I - \overline{H}_R}{\overline{H}_I} \qquad (2)$$

is equal to 1.33. For the sample with $x = 0.75$, $\overline{H}_I < \overline{H}_R$. The results obtained with method I were

TABLE II. Best-fit parameters describing the isomer shifts in $Cu_2MnAl_{1-x}Sn_x$ compounds. $I(0)$ stands for the isomer shift ascribed to an Sn atom with no Sn atoms in the first coordination shell, ΔI is a change of the isomer shift per one Sn atom, $\overline{IS}$ describes the average isomer shift, and Γ stands for the linewidth of the outermost line.

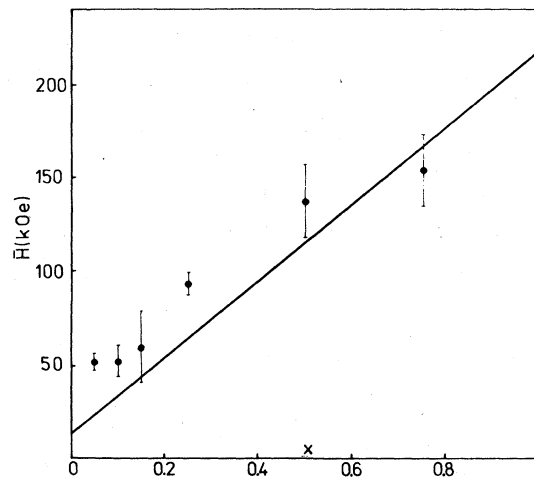| x	I(0) (mm/s)	ΔI (mm/s)	$\overline{IS}$ (mm/s)	Γ (mm/s)
0.05	1.72 ±0.05	−0.003 ±0.019	1.71 ±0.10	2.04 ±0.47
0.10	1.76 ±0.03	−0.005 ±0.014	1.75 ±0.06	2.17 ±0.37
0.15	1.81 ±0.06	−0.011 ±0.022	1.78 ±0.12	2.76 ±0.84
0.25	1.85 ±0.04	−0.015 ±0.010	1.79 ±0.10	1.68 ±0.20
0.50	1.73 ±0.11	−0.014 ±0.011	1.62 ±0.19	2.24 ±0.51
0.75	1.74 ±0.15	−0.005 ±0.011	1.68 ±0.19	2.25 ±0.45

FIG. 3. Average hyperfine field as a function of tin content is presented. The full line shows its calculated values, assuming a random substitution of Al atoms by Sn ones. The full circles stand for the experimental data.
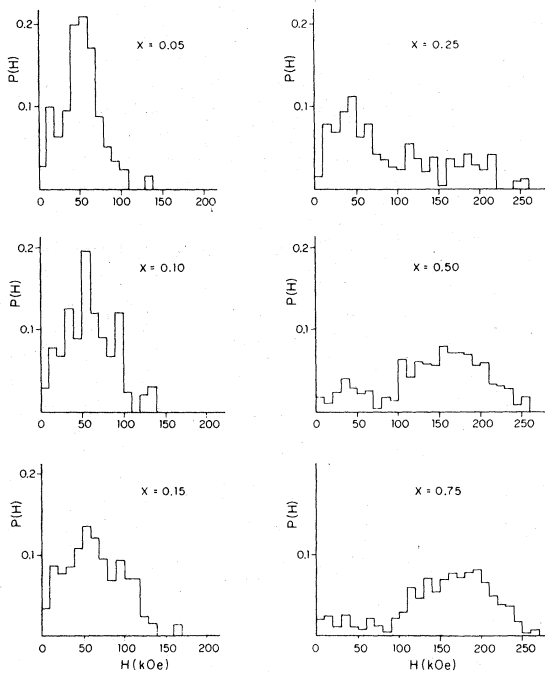
FIG. 4. Field distributions obtained from the Mössbauer spectra shown in Figs. 1(a) and 1(b).

supported by fitting the spectra using the independent method II. This method gave the field distributions as well as the average fields. The former are presented in Fig. 4, while the latter are collected in Table I and labeled as $\bar{H}_{II}$.

2. The isomer shifts

The values of the parameters describing the isomer shifts are presented in Table II. They are given relative to the center of an iron foil spectrum. $I(0)$ stands for the IS of those Sn atoms which have no Sn atoms in the first coordination shell, $\Delta I = I(1) - I(0)$, and $\overline{IS}$ is the average value of the IS as obtained from the following formula:

$$\overline{IS} = \left[\sum P(m,x) I(m) / \sum P(m,x) \right] . \quad (3)$$

One can see that both $I(0)$ and IS depend slightly on tin content, i.e., their values increase with increasing tin concentration up to $x = 0.25$. At this concentration the two quantities reach their maxima, to decrease for higher-x values. The values of ΔI are negative and are rather constant to within the errors. This means that the density of s-like electrons within the Sn nuclei decreases when the Al atoms are substituted by Sn ones.

D. Comparison of the obtained values for the hyperfine field with the models predictions

1. Blandin-Campbell model

This model formulated by Blandin and Campbell,[7] representing a modification of the Caroli-Blandin model,[6] leads to the following formula for the hyperfine field:

$$H_{hf} = -\frac{J\Omega_0 K}{8\pi\mu_B} \sum_{i/1}^{N} \langle s_z(R_0^i) \rangle \frac{\cos(2k_F R_0^i + 2\delta_0)}{(R_0^i)^3} , \quad (4)$$

where J is the exchange integral, Ω_0 is the atomic volume, K is the Knight shift, $<s_z>$ is the impurity spin, k_F stands for the Fermi wave-vector, $2\delta_0 = \frac{1}{4}(\pi Z_{sc})$ is the impurity phase shift, Z_{sc} is the excess charge to be screened, and R_0^i stands for the distance to the ith impurity. This formula was used to calculate H_{hf} as a function of x for the compounds studied. It was assumed that J, Ω_0, K, s_z, k_F, $2\delta_0$ change linearly between $x = 0$ and $x = 1.0$ (for $x = 0$ and $x = 1.0$ the experimentally determined values for all these quantities except J were used). The latter was determined from formula (4), using the known values of $H_{hf} = +200$ kOe for Cu_2MnSn, which gave the value of $J(x = 1)$, while the value of $J(x = 0)$ was determined, assuming that for $x \rightarrow 0$

$$H_{hf} = \begin{cases} +200 \text{ kOe[curve } a] \\ +68 \text{ kOe[curve } b] , \\ -68 \text{ kOe[curve } c] \end{cases}$$

[for curves (b) and (c) see Ref. 12]. All these three predictions are illustrated in Fig. 5. The summation has been done up to $N = 3$.
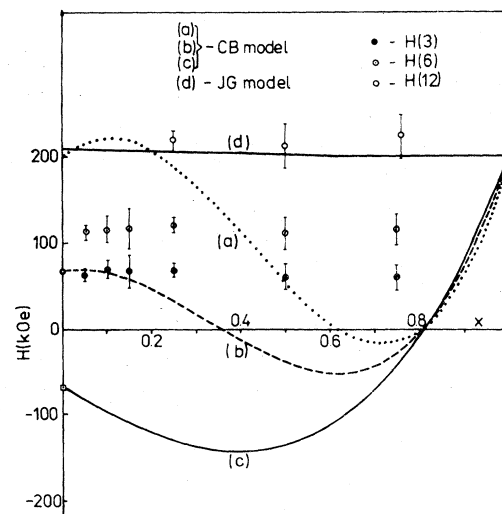

FIG. 5. Measured hyperfine fields vs tin concentration together with the predictions based on the JG model—curve d as well as on the BC model—curves $a-c$.

2. Jena-Geldart model

The authors of this model derived the following formula for the field:

$$H_{\text{hf}} = -\frac{8}{3}\pi\mu_B\alpha^2 P(0) , \tag{5}$$

where $\alpha^2 P(0)$ is the local spin polarization depending on k_F, Z_{sc}, and a_0 (a_0 being the lattice parameter). The numerical values of the field at Sn sites versus x were calculated using a linear approximation for $k_F(x)$, $Z_{sc}(x)$, and $a_0(x)$. The result of this calculation is presented together with the predictions by BC model in Fig. 5. One may readily see, that contrary to CB-model prediction, the JG model gives an almost constant field at Sn site. This shows that, in fact, the predictions of these two models are different, when applying them to a given system.

Now, what about the experimental results? As it was presented in Secs. III A—III C 1, each of the studied compounds is characterized by at least 8 sites having different field values. This makes it difficult to compare these results directly with the models. On the other hand, however, this nonhomogeneity of the compounds cannot be predicted or explained by the models. As for the JG model, its basic assumption is the existence of a uniformly polarized magnetic background. This means, that this model predicts only one value of the field at a given impurity situated in this background. This, however, remains in disagreement with the present results, which show that there is a possibility of coexistence of different fields at Sn sites in a given compound. Thus, this model fails to describe the fields observed in $Cu_2MnAl_{1-x}Sn_x$ alloys. Concerning the CB model, it predicts a pronounced dependence of the field at the Sn site on tin concentration. This also is not what has been observed for the studied samples, where the field is a quantity well defined for a given Sn configuration and its value does not depend on Sn content.

Then, how can one explain the results which have been observed? To try to give an explanation, let us first of all note that the most characteristic feature determining the field at an Sn site is the fact, that its value depends only on how many Sn atoms are situated in the first coordination sphere (relative to Sn). The more of them there are, the greater the value of the field. Each Sn atom added to this sphere increases the field by ~ 17 kOe. This indicates that there is a direct connection between the number of Sn atoms and the value of the field. Next, let us note that the field, for a given configuration, does not depend on tin concentration in the compounds. This points to a strong local character of the studied phenomena, i.e., a local character of the spin polarization, particularly at a Sn site. Such polarization might be caused, for example, by a transfer of some amount of s-like electrons from Sn atoms to a Cu one, which is the only atom among the ones constituting the sytem, possessing one valence electron (while the other have two). However, to cause the spin polarization by this mechanism, it would be necessary that the number of s electrons with spin-up and with spin-down orientation are not equal. In particular, only spin-up or spin-down electrons may be involved in this process. This may be deduced from the fact that substitution of the more Al atoms by Sn ones, increases the value of the field, which is positive (the sign of the field has been determined for $x = 0.05, 0.10, 0.15$, and 0.25). This means that less spin-up s-like electrons has to be transferred from each Sn atom.

Such electron transfer phenomenon should be reflected in a decrease of the s-like charge density at the Sn site, which in turn should change the isomer-shift value. Hence, the 13 tin configurations should have different values of IS. Our results presented in Table II supply firm evidence for that, i.e., one observes that the isomer shift for a particular configuration of atoms depends on a number of Sn atoms, which have been substituted for the Al ones. On the average, the IS decreases by 0.09 mm/s per Sn atom substituted.

The evident dependence of both the hyperfine field and the isomer shift on the number of Sn atoms implies, that substitution of Al atoms by Sn ones causes changes both in spin and charge densities in a site occupied by the probe Sn atom. Furthermore, because the field increases, while the isomer shift decreases with the increasing number of tin atoms, the polarization of electrons increases and the charge density decreases. This seems to be a reasonable evidence for spin and charge transfer from Sn atoms.

One can estimate the lower limit of the amount of s-like electrons transferred, assuming the same proportionality constant as did other authors, see Ref. 10. They showed that a change of 0.04 electrons/μ_B caused a change of $H_{\text{hf}} \approx 155$ kOe. In the compounds studied one Sn atom increased the field by ~ 17 kOe. This is equivalent to the transfer of 0.004 s-like electrons with spin down. Since in the $Cu_2MnAl_{1-x}Sn_x$ system there are about two s-like electrons per atom, then the substitution of one Al atom by an Sn one causes $\sim 0.2\%$ change in spin density at the site occupied by the probe atom.

IV. SUMMARY AND CONCLUSIONS

To summarize, we would like to emphasize that the results obtained by the present investigation for $Cu_2MnAl_{1-x}Sn_x$ compounds have enabled us to state that these compounds exhibit a very localized character of ferromagnetism. This feature cannot be explained either by the CB model or by the JG model.

Furthermore, the results are quite different from the ones obtained for Sn atoms substituted into In sites in the Cu_2MnIn alloy, where the field at the Sn site was determined to be equal to $+196$ kOe[3], although the Sn content was only 1 at.%. To explain this value, one has to suppose that the compound was completely ordered or that it exhibits a completely different character when changing Al by In, namely, the itinerant one. It seems that the former is very unlikely, due to the low-Sn concentration, so the probability of forming only the configuration with 12 Sn atoms should be very small. Thus the latter might be the case. If so, the group of compounds known as the Heusler alloys, exhibit different aspects of ferromagnetism, depending on the elements constituting these systems. Probably all the alloys could be classified into three groups, according to whether their ferromagnetic behavior exhibits: (a) localized; (b) itinerant; (c) localized-itinerant character. Future study on these alloys should concentrate on trying to establish if this hypothesis is true, and if so, to establish the members of each of the group mentioned above. This may be done by systematic study of each of the known Heusler alloys upon changing content of one of the constituting elements, as it was done in the present investigation.

Such a classification, if successful, would prove that it is not possible to describe all these systems with only one model and would show which compounds need localized, or itinerant, or localized-itinerant description. This, in connection with the properties of the elements used to build up these compound, would probably help to clear our understanding of the phenomenon of ferromagnetism.

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