Magnetic Moment and Curie Temperature of Amorphous (Co_<1-x>Mn_x)_<100-y>B_y Alloys

Magnetic Moment and Curie Temperature of Amorphous $(Co_{1-x}Mn_x)_{100-y}B_y$ Alloys *

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Synopsis

Measurements have been made of the magnetic moment and the Curie temperature of Co-Mn-B amorphous alloys with wide Mn and B concentrations. The magnetic moment decreases monotonically with increasing Mn concentration for the alloys with low B concentrations, while it increases initially and then decreases for the alloy with high B concentrations. Ferromagnetic moment vanishes at about Mn/(Co + Mn) = 0.4 irrespective of B concentration. The Curie point also reaches zero absolute temperature near the same Mn concentration. The upwards convex curves of magnetic moment vs. Mn concentration in the present amorphous alloys are very different from that of the crystalline Co-Mn alloys, but rather similar to that of the $(Co, Mn)_2B$ intermetallic compound. These composition dependences are analyzed in terms of the local environment effect.

I. Introduction

The magnetic properties of various metal-metalloid amorphous alloys have been investigated. It has been found that the ferromagnetic behaviour for the 3d-metal-metalloid amorphous alloys are similar to those of the corresponding crystalline binary (or ternary alloys. Mizoguchi[1)] has shown that the composition dependence of the magnetic moment of the 3d-metal-metalloid amorphous alloys have the same trend to the well known Slater-Pauling curve even though the curves for amorphous alloys locate slightly low position compared to the Slater-Pauling curve. This is reasonable because metal atoms in the amorphous structure are dense randomly packed and the exchange interaction is important between nearest neighbour atoms and therefore

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the lack of structure scarcely influences the magnitude of the magnetic moment. Simply the composition dependences of the magnetic moment for amorphous alloys are sometimes well explained by the rigid band model under consideration of electron transfer from metalloid atoms. The Slater-Pauling curve has several branches which consist of several binary alloy systems containing mainly Mn or Cr atom because of its antiferromagnetic coupling or disappearance of ferromagnetism. Co-Mn binary alloys belong to one of such branches in which the magnetic moment decreases nearly linearly as increasing Mn concentration as shown in Fig. 1. While as shown by Mizoguchi et al.[1] the trend of the composition dependence of the magnetic moment of Co-Mn-P-B amorphous alloys is different from that of crystalline Co-Mn alloys, but it is rather similar to that of $(Co, Mn)_2B$ intermetallic compound concerning that both the Co-Mn-P-B and the $(Co, Mn)_2B$ have a broad maximum on their curves as shown in the same figure.

Wohlfarth[2] suggested recently that the curve of the composition dependence of the magnetic moment for two crystalline borides (TM, $TM)_2B$ and (TM, TM)B (where TM denotes a transition metal) behaves as if the Slater-Pauling curve shifts by 1 and 2 effective atomic number, respectively. This behaviour also can be expected to hold for the amorphous alloy because the trend of the composition dependence of the magnetic moment of the amorphous Co-Mn alloys containing metalloid atoms is rather similar to that of the crystalline Ni-Mn binary alloys, which may imply that the effective atomic number of such an amorphous alloy shifts by some fractions. Thus, it is interesting to investigate the B dependence of the magnetic moment for the several Co-Mn amorphous alloys.

The present paper is an extension of our previous paper[3], where we have investigated the influences of Mn and B concentrations on the magnetic moment of Co-Mn-B amorphous alloys, and also analyzed the change of the magnetic moment as changing Mn and B concentrations in terms of the local environment model which has been constructed by Kouvel[4]. In the present paper we have further extended our discussion about the interpretation of the behaviour of the Mn composition dependence of the magnetic moment for the present amorphous alloys. And we have also discussed the composition dependence of the Curie temperature.

II. Experimental procedure

Amorphous alloy ribbons $(Co_{1-x}Mn_x)_{100-y}B_y$ $(0 \leq x \leq 0.5,\ 11 \leq y \leq 33)$ were produced by a rapid quenching method from the melt using a single

roller technique. The specimens thus obtained were about 0.5 ∿ 1 mm width and 20 ∿ 30 μm thickness. All the specimens were confirmed to be in the amorphous state by X-ray Debye-Scherrer method.

Magnetic moment at 4.2K and temperature dependences of magnetization and Curie temperature were measured by using a conventional magnetic balance with applying magnetic field up to 8000 Oe.

Ⅲ. Results and Discussions

Fig. 2 shows the temperature dependence of the magnetization for the amorphous $(Co_{1-x}Mn_x)_{80}B_{20}$ ($x = 0.1 \sim 0.4$) alloys. As shown in this figure, the magnetization decreases monotonically as increasing temperature from 4.2K except for the case of $x = 0.4$. In the high temperature region (above 700K), however, the crystallization occurs and then the magnetization curve becomes very complicated. Fig. 3 shows such a complicated behaviour of the magnetization vs. temperature in high temperature range for the samples $(Co_{0.8}Mn_{0.2})_{100-y}B_y$ ($y = 12$, 20 and 28). As Takahashi et al.[5] already suggested, the

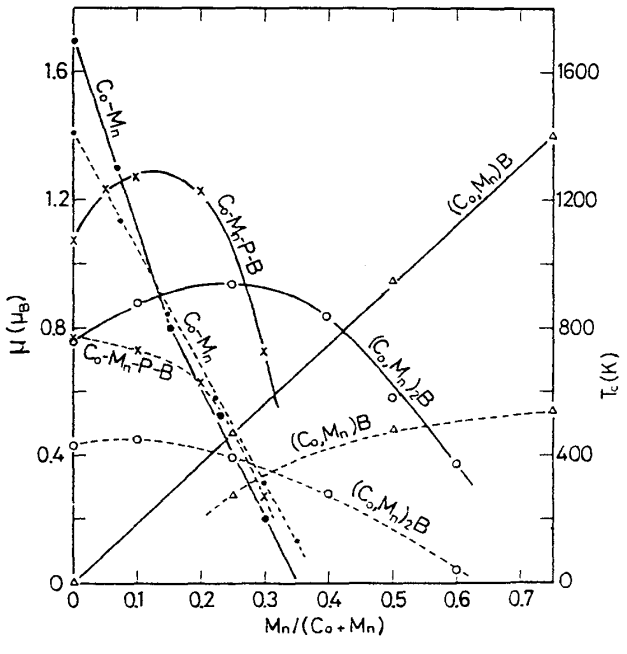

Fig. 1 Mn composition dependence of magnetic moment (full lines) and Curie temperature (broken lines) for various Co-Mn alloys and compounds.

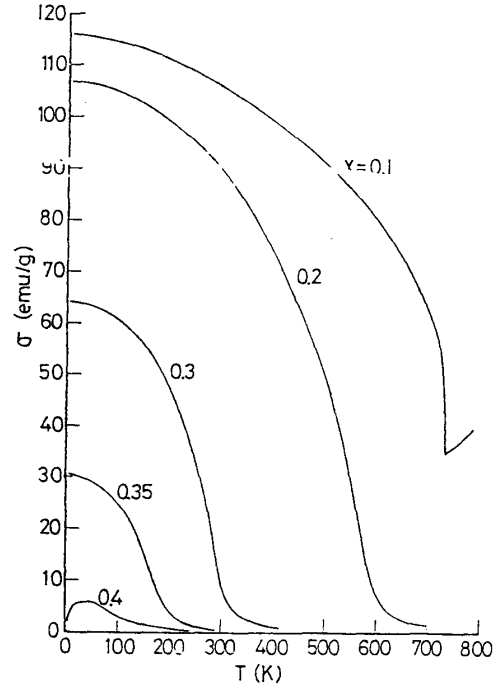

Fig. 2 Temperature dependence of the magnetization (σ) for amorphous $(Co_{1-x}Mn_x)_{80}B_{20}$ alloys.

crystallization process of the amorphous Co-B alloys are not simple because a sample takes a mixed structure of Co, Co_3B and Co_2B depending on the temperature. In the present amorphous alloys, the crystallization process is further complicated because of containing two magnetic elements, that is, after crystallization, the sample may take a mixed structure composed by Co-B, Mn-B and Co-Mn-B compounds. In the low temperature region, the $(Co_{0.6}Mn_{0.4})_{80}B_{20}$ alloy behaves differently from other alloys as shown in Fig. 2. This behaviour of the magnetization vs. temperature is rather similar to that of amorphous Ni-Mn-Si-B alloys[6]. Fig. 4 shows the temperature dependence of the magnetization for the samples $(Co_{0.6}Mn_{0.4})_{100-y}B_y$ (y = 12, 20 and 28). In the figure, $(Co_{0.6}Mn_{0.4})_{88}B_{12}$ behaves ferromagnetically down to low temperature (about 10K) but below 10K the magnetization suddenly drops. This behaviour seems to be explained that the sample takes an another magnetic state at a very low temperature. The magnetization vs. temperature curves for the samples y = 20 and 28 which are nearly same each other suggest that both samples are not ferromagnetic but rather mictomagnetic at low temperatures.

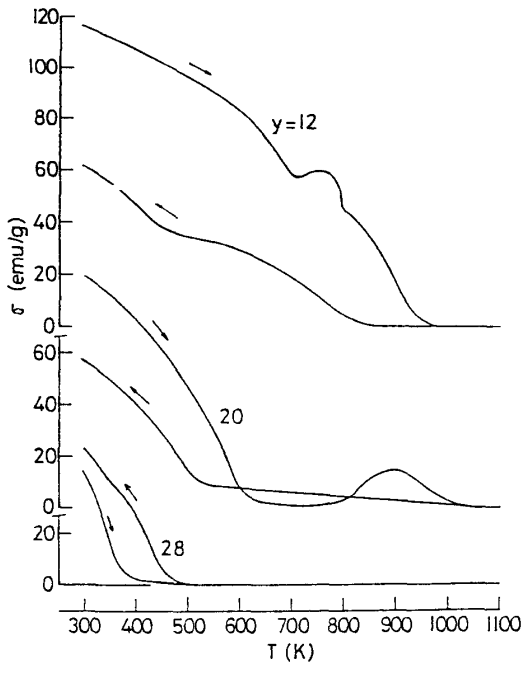

Fig. 3 Temperature dependence of the magnetization for amorphous $(Co_{0.8}Mn_{0.2})_{100-y}B_y$ (y = 12, 20 and 28) alloys.

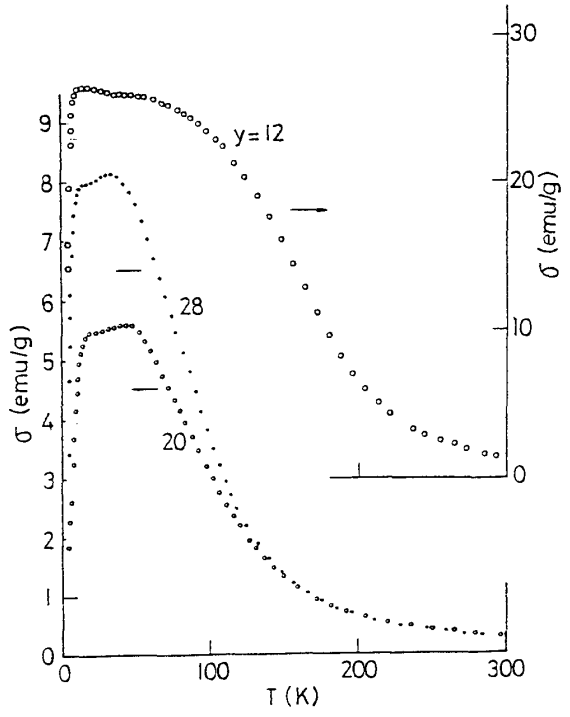

Fig. 4 Temperature dependence of the magnetization for amorphous $(Co_{0.6}Mn_{0.4})_{100-y}B_y$ (y = 12, 20 and 28) alloys.

Figs. 5 and 6 show the Mn composition dependence of the magnetic moment (μ) and the Curie temperature (T_C), respectively, where the values at x = 0 in both figures have been reffered from the data of Watanabe et al.[7] and of Takahashi et al[5]. It has to be noted that as the present sample has a crystallization temperature around 700K, all the Curie points located above 700K are obtained by extrapolation. From these figures it is easily seen that the curves of Mn composition dependence of the magnetic moment are upwards convex for all B concentrations. Besides an interesting fact is that as increasing the Mn composition the curves for y = 28 and 32 initially slightly increase. As Mn concentration further increases the magnetic moment quickly decreases to zero at about x = 0.4, regardless of B concentration. The same trend is also shown in the Mn composition dependence of the Curie temperature, that is, Curie temperature also decreases to zero absolute temperature near x = 0.4, irrespective of B concentration.

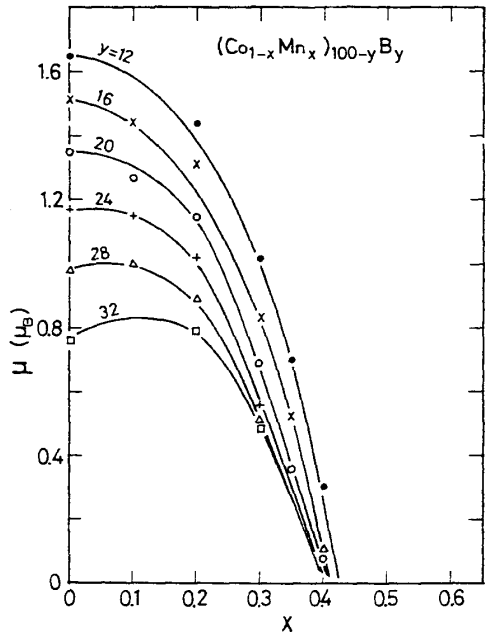

Fig. 5 Mn composition dependence of the mean magnetic moment (μ) per [Co, Mn] atom at 4.2 K for the amorphous $(Co_{1-x}Mn_x)_{100-y}B_y$ alloys.

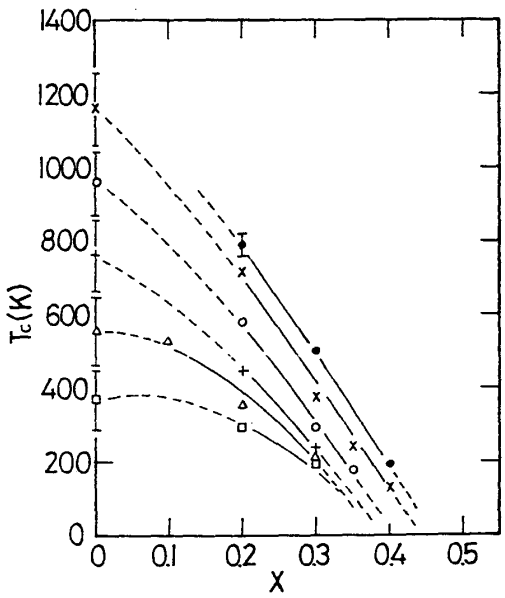

Fig. 6 Mn composition dependence of the Curie temperature (T_C) for the amorphous $(Co_{1-x}Mn_x)_{100-y}B_y$ alloys.

These results point out some characteristics as follows:

1) The upper convex curves of the magnetic moments vs. Mn concentration for the present amorphous alloys are quite different from a linear change in μ vs. x for the corresponding crystalline $Co_{1-x}Mn_x$ alloy (Fig. 1). The slight increasing behaviour in μ with increasing x for the present amorphous alloys with high B content (y = 28 and 32)

in the Co rich side is rather similar to the Mn composition dependence of μ for the $(Co_{1-x}Mn_x)_2B$ intermetallic compound as shown in Fig. 7. This implies that the local environment effect of Mn atoms is effective to explain the initial increasing of the magnetic moment of the present amorphous alloy.

2) Compared with the crystalline $(Co, Mn)_2B$ compound, the maximum value of the magnetic moment for the present amorphous alloy with $y = 32$ is smaller than that for the compound. And the critical Mn concentration of $x = 0.4$ for the present amorphous alloys is lower than that for the same compound (about $0.6 \sim 0.7$). These differences may be attributed to the fact that the local environment of constituent atoms is different between an amorphous state and a compound state.

3) Both the magnetic moment and the Curie temperature drop to zero at about $x = 0.4$ irrespective of B concentration. This critical behaviour suggests that as increasing Mn concentration the number of Mn-Mn pairs which have negative exchange interactions increases and then the compensation of the total exchange interactions takes place at a certain Mn concentration, which may be depend on B concentration. But it should be noted that the critical Mn concentration of the present amorphous alloys is not so much different from that of the crystalline Co-Mn binary alloy ($x \simeq 0.35$, see Fig. 1) in spite of the large difference of the Mn composition dependence of the magnetic moment between both the alloys.

Above characteristics lead us to the following considerations: In order to analyze the magnetic properties of the present amorphous alloys, the local environment effect of magnetic atoms must be taken into account. Because the local environment model sometimes gives a good approximation to explain such a magnetic behaviour as mentioned above. The application of this model is already done for several crystalline intermetallic compounds containing Mn atoms such as $(Co, Mn)_2B$ by Kadomatsu et al.[9] and $(Fe, Mn)_2B$ by Shigematsu[10] in order to explain the Mn composition dependence of the magnetic moment. Kadomatsu has well explained the composition dependence of the magnetic moment for $(Co, Mn)_2B$ intermetallic compound using the model.

According to Kadomatsu's expression, mean magnetic moment $\mu(x)$ of $(Co_{1-x}Mn_x)_2B$ compound per metal atom can be exhibited as

$$\mu(x) = \sum_{n=0}^{N} \frac{(N-n)\mu_{Co} + n\mu_{Mn}}{N} \cdot P(n, x)$$

where $P(n, x) = {}_NC_n x^n (1-x)^{N-n}$ is a binomial distribution function which is the probability of finding a Mn atom at x, N is the number of near neighbour metal atoms and μ_{Co} and μ_{Mn} are the magnetic moment

of Co and Mn atoms, respectively.

Now we use the same expression as Kadomatsu's based on the local environment model in order to obtain the Mn composition dependence of the magnetic moment of the present amorphous alloys. The values of μ_{Co} are deduced by Watanabe's value[7] in Fig. 5. And the value of μ_{Mn} is determined by extraporation of initial slope of μ vs. x curve to x = 1 in Fig. 5. These values of μ_{Mn} thus obtained are shown in Fig. 8 which also include the μ_{Mn} values of the two compounds, MnB[8] and Mn_2B[9].

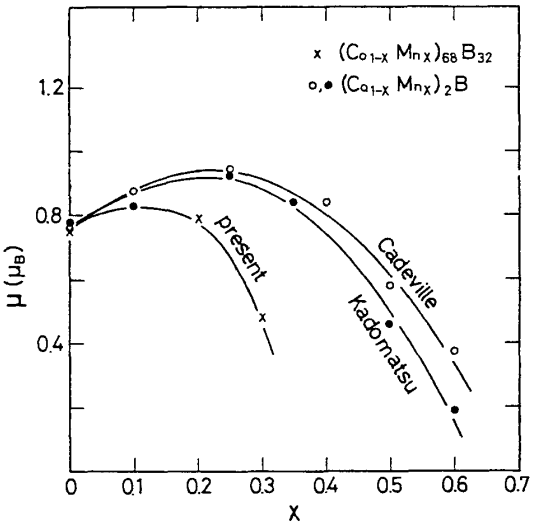

Fig. 7 Comparison between mean magnetic moments per [Co, Mn] for the amorphous alloys $(Co_{1-x}Mn_x)_{68}B_{32}$ and for the intermetallic compound $(Co_{1-x}Mn_x)_2B$ after Cadeville et al.[8] and Kadomatsu et al.[9]

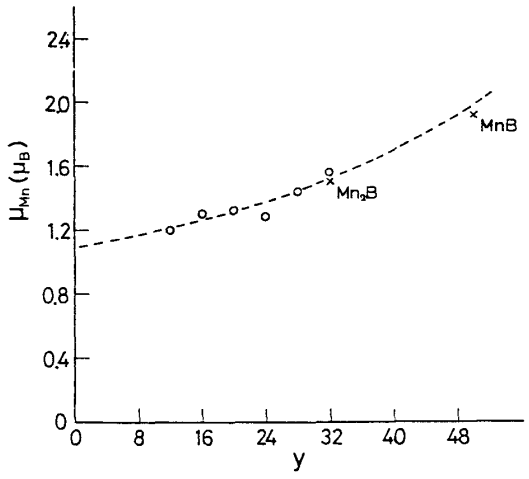

Fig. 8 Extrapolated values of the magnetic moment of Mn(μ_{Mn}) as a function of B concentration.

The calculation was done under the following assumptions:

a) Each metal atom has 12 near neighbours (N = 12) on the average. The contribution of each neighbour to the magnetic moment is same, regardless of the distance between the central atom and the surrounding atoms.

b) The coupling of the magnetic moment is ferromagnetic between Co-Co and Co-Mn, and antiferromagnetic between Mn-Mn.

c) When a central metal atom under consideration is surrounded by more than n_0 Mn neighbours, it loses the ferromagnetic moment or couples antiferromagnetically with neighbour atoms according as the central atom is Co or Mn. Therefore the summation in the above equation must end at $n = n_0 - 1$.

d) The values of μ_{Co} and μ_{Mn} do not change even if Mn concentration changes.

The assumption (a) is supported by the fact that many experimental results on the structure of metal-metalloid amorphous alloys suggest that the coordination number of near neighbour metal atom is close to 12[11]. And (b) may be reasonable in the present case, because if we take a negative coupling between Co and Mn atoms the calculated curves of $\mu(x)$ would not explain the experimental upward convex curves. (Concerning to the sign of Co-Mn coupling, we will discuss later). Kadomatsu et al.[9] have already obtained a positive value of the Co-Mn coupling in the $(Co, Mn)_2B$ compound by using the pair interaction model.

One of the results of the calculation using above equation is illustrated in Fig. 9 for the case of $y = 20$. In the figure it is clearly shown that experimental points lie close to $n_0 = 4$ line. We also obtained the best fit curve for other B-concentration alloys with $n_0 = 4$. The results of calculation in the case of $n_0 = 4$ are illustrated in Fig. 10. The experimental results of the change of magnetic moments vs. Mn concentration can be qualitatively explained in terms of these calculated curves. This implies that the value $n_0 = 4$ is reasonable in the present amorphous alloys. The present value $n_0 = 4$ is rather smaller than $n_0 = 6$ for $(Co, Mn)_2B$ compound which has been deduced by Kadomatsu et al[9]. This difference may be attributed to the difference of the local environment structure of the array of atoms between in the present amorphous alloy and in the $(Co, Mn)_2B$ compound.

Now we turn to our discussion for the composition dependence of the Curie temperature of the present amorphous alloys. The simplest approximation to analyze it is the pair interaction model[12] where the Curie temperature is determined by the sum of nearest neighbour pair interactions, which is expressed as follows:

$$T_C = P_{AA}T_{AA} + P_{AB}T_{AB} + P_{BB}T_{BB}$$

where P_{AA}, P_{AB} and P_{BB} are the relative number of A-A, A-B and B-B metal pairs, and T_{AA}, T_{AB} and T_{BB} are the exchange interaction energy $(-2J_{ij}S_iS_j)$ in unit of degree between A-A, A-B and B-B, respectively. So we rewrite the above equation in the case of present alloy as follows:

$$T_c(x, y) = (1-x)^2T_{CoCo}(y) + 2x(1-x)T_{CoMn}(y) + x^2T_{MnMn}(y)$$

Now, we estimate these interaction energys very roughly as a

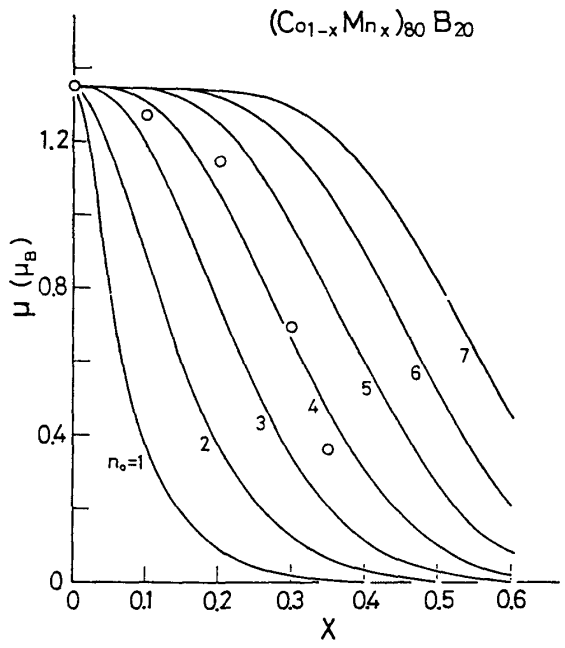

Fig. 9 Calculated curves of mean magnetic moment for the amorphous $(Co_{1-x}Mn_x)_{80}B_{20}$ alloy. Circles show the experimental results.

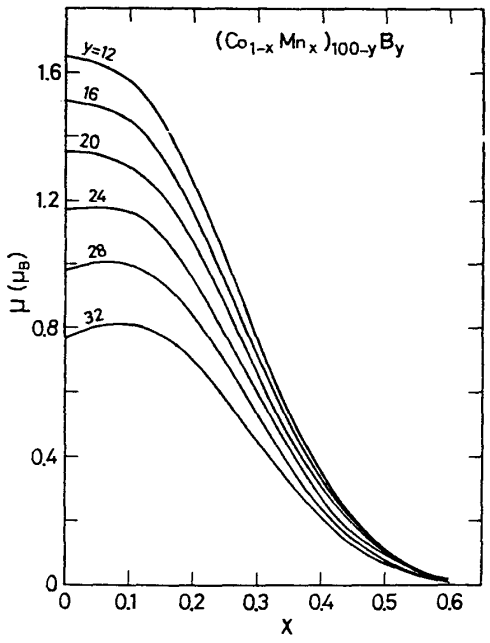

Fig. 10 Calculated curves of $n_0 = 4$ based on the local environment model for the amorphous $(Co_{1-x}Mn_x)_{100-y}B_y$ alloys.

function of B concentration using the experimental results. For y = 0, we used the data of Takahashi et al.[5], and also in the high temperature region we deduced T_C by extrapolating their data to that region where errors are estimated about $T_C \pm 100K$.

The result is shown in Fig. 11. Because of a scant experimental points and the extrapolated values in high temperature region, the result are very scattered for T_{MnMn}. In this figure the Co-Co interaction is positive and decreases as B concentration increases (T_{CoCo} (y) is equal to the Curie temperature of $Co_{100-y}B_y$), while Mn-Mn interaction seems to be nearly constant and takes very large negative value irrespective of B concentration. But because of the large ambiguity (which appears in the figure by error bar), it can not be confirmed whether $T_{MnMn}(y)$ goes to positive direction or not, or keep constant. The T_{CoMn} interaction is small and positive for all B concentrations and roughly $T_{CoMn}(y)$ increases slightly as increasing B concentration. As discussed above, these positive values are reasonable to explain the upper convex curve of Mn composition dependence of the magnetic moment in Fig. 5. That is, the results are consistent with the composition dependence of the magnetic moment.

Thus, as discussed before, we have attempted to explain the Mn composition dependence of the magnetic moment by using the local

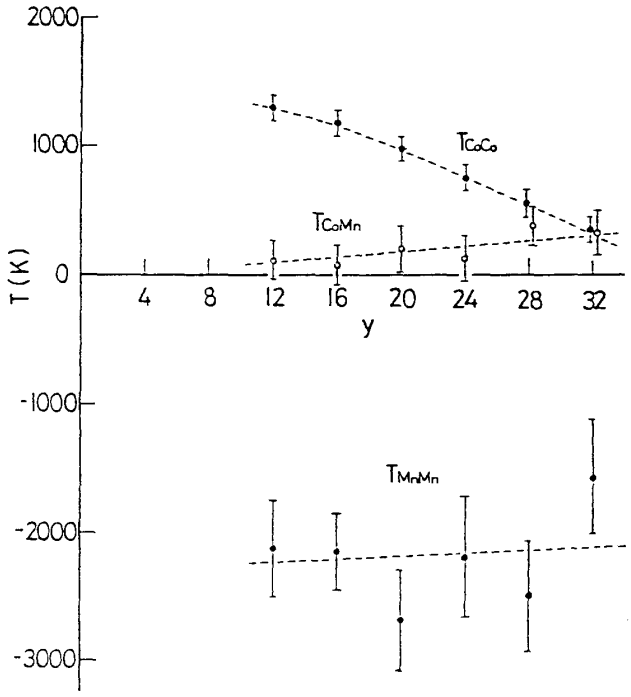

Fig. 11
Calculated values of T_{CoCo}, T_{CoMn} and T_{MnMn} as a function of B concentration for the amorphous $(Co_{1-x}Mn_x)_{100-y}B_y$ alloys.

environment model. The basic magnetic properties of the present amorphous $(Co_{1-x}Mn_x)_{100-y}B_y$ alloys may be understandable qualitatively within the scope of the local environment model and the pair interaction model. As shown in Fig. 7, both the magnetic moment and the Curie temperature in the present amorphous $(Co_{1-x}Mn_x)_{68}B_{32}$ alloys dropped to zero with less Mn concentration than in the $(Co_{1-x}Mn_x)_2B$ compound. The reason is a difference of local environment structure between present amorphous alloys and $(Co, Mn)_2B$ compound. In other words to say, the couplings between Co-Co, Co-Mn and Mn-Mn are different between both the materials. (In the case of $(Co_{1-x}Mn_x)_2B$, $T_{CoCo} \simeq 430K$, $T_{CoMn} \simeq 600K$ and $T_{MnMn} \simeq -930K$). But detailed discussion about the information concerning to the individual constituents must be necessary in future.

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