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Concentration dependence of the Co moment in amorphous alloys of Co with Y, La, and Zr

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The concentration dependence of the Co moment has been measured in amorphous $Y_{1-x}Co_x$, $La_{1-x}Co_x$, and $Zr_{1-x}Co_x$ alloys ($0.33 \leq x \leq 0.88$). For the amorphous alloy systems the concentrations of Y, La, or Zr at which the Co moment disappears is much higher than for the crystalline systems. Furthermore the critical concentration is the same for Y and La ($1-x \approx 0.5$) but lower for Zr ($1-x \approx 0.4$). The result that Y and La yield similar data indicates that the size of the nonmagnetic atom does not play a significant role in the magenetic properties. This is in contrast to the results for amorphous YFe and LaFe alloys. The lower critical concentration for the Zr alloys suggests a charge-transfer mechanism for the reduction of the Co moment upon alloying. The data were found to fit a simple charge-transfer model in which Y or La contributes about 1.4 electrons to the Co *d* states while Zr contributes 2.2. However, it was also observed that the Co moment was proportional to $(x-x_0)^{1/2}$, where x_0 is the critical concentration of Co, and that the Co-Co exchange constant was independent of concentration. These latter results suggest that the Co moments are quite localized in the amorphous alloys.

I. INTRODUCTION

Recent developments in amorphous magnetic materials, particularly those alloys containing rare earths (R) and transition metals (M) have drawn considerable attention.[1-6] The R-M alloys present a convenient opportunity to study magnetic order in structurally amorphous materials because they are easily produced, and because the possible combinations of R and M constituents and the large range in x for $R_{1-x}M_x$ alloys include very diverse types of magnetic behavior. In addition, the crystalline R-M alloys exist in a number of different compositional phases. This allows the direct comparison of the magnetic behavior of amorphous alloys to the behavior of corresponding crystalline compounds. Previous studies have more often been concerned with amorphous R-Fe alloys where the variety of magnetic phenomena observed is richer and, perhaps, more confusing.[7-11] In spite of the limited amount of data available for the amorphous R-Co alloys, a number of interesting results have emerged. For example, Tao *et al.*,[12,13] Heiman and Lee,[6,14] and Jouve *et al.*[15] have shown that the magnetic ordering temperature (T_c) is higher for the amorphous alloys than for their corresponding crystalline counterparts. These results contradicted most early theories of amorphous ferromagnetism.[16-19] Tao *et al.*[12,13] explained the increased T_c as due to the fact that the reduced density of the amorphous alloys reduces the amount of charge transfer from the R into the Co *d* states. Thus for any given concentration, the Co moment and T_c are larger in the amorphous state. In the absence of any alternative theories, this reduced charge-transfer model appears to have gained acceptance.

In the case of non-*S*-state R-Co alloys, the work of Coey *et al.*[20] has shown that local anisotropy effects can give rise to complications which result from randomized spin structures which they have chosen to call "sperimagnetic." In spite of this scattered spin structure, the temperature dependence of the total magnetization could be described by a mean-field model of ferrimagnetism with T_c higher than the corresponding crystalline compounds.

When the properties of the amorphous R-Co alloys are contrasted to those of the amorphous R-Fe alloys, it is clear that the magnetic behavior of the M constituents is dramatically different. One complication in determining the magnetic properties of the Co atoms is that in general there are two magnetic constituents in these alloys and further that the R constituent can have a very complicated spin arrangement. This complication makes it particularly difficult to obtain values for the atomic moments of the M. Because the coupling in these alloys is usually ferrimagnetic, the bulk magnetization which one measures is the small difference between two large "subnetwork" magnetizations $M_{\text{total}} = M_R - M_{\text{Co}}$. Thus any small uncertainty in composition or in the collinearity of the spins can result in a very large error in the atomic moments.

In this paper we have simplified this situation by selecting Co-based alloy systems in which the Co atom is the only magnetic constituent. We have determined how the magnetic moment of Co changes upon alloying with the nonmagnetic elements Y, La, and Zr. In this series La is the only true R; however, in practice Y is generally selected as a nonmagnetic substitute for Gd since its outer electron configuration is similar to that of the R and its atomic radius ($R_{\mathrm{Y}} = 1.80$ Å) is closer to that of Gd ($R_{\mathrm{Gd}} = 1.79$ Å) than is the case for the nonmagnetic true R atoms La ($R_{\mathrm{La}} = 1.87$ Å) and Lu ($R_{\mathrm{Lu}} = 1.74$ Å). Because their outer electron configurations are similar, Y and La are expected to have the same valence state (nominally 3+). Zr is next to Y in the Periodic Table and thus contains an additional outer electron and is expected to have a higher valence state (nominally 4+). Zr is also smaller ($R_{\mathrm{Zr}} = 1.60$ Å). From our results we are thus able to assess the effects of size and charge state upon the magnetic interactions of the Co atom in the amorphous R-Co alloys and compare these effects with the results for the crystalline alloys.

II. EXPERIMENTAL

Samples were prepared in the form of thin films; $3\,000 \leq t \leq 5\,000$ Å. The films were deposited on fused-quartz substrates by the use of separate electron-gun evaporation sources for each of the elemental constituents. Rates were controlled and feedback stabilized with ionization-type rate monitors. The vacuum system operated with a base pressure of 7×10^{-9} Torr, and pressure during deposition was maintained at less than 9×10^{-8} Torr.

All films were examined by x-ray diffraction and found to be amorphous. Occasionally films were checked by electron diffraction, and their amorphous nature was confirmed. The chemical compositions of all films were determined by electron-probe x-ray microanalyzer techniques for thin films.[21,22] The accuracy of the results is expected to be better than 5 at.% relative. In fact, the results generally agreed with the rate monitor determinations to within 2 at.%. Magnetization measurements were carried out from 4.2 to 300 K on a vibrating sample magnetometer in fields up to 20 kOe.

III. RESULTS AND DISCUSSION

Magnetization curves as a function of applied field are shown in Fig. 1 for a typical sample from each series of alloys. It is seen that the samples are easy to saturate in low magnetic fields so that it is likely that the Co moments are fully aligned. The observed magnetizations at 4.2 K, which are measured in emu/cm^3, are converted to moment per Co atom by assuming an alloy density that is a linear combination of the elemental densities in proportion to their concentrations [i.e., $\rho_{\mathrm{alloy}} = x\rho_{\mathrm{Co}} + (1-x)\rho_R$]. The results are summarized in Fig. 2, which shows the concentration dependence of the Co moment. The heavy solid line is the moment for the crystalline YCo compounds.[23] (The results for crystalline LaCo alloys[23] are nearly equivalent.) The broken lines indicate the general trends for the amorphous alloys. Three features should be noted. First, while the concentration of R at which the moment disappears in crystalline YCo (or LaCo) alloys is less than 30 at.%, the critical concentration in the amorphous YCo (LaCo) alloys is over 50 at.%. Second, unlike the situation with amorphous YFe and LaFe alloys,[8] there are no significant differences between amorphous YCo and LaCo alloys. Third, the critical concentrations of R for amorphous YCo (LaCo) alloys are higher ($\approx$50 at.%) than for amorphous ZrCo alloys ($\approx$40 at.%). These results show that the size of the R atom plays almost no role in the properties of the amorphous R-Co alloys; but

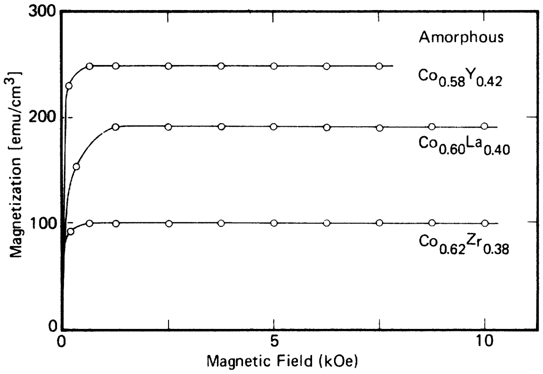

FIG. 1. Typical results for magnetization as a function of applied field for a representative sample from each alloy system. Since the samples saturate easily, it is likely the Co moments are fully aligned.

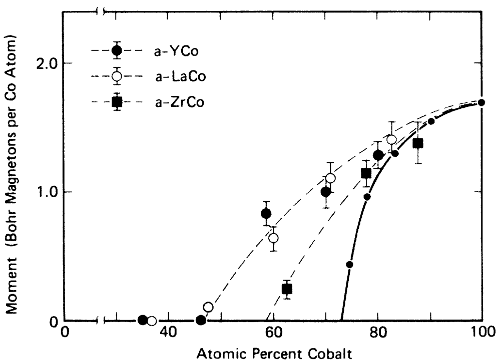

FIG. 2. Concentration dependence of the Co moment for the amorphous YCo, LaCo, and ZrCo alloys. The heavy solid line shows the concentration dependence of the Co moment for crystalline YCo alloys taken from Ref. 19 (the data for crystalline LaCo alloys are nearly identical). The broken lines are intended merely to indicate the trend of the data.

rather that the key feature is the charge state of the *R* atom. This indicates that the differences between amorphous and crystalline *R*-Co alloys are due to a reduction of the filling of Co 3*d* states by *R* electrons in the case of the amorphous material, as had been proposed by the reduced charge-transfer model.[12,13]

The data can be compared to a simple charge-transfer model by plotting Co moment versus the number of *R* atoms alloyed with one Co atom [i.e., $(1-x)/x$]. This is shown in Fig. 3. Figure 3(a) shows the result for the amorphous ZrCo alloys, the solid line is characterized by the equation $\mu_{\text{Co}} = 1.7 - 2.21[(1-x)/x]$. The agreement between the data and this equation is reasonable and implies a charge transfer of 2.21 electrons per Zr atom, considerably less than expected for the quadrivalent Zr atom. It is worth comparing this result with crystalline ZrCo alloys. The data[24,25] are limited, but crystalline ZrCo_2 apparently has no moment, whereas the amorphous value is nearly $0.6\mu_B$/Co atom.

Figure 3(b) shows the results for amorphous YCo and LaCo. The solid line is given by the equation $\mu_{\text{Co}} = 1.7 - 1.41[(1-x)/x]$. Once again the agreement is reasonable and implies a charge transfer of 1.41 elections per Y (La) atom, also considerably less than expected for a nominally trivalent atom. Thus, in the amorphous *R*-Co alloys the apparent charge transfer is roughly half that expected by simple valence arguments.

Results for the Co moment in amorphous GdCo alloys are also plotted in Fig. 3(b). The data plotted here are due to Taylor and Gangulee.[26] It is important to remember that the measured magnetization in GdCo is the difference between the "subnetwork" magnetizations. Thus, to obtain the Co moment, one must assume a Gd moment and spin orientation. The data of Taylor and Gangulee[26] shown here differ somewhat from those reported by Tao *et al.*[12,13] or Heiman and Lee.[14] Whereas the moments in Refs. 12, 13, and 14 were obtained from the 4.2-K magnetization, the data shown here may be more reliable since they are the result of a fit of the temperature dependence of the magnetization to a mean-field model. The interesting thing to note is that the Co moments in the amorphous GdCo alloys are remarkably similar to those for the amorphous YCo and LaCo alloys, except for a slight shift upward. In view of the large uncertainty associated with the moment determinations it is not clear that this shift is significant. {Taylor and Gangulee[26] noted that the best fit to a charge transfer model requires a form $\mu_{\text{Co}} = 1.7 - 1.86[(1-x)/x]^{3/2}$.} Although the addition of another parameter produces a better mathematical fit, the physical significance of the exponent $\frac{3}{2}$ is lacking. In view of this and the uncertainties in the data, a linear fit as shown in Fig. 3(b) does not seem unreasonable.

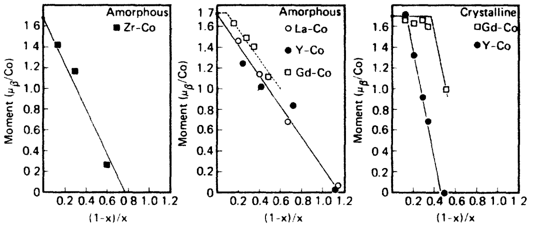

FIG. 3. Co moment plotted against the number of *R* atoms alloyed with a Co atom [i.e., vs $(1-x)/x$]. (a) ZrCo; the straight line is characterized by the equation $\mu_{\text{Co}} = 1.7 - 2.21[(1-x)/x]$. (b) YCo and LaCo; the solid straight line is characterized by the equation $\mu_{\text{Co}} = 1.7 - 1.41[(1-x)/x]$. The results for GdCo due to Taylor and Gangulee (Ref. 26) are included for comparison. (c) Crystalline YCo and GdCo; the data here are from Refs. 19 and 23.

It is interesting to compare the results for the amorphous alloys in Fig. 3(b) with the data for their crystalline counterparts, shown in Fig. 3(c). Figure 3(c) is essentially the same as that due to Lemaire.[27] While the crystalline Co moments fall on a straight line, they do not fit a simple charge-transfer model, because there appears to be a critical concentration of *R* before any reduction of the Co moment occurs, and this concentration depends on the de Gennes factor of the *R*. Also, the linear fit to those data implies a charge transfer of 4.7 electrons per atom from Y to Co. On the other hand, Lemaire notes that the disappearance of the Co moment near 30-at.% Y [i.e., $(1-x)/x \simeq 0.45$] implies an *average* charge transfer of three electrons per Y atom as expected from simple valence arguments. A final important feature to note is that the difference in Co moments between YCo and GdCo alloys is much more pronounced in the crystalline materials.

While the agreement of the data to the mathematical formulation of a charge transfer model is quite good, the fact that the fit shows that the *R* transfers only about one-half the expected number of electrons requires further discussion. Because the fit is good for all values of *x*, the suggestion of Tao *et al.*[12,13] that the increased density of the Laves phase $R\text{-Co}_2$ compounds is responsible for the difference between the crystalline and amorphous material does not seem valid. The observed results could be due to a generally altered band structure. Richter *et al.*[28] have shown that structure fluctuations alter the idealized density of states for Ni by decreasing the peak near the high-energy end and simultaneously producing a tail extending to higher energies. A similar result would be expected for Co. This effect is in the right direction to explain the observed results; however, to explain the data fully, it is also required that, in going from the crystalline to the amorphous state, the density of states for the *d* and *s* electrons of Y, La, and Zr move down in energy, producing more of an overlap with the Co *d* states.

The fact that the resistivity of these alloys is very large[29] ($\rho \approx 200$ $\mu\Omega$ cm at room temperature) indicates an electron-mean-free path of the order of the atomic spacing. Thus a more localized picture would seem appropriate for the amorphous alloys. The assumption of more localized electrons has an immediate advantage for a charged-transfer model. Cargill[30] has shown for the case of amorphous GdFe that each *M* atom has one-half the number of *R* nearest neighbors when compared to the crystalline alloys. Thus, the combination of more localized electrons and one-half the number of *R* nearest neighbors in the amorphous alloys fit the data quite well.

Additional support for a localized picture comes from the behavior of the Co-Co exchange constant J_{Co}. We use the formula $J_{\text{Co}} = 3kT_C/2ZS(S+1)$, where $Z = 12x$ is the average number of Co nearest neighbors. One problem with the Co alloys is that for $x > 0.70$, T_c is above the crystallization temperature and cannot be conveniently determined. For the data near $x = 0.60$, we find $J_{\text{Co}} \approx 2.0 \times 10^{-14}$ erg. This is almost identical to the results of Taylor and Gangulee[26] and Hasegawa[31] for the more Co-rich amorphous GdCo alloys, as well as that calculated from the data of Jouve *et al.*[15] It is also the same as the results calculated from amorphous-Co metalloid alloys.[32] The concentration dependence of J_{Co} in the crystalline and amorphous *R*-Co alloys can be seen in Fig. 4. Thus, while J_{Co} increases with *R* concentration in the crystalline alloys, it is independent of concentration in the amorphous alloys. This is consistent with the idea that long-range interactions or structure effects are absent in the amorphous materials, and that J_{Co} depends only on pairwise nearest-neighbor exchange. Theoretical support for this comes from the work of Madhukar[33] and Kaneyoshi,[34] who show that one expects a very short-range indirect-exchange interaction in amorphous materials. All these results are thus consistent with a more localized moment behavior in the amorphous alloys.

One would prefer the model describing the amorphous *R*-Co alloys to be consistent with the results for the *R*-Fe alloys. A problem with the reduced-charge-transfer model is that it does not appear to apply to the amorphous *R*-Fe alloys. This was explained by Tao *et al.*[12] as due to the fact that both spin-up and spin-down states are unoccupied in the Fe alloys, whereas only spin-down states are unocupied in the Co alloys. Thus, while the charge-transfer model is not necessarily in conflict with the amorphous *R*-Fe results, it is not directly applicable to that case.

Reduced-charge transfer is by no means the only interpretation of the data available. In the discussion of local environment effects on the magnetic moment of alloys, either in terms of a virtual bound-state model[35] or a nearest-neighbor chemical model[36] it has been shown that the concentration dependence of the Co moment is expected to take the form $\mu_{\text{Co}} = \mu_0(x - x_0)^\alpha$, where x_0 is some critical concentration and α is on the order of $\frac{1}{2}$. Figure 5 shows the square of the Co moment plotted against Co concentration for both the crystalline and amorphous *R*-Co alloys. It is interesting to note that the amorphous data can be described by a straight line, whereas the crystalline data cannot. The straight-line fit to the amorphous YCo-LaCo data yields the equation $\mu_{\text{Co}} = 2.335(x - 0.47)^{1/2}$. Similarly, a fit to the ZrCo data gives $\mu_{\text{Co}} = 2.69(x - 0.60)^{1/2}$. Whether these

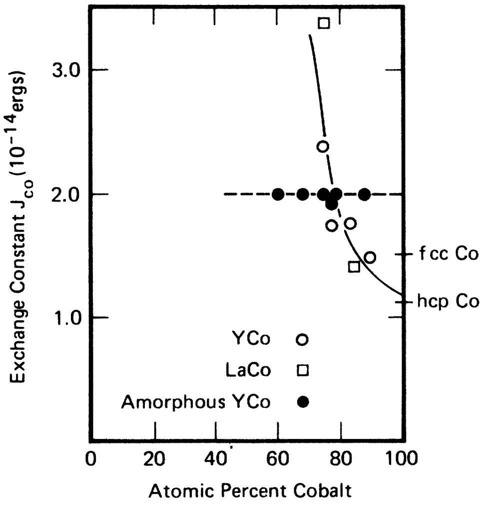

FIG. 4. Concentration dependence of the Co-Co exchange constant J_{Co}. Although J_{Co} increases upon alloying in the crystalline case, it is independent of concentration for the amorphous alloys.

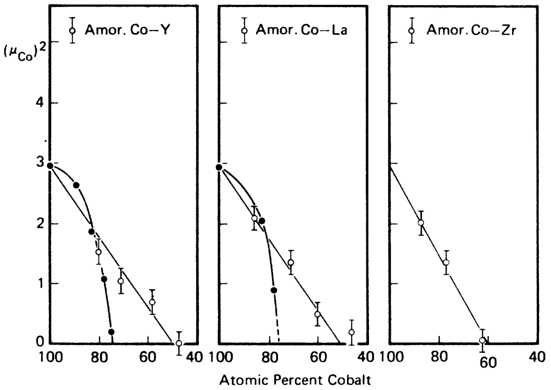

FIG. 5. Square of the Co moment vs the Co concentration for crystalline and amorphous alloys. Note that while the amorphous data approximate a straight line, the crystalline data (full circles, heavy solid lines) do not.

equations or the charge transfer equations {i.e., $\mu_{\text{Co}} = 1.7 - 1.41[(1-x)/x]$ and $\mu_{\text{Co}} = 1.7 - 2.21 \times[(1-x)/x]$} provide the correct description of the results cannot be resolved by the quality of the fit. This is not because of the uncertainty in the data, but rather is because the models predict the same values (within $0.02\mu_B$) for μ_{Co}. This similarity in result is surprising in view of the dissimilarity of mathematical form. Thus, whether the reduced-charge-transfer model or the local-environment model is correct can never be determined from the moment behavior alone.

One argument which seems to support the nearest-neighbor chemical model is the work of Coey *et al.*,[37] which indicates that the Fe moment in amorphous YFe alloys is a direct function of the number of Fe neighbors, and that the moment distribution can be described by simple statistics expected for a binomial distribution of the nearest neighbors. This in fact suggests a very simple explanation for the observed difference between amorphous and crystalline magnetic moments, namely, the statistical distribution of local environments in the amorphous materials. Thus, while crystalline YCo_2 is not magnetically ordered, amorphous YCo_2 may have some Co sites which are more characteristic of those in YCo_3 or YCo_5, etc. (which are magnetically ordered), giving rise to an inhomogeneous moment distribution with a net magnetic moment. Detailed comparison of such a model to the observed moments is complicated, but a simple statistical analysis suggests that such an effect would probably not be the whole explanation. For example, in the case of amorphous $\text{Y}_{0.40}\text{Co}_{0.60}$, on a statistical basis one would expect less than 25% of the Co sites to have local environments similar to those in the magnetically ordered crystalline phases. If one generously assumes that all these Co sites develop the full Co moment of $1.7\mu_B$, one would expect a maximum Co moment of about $0.4\mu_B$ for amorphous $\text{Y}_{0.40}\text{Co}_{0.60}$, which is only about one-half the observed value. Such an argument is not conclusive, of course. For example, it is possible for Co clustering to raise the observed moment; however, what data do exist show that the amorphous materials are very uniform and describable by simple statistics.[30,37,38] Thus, although the data strongly suggest that the Co moment is localized in the amorphous alloys, there is still some choice available for the formulation of the concentration dependence of μ_{Co}.

As a final sidelight, another aspect of the data is apparent in Fig. 5. Whereas the Co moment is higher in the amorphous material for $x < 0.8$, it is lower than the crystalline moment for $x > 0.8$. Although the data are not conclusive on this point, this same result has been noted in the case of amorphous GdCo alloys by Tao *et al.*[13] The significance of this feature, if any, is not understood.

IV. SUMMARY

We have measured the concentration dependence of the Co moment in amorphous $\text{Y}_{1-x}\text{Co}_x$, $\text{La}_{1-x}\text{Co}_x$, and $\text{Zr}_{1-x}\text{Co}_x$ alloys. We find that there are no significant differences between YCo and LaCo alloys, that the R concentration at which the Co moment disappears is much higher in the amorphous alloys than in their crystalline counterparts, and that the critical concentration is higher for Y and La than for Zr. These results show that in contrast to the situation in amorphous R-Fe alloys, the size of the R atom does not play a significant role in the properties of these Co-based materials, but rather that the charge state of the R-type atom does. This observation, coupled with the differences between crystalline and amorphous alloys, suggests that charge transfer from the R atom to the Co atom is reduced in the amorphous alloys. In fact, it is found that the data for the amorphous material fit a simple reduced charge-transfer model quite well. The reduction of the charge transfer is seen to result from more highly localized electrons coupled with a reduction in R nearest neighbors, as reported by Cargill.[30] This is not the only interpretation available, however; it has been shown that behavior of μ_{Co}^2 vs x and the concentration independence of the Co-Co exchange constant could be indicative of a localized virtual bound-state formalism or a nearest-neighbor chemical model or a simple statistical model. Although there is some choice in the detailed formulation of the concentration dependence of the Co moment, all results indicate a localized Co moment.

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