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Magnetism in ordered and amorphous YCo_3 and YFe_3

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Local magnetic moments on cobalt atoms in ordered and amorphous YCo_3 differ dramatically, whereas those on iron atoms in ordered and amorphous YFe_3 do not. Our energy-band calculations for these systems show that YCo_3 in the Cu_3Au model structure has an equilibrium lattice constant which lies within a few percent of a volume-induced magnetic instability, whereas the equilibrium lattice constant for YFe_3 lies in a region of stable magnetism. The calculations suggest that the difference in the magnetic moment of ordered and amorphous YCo_3 is a consequence of this magnetic instability and a difference in the atomic densities of the two forms of this material. This density difference is sufficient to lower the moment for ordered YCo_3 but not for ordered YFe_3.

INTRODUCTION

Our understanding of the magnetic properties of metals and alloys has recently been elucidated by a generalization of the Slater-Pauling construction[1] which expresses the magnetic moment as a sum of an integer contribution called the magnetic valence and a small noninteger *sp* contribution. The success of this generalization depends on the full occupation of up-spin *d* states (i.e., strong magnetism) and the constancy of the *sp* contribution to the magnetic moment. The utility of this generalization is its general applicability to large classes of crystalline materials of different structural types as well as to their amorphous analogs. In particular, the theory predicts that ordered and amorphous systems of the same composition should have approximately the same magnetic moment with the only difference being due to small differences in the *sp* contribution.

The general agreement between the experimentally determined local moments for ordered and amorphous Y-Fe alloys is an example of this prediction. (Since amorphous Y-Fe alloys are spin-glasses,[2] a local probe such as Mössbauer spectroscopy is used to determine the moment.[3]) The large difference between the magnetic moments of ordered and amorphous YCo_3, on the other hand, indicates that the central assumption responsible for the simplicity of the generalized Slater-Pauling theory[4,5] (that the majority-spin *d* bands are fully occupied) is violated for crystalline YCo_3. That is, although iron and cobalt occupy adjacent positions in the Periodic Table, their magnetic properties are surprisingly different when they are combined with yttrium. In particular, why should ordered YCo_3 have a much lower moment than amorphous YCo_3, while ordered and amorphous YFe_3 have the same moment, and why should Y-Co alloys with low yttrium concentration have similar moments in the crystalline and amorphous[4,5] forms?

As a first step in understanding the observed differences in the magnetic properties, we have performed paramagnetic and spin-polarized energy-band calculations as a function of lattice constant for YCo_3 and YFe_3 in the ordered Cu_3Au structure. The calculations are based on the local-spin-density treatment of electronic exchange and correlation and use the augmented-spherical-wave method[6] to solve the single-particle equations. The Cu_3Au structure is fcc-like and consists of a large gold atom in a 12-atom cage of copper atoms. Ordered YCo_3 and YFe_3 both assume the $PuNi_3$ structure type,[7,8] which is a complicated Laves-type form bearing little resemblance to the Cu_3Au structure. In the amorphous form, however, these materials are expected to have a high degree of fcc-like short-range order[9] and to exhibit fcc-like coordination numbers.[10] To this extent, the Cu_3Au calculations should be more relevant to the amorphous systems than to the ordered systems, although the Cu_3Au structure does not permit the degree of relaxation expected for amorphous materials made up of constituents which have large differences in atomic sizes.

CALCULATIONS

Our calculated results for YCo_3 and YFe_3 are shown in Figs. 1 and 2, respectively, where we plot total energy and

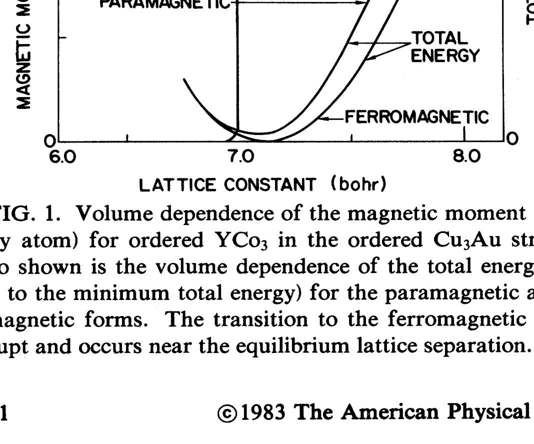

FIG. 1. Volume dependence of the magnetic moment (μ_B per alloy atom) for ordered YCo_3 in the ordered Cu_3Au structure. Also shown is the volume dependence of the total energy (relative to the minimum total energy) for the paramagnetic and ferromagnetic forms. The transition to the ferromagnetic state is abrupt and occurs near the equilibrium lattice separation.

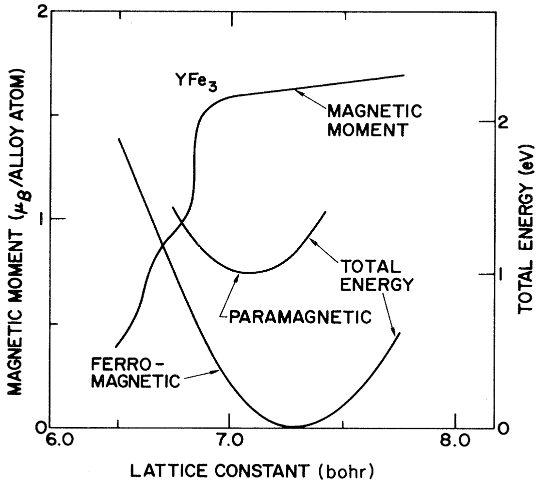

FIG. 2. Volume dependence of the magnetic moment (μ_B per alloy atom) for ordered YFe$_3$ in the ordered Cu$_3$Au structure. Also shown is the volume dependence of the total energy (relative to the minimum total energy) for the paramagnetic and ferromagnetic forms. The transition to the ferromagnetic state is gradual and occurs at reduced lattice constants.

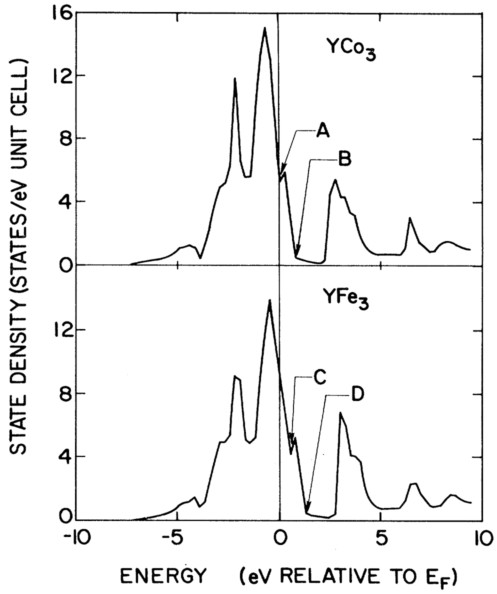

FIG. 3. State densities for paramagnetic YCo$_3$ and YFe$_3$ in the Cu$_3$Au structure. For YCo$_3$, the Fermi energy falls in a local minimum labeled *A*. In the spin-split case, the majority-spin state density is shifted to lower energy so that the Fermi energy falls to location *B* yielding the full cobalt moment. For YFe$_3$, the spin-split case can result in the Fermi energy being "pinned" at the local minimum labeled *C*, yielding a "weak" moment. For large lattice separations, the Fermi energy is shifted to location *D* yielding the full Fe moment. YCo$_3$ is therefore either fully magnetic or nonmagnetic, depending on the lattice separation. YFe$_3$, on the other hand, exhibits a region of "weak" magnetism at reduced lattice separations.

magnetic moment as a function of lattice constant. The lattice constant corresponding to the minimum in the total energy represents the theoretical equilibrium lattice constant for the paramagnetic and ferromagnetic states. For both YCo$_3$ and YFe$_3$, the ferromagnetic state has a larger equilibrium lattice constant and a lower minimum total energy indicating that, in the Cu$_3$Au structure, the ferromagnetic state is preferred. We note that the equilibrium lattice constants for *paramagnetic* YCo$_3$ and YFe$_3$ are approximately equal (reflecting the fundamental size similarity of the Periodic-Table neighbors, Fe and Co), whereas the lattice constant for ferromagnetic YFe$_3$ is approximately 0.15 bohr larger than that of ferromagnetic YCo$_3$. The larger value for the iron case is a direct consequence of the larger moment associated with the iron compound as compared with the cobalt compound and the resulting internal magnetic pressures.[11] As Figs. 1 and 2 show, the two systems exhibit interesting differences. The energy difference between the paramagnetic and ferromagnetic states is small for YCo$_3$, but large for YFe$_3$, indicating that YCo$_3$ is just barely magnetic, while YFe$_3$ has a strong preference for magnetism. Indeed, at lattice constants only slightly smaller than the equlibrium values, the energy curves for paramagnetic and ferromagnetic YCo$_3$ merge and the system no longer prefers the magnetic state. YFe$_3$, on the other hand, remains magnetic even for lattice constants much smaller than the theoretical equilibrium value.

The weakly increasing magnetic moment represented by the plateau beyond the critical lattice constant is characteristic of *d*-band magnetic systems and corresponds to full polarization of the up-spin *d* electrons, a condition generally referred to as "strong magnetism." In this region, the system is well behaved and can be described in terms of the generalized Slater-Pauling construction. Below the critical volume, the moment drops precipitously and the system abruptly becomes paramagnetic, as in the case of the YCo$_3$, or the moment gradually falls to zero, as in the case of the YFe$_3$. The low-volume region below the plateau which does not support the full moment of the system corresponds to a region of "weak magnetism." With these definitions YCo$_3$ is a strong ferromagnet at the equilibrium volume, even though it is on the verge of undergoing a moment instability. YFe$_3$, on the other hand, is a strong ferromagnet, but can become a weak ferromagnet at reduced volumes.

The relevant differences between YCo$_3$ and YFe$_3$ are apparent in the calculated paramagnetic state densities shown in Fig. 3. Note first that the state densities for the two compounds are fundamentally very similar, implying that rigid-band theory is an appropriate perspective. The *important* difference between the two compounds is the valence difference between cobalt and iron. Because the Fermi level for both systems falls in a region of generally decreasing state density, the larger valence of cobalt causes the Fermi-level state density in YCo$_3$ to be smaller than that of YFe$_3$. The importance of the greater valence of cobalt is that it brings the Fermi-level state density of YCo$_3$ precariously close to the critical "Stoner" value, below which ferromagnetism is no longer possible. Note that increasing the valence still further, by going from cobalt to nickel, eliminates ferromagnetism altogether. (YNi_3, both experimentally and theoretically, is paramagnetic.) The central point in our analysis is that the valence of cobalt, in conjunction with the approximately rigid-band character of the state density, brings the Fermi level to a position where ferromagnetism is just barely possible. This implies that the magnetic moment of YCo_3 becomes very sensitive to small volume changes, because of concomitant changes in *d*-band widths. Figure 1 demonstrates this sensitivity.

The calculated paramagnetic state densities for the Cu_3Au structure exhibit small features labeled *A* and *C* in Fig. 3. In the YCo_3 case, the paramagnetic Fermi level falls in the shallow minimum at *A* so that when this system spin-splits, the majority-spin state density will be occupied up to the deep minimum labeled *B* at about 1 eV. Thus, YCo_3 will be either fully magnetic or fully nonmagnetic. For YFe_3 the paramagnetic Fermi level occurs at a lower energy where the state density is larger. When this system spin-splits, the Fermi level can either be "pinned" in the local minimum labeled *C* (yielding a low moment), or find the deep minimum labeled *D* and yield the full (strong) moment. The single-step behavior of the magnetic moment of YCo_3 and the approximate two-step behavior of YFe_3 is seen to be a direct consequence of the details of the leading edge of the state densities.

We do not believe that the small anomalies at *A* and *C* in Fig. 3 are significant in the real systems, because the real systems exist in structures which differ from the Cu_3Au structure. For the real systems, we focus only on the gross features of the band structures, namely the deep gap at *B* and *D* above the Fermi level, the roughly triangular-shaped state densities, and the relative location of the Fermi level. Thus the basic difference between the two systems is the location of the Fermi level in the trailing edge of the main *d*-band peak. In going from YFe_3 to YCo_3 (and on to YNi_3), the systems must progressively accommodate three additional electrons per formula unit. Therefore, even in the real systems, the Fermi level should move to higher energy in the *d* bands and the Fermi-level state density should progressively decrease in going from iron to cobalt and on to nickel. Since the magnetic moment corresponding to the plateau region in Figs. 1 and 2 can be expected to be proportional to the area of the unoccupied portions of the main *d* bands, the iron system has a higher moment than the cobalt system. The nickel system would be nonmagnetic because its Fermi-level state density is too low to allow for a transition to the magnetic state. That is, the moments for the real systems should be accurately given by Friedel's formula, provided only that they are strong ferromagnets.[12]

Because of the structural differences between our Cu_3Au calculations and the experimental systems, we also must not attach great significance to the calculated lattice constants, which in fact indicate a density larger than observed in either the crystalline or amorphous forms. But we do believe that the trends shown in Figs. 1 and 2 between iron and cobalt will persist: greater stabilization energy and hence larger lattice parameter, as well as lower critical volume, for the iron relative to the cobalt compounds.

COMPARISON TO EXPERIMENT

Our calculated magnetic moment for ordered YCo_3 at theoretical equilibrium is 0.82 Bohr magnetons per alloy atom. This value is in excellent agreement with the experimental value of 0.80 Bohr magnetons obtained for amorphous YCo_3 and in disagreement with the crystalline YCo_3 results.[4,5] The agreement for the amorphous case indicates, in contrast to earlier suggestions,[4,5] that the average cobalt moment need not be obtained by averaging local configurations, but rather that the amorphous system exhibits the full cobalt moment predicted by the Friedel formula.[12] This prediction is structure independent, and the fcc calculation presumably corresponds to one of many different local environments which would give the same result. On the other hand, the closeness of the ferromagnetic minimum in Fig. 1 to the critical volume suggests that the reason for the discrepancy with the crystalline data is the denser packing in the crystalline case.

Unfortunately there is insufficient density data in the literature to confirm this supposition directly. However, density data on related crystalline compounds yield indirect support to our contention. In particular, the densities[13] of crystalline YCo_5 and YFe_5 imply average atomic volumes 4% and 7% less than Vegard's law, and those of YCo_2 and YFe_2 yield volumes 17.5% and 12% less than Vegard's law (assuming a density of 7.8 g/cm^3 for Fe, as for bcc Fe or magnetic fcc Fe extrapolated from FeNi alloys). Our calculations indicate deviations in the same direction for the fcc-like Cu_3Au structure.

Although densities of the amorphous analogs have not been reported, data exists[13] for GdCo and TbFe, both crystalline and amorphous. Crystalline Gd_2Co_{17}, $GdCo_5$, and Gd_4Co_3 lie within 3% of Vegard's law, but just in the region we are interested, crystalline Gd_2Co_7, $GdCo_3$, and $GdCo_2$ have average atomic volumes 13%, 11%, and 15% less than Vegard's law, respectively. The similarity in these deviations to the YCo_2 and YFe_2 data suggests that gadolinium behaves very similarly to yttrium in these systems. In fact, both gadolinium and terbium are well known to be similar in size and chemical properties to yttrium. Therefore we propose to use density data on these systems to deduce the behavior of the yttrium systems.

Turning now to the amorphous data, we find that amorphous GdCo alloys[14] have deviations of less than 3% below Vegard's law, again implying less dense packing than in the crystalline compounds. Similarly $TbFe_2$ is reported[15] to be 13% less dense in the amorphous than crystalline form. Furthermore, these differences cannot be attributed to magnetic volume effects, since both the crystalline and amorphous GdCo and TbFe systems remain strongly magnetic throughout the relevant composition range.

These data suggest that the likely cause of the moment differences between amorphous and crystalline YCo_3 is the difference in average atomic volumes, which becomes important because the system is close to the critical density for collapse of magnetism. We propose that amorphous YCo_3 is on the plateau of Fig. 1 while crystalline YCo_3 is on the edge. Further evidence for this supposition comes from the observation of a large magnetovolume effect,[5] which would be expected in the critical region of Fig. 1. One can also understand why the moment in other Y-Co compounds which contain less yttrium are much more similar to their amorphous analogs. In these cases the equilibrium lattice constant will be shifted further away from the critical value, approaching the more stable case of pure cobalt. Then, the strong nonlinearity of Fig. 1 ensures that the moment of the crystalline compounds will rise rapidly to its strongly magnetic Friedel value on the plateau.

Turning now to the iron case, for YFe_3 we calculate a magnetic moment of 1.6 Bohr magnetons per alloy atom, while the experimental value for both the crystalline and amorphous form is 1.3. Our calculations for the fcc structure indicate strong magnetism far from the critical volume for moment collapse. This means that iron moments with this kind of environment (eight iron nearest neighbors and four yttrium nearest neighbors) will have little sensitivity to volume. That is, the same volume differences that had such a drastic effect in the cobalt system should play a weaker role here, so that both crystalline and amorphous YFe_3 have the same moment.

On the other hand, although our calculations indicate strong magnetism for YFe_3, the measured magnetic moment is approximately 20% less than our calculated value. It might at first be thought that this difference could arise from the spin-glass behavior in amorphous Y-Fe since antiferromagnetic alignment reduces the size of the participating moments in the two-site Anderson model, for example.[16] Nevertheless, neutron studies indicate a ferromagnetic correlation length of the order of 10 Å throughout the spin-glass region[3] and the paramagnetic Curie temperature is strongly positive. These results suggest that the microscopic magnetic interactions are predominantly ferromagnetic even though macroscopic behavior of amorphous Y-Fe is spin-glass-like, and they justify our comparison to a ferromagnetic calculation.

A more plausible explanation of the 20% discrepancy in our view is as follows: There is considerable evidence that the iron moment will decrease below the Friedel formula, *both* at increased iron concentrations (fcc iron is antiferromagnetic), and at decreased iron concentration.[12] Therefore, in contrast to the usual situation in which the effects of stoichiometry fluctuations tend to average to zero, such fluctuations in YFe_3 will necessarily reduce the magnetization. Experimental evidence for this in the Y-Fe system comes from the moment behavior which pulls below the Friedel line at high iron concentrations[12] and from the broad Mössbauer hyperfine field distributions at high solute concentrations.[3] Thus we suggest that for both amorphous and ordered systems, there is a distribution of local environments which contribute reduced moments and cause the average to deviate downward from the strongly ferromagnetic prediction of our calculation. In other words, this system, although insensitive to volume, is somewhat sensitive to composition or local environment. We take the approximate equality of amorphous and crystalline moments as evidence for a preponderance of fcc-like local environments, but with about 20% of the local sites having deviations which cause the moment to drop by about 20% from its predicted value.

In summary, the interesting contrast between amorphous and crystalline Y-Co and Y-Fe alloys can be understood on the basis of theoretically derived moment-versus-volume curves, coupled with the experimentally observed density differences between amorphous and crystalline states.

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