Magnetic and magnetovolume properties of RCo$_2$ compounds and alloys from energy band structure

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Abstract. A quantitative description of the magnetic behaviour is obtained for the itinerant electrons of the rare-earth–cobalt Laves-phase compounds. This is accomplished by fitting the results of a fixed-spin-moment calculation of the electronic energy of YCo$_2$ to a power series in the magnetization for several different volumes and by coupling to the rare earth spins in molecular field theory. The $T = 0$ itinerant moments are obtained for the RCo$_2$ series and the alloy Y$_{1-x}$Gd$_x$Co$_2$. The spontaneous volume magnetostriction of RCo$_2$ is also estimated. The results are compared with experiment.

1. Introduction

Scientific interest in the RCo$_2$ (R = rare earth) series of compounds and in pseudobinary alloys R$_{1-x}$R$'_x$Co$_2$ has continued, seemingly unabated, since the discoveries in the sixties that, in these materials, the Co moment is a strong function of the spin of the rare earth constituent [1]. Although YCo$_2$ proved to be non-magnetic, it behaves like a strongly enhanced paramagnet [2]. In addition, this compound exhibits an increase in its susceptibility with increasing magnetic field, an unusual property which prompted the prediction of the metamagnetic behaviour for YCo$_2$ in large magnetic fields [3]. Although laboratory fields are too weak to make YCo$_2$ ferromagnetic, if Y is replaced by a magnetic rare earth component, the molecular fields generated by the rare earth ions are strong enough to cause the appearance of magnetism in the Co sublattice. In fact, Bloch and Lemaire [4], using a two-sublattice model and measured susceptibility values and Curie temperatures, calculated a moment of 0.91 μ_B for Co in GdCo$_2$ and 0.26 μ_B for Co in PrCo$_2$. In their description the Co moment is simply proportional to the spin of the rare earth, a consequence of the assumption of weak ferromagnetism in the Co sublattice. In a further development Bloch et al [3] showed that the first-order magnetic transitions that occur in ErCo$_2$, HoCo$_2$ and DyCo$_2$ could be explained if the Co susceptibilities of these compounds showed the same increases with field as that seen in YCo$_2$. These authors developed a Landau-type expansion for the energy of the Co sublattice which in turn was coupled to the rare earths via molecular field theory. A temperature-dependent coefficient of the fourth-order term in this expansion, negative at low temperatures and positive above 200 K, was used to explain both the first-order nature of the magnetic transitions in the above-named compounds and the second-order transitions observed in TbCo$_2$ and GdCo$_2$. This change in sign of the fourth-order term

further implies the special field and temperature dependences of the magnetization now known to occur in YCo_2.

Another interesting feature of the Co compounds and alloys is the invar-like behaviour observed in the RCo_2 series [5]. This large change in volume near and below the Curie point is associated with the formation of a magnetic moment on the Co atoms. The equilibrium size of this moment should then depend on the ability of the lattice to adjust its volume but, more importantly, upon the response of the itinerant electrons to changes in volume as well as changes in their magnetic polarization. The latter property is determined, at low temperature, by the moment and volume dependence of the energy band structure. Schwartz and Mohn [6] have used the fixed-spin-moment method of energy band calculations to investigate the energy surface of YCo_2 as a function of volume and magnetization. This method is discussed in detail in their paper and a later paper by Moruzzi *et al* on Fe, Co and Ni [7]. In this method the total energy, E, of a system is determined by a local density approximation band structure calculation with volume, V, and magnetic moment, m, constrained to given values. This simulates both applied pressure, $P = (\delta E/\delta V)_m$, and applied magnetic field, $H = (\delta E/\delta m)_V$, in completely equivalent ways. The $E(m)$ curves for three different lattice constants reported in [6] are shown in figure 1, referenced to an energy zero at the calculated paramagnetic equilibrium volume. The dependencies of E on m are consistent with metamagnetic behaviour for lattice constants between 13.4 au and 13.6 au, and indicate ferromagnetic behaviour for larger lattice constants. In this paper we have attempted to incorporate the effects of volume changes on the magnetic properties of the compounds with magnetic rare earths, using the results of these energy band calculations of YCo_2, combined with a molecular-field description of the coupling of rare earth spin to the cobalt sublattice. In addition, we have estimated the spontaneous volume change on going from $m = 0$ to the equilibrium value of m.

2. Calculations

In order to calculate the magnetic behaviour of the RCo_2 compounds using the YCo_2 total energy surface we need to interpolate/extrapolate the energy curves shown in figure 1. We have fit these energy curves via a least-squares procedure to a sixth-order Landau expansion in m allowing each of the Landau coefficients to vary linearly with lattice constant. The computed fits are shown as dashed lines in figure 1. (The fit was equally good for the fourth lattice constant reported in [6], $r = 14.0$ au.) A contour plot of the reconstructed energy given by this analytic fit is shown in figure 2. This energy surface is strikingly similar to that obtained by fixed-spin-moment calculations for FCC Fe in [7] (and fit by a similar Landau expansion by Entel and Schroter [8]) and suggests that, in addition to the metamagnetic transition predicted for large fields, a transition to ferromagnetism will occur at an expanded lattice constant. Such behaviour has been observed for $Y(Co_xAl_{1-x})_2$ alloys that are ferromagnetic for $x > 0.12$ [9].

We now adopt the conventional point of view that the YCo_2 compound represents the behaviour of the d (and s–p) itinerant electrons for the entire RCo_2 series, and that the substitution of a rare earth for Y introduces only the (local) 4f magnetic properties. From our fit to the energy surface we obtain an analytic expression for the zero-temperature free energy of the d electrons

$$F_d = (K/2)(r - r_0)^2 + am^2 + bm^4 + cm^6. \tag{1}$$

Retaining the notation of [6] the energy, F, and moment, m, are referenced to the
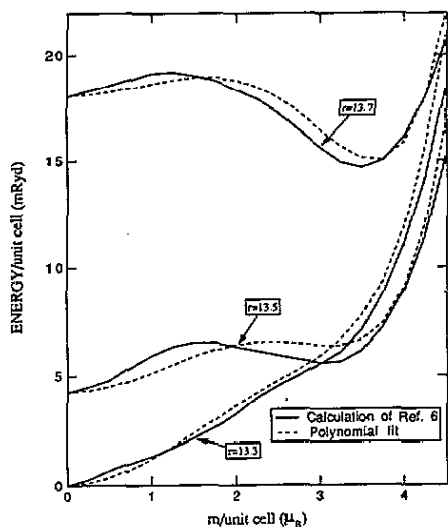
Figure 1. The electronic energy versus magnetic moment for the two-formula-unit primitive cell of YCo_2 as calculated by the fixed-spin-moment method (FSM) [6] (solid lines) and a polynomial fit (dashed lines) for three separate values of the cubic lattice constant. The values for the fitting parameters are given in (3) in the text. Meta-magnetic behaviour is indicated for lattice constants between 13.4 and 13.6 au and ferro-magnetism is indicated for larger lattice constants.
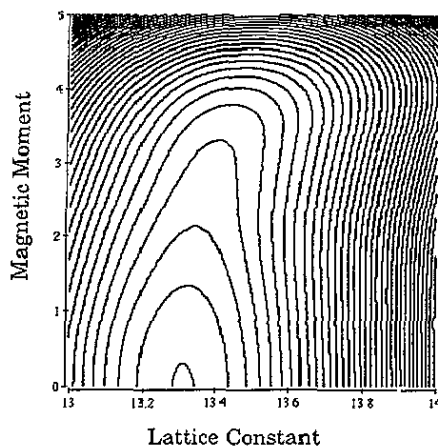
Figure 2. Contour plot of the fitted FSM energy surfaces as in figure 1 in the magnetization lattice parameter plane based on the results of Schwarz and Mohn [6]. The difference between any two contours is 1.625 mRyd. The contours display the invar-like behaviour as has been displayed for FCC Fe[7] and for Fe₃Ni [14].

primitive unit cell containing two formula units, but r is the cubic unit cell lattice constant (and $r_0 = 13.3$ au). K is obtained from a fit to the calculated paramagnetic total energies as a function of lattice constant [6] and has the value 239 mRyd au^{-2}. The Landau coefficients, a, b, and c, depend linearly on r as

$$a = 1.40 \, (14.21 - r) \text{ mRyd } \mu_B^{-2}$$
$$b = -0.105 \, (r - 12.20) \text{ mRyd } \mu_B^{-4} \quad (2)$$
$$c = 0.0035 \, (r - 11.85) \text{ mRyd } \mu_B^{-6}.$$

Following Bloch *et al* [3] we can obtain a Gibbs free energy, G, for the itinerant electron system in the field, h, introduced by a rare earth 4f moment with spin $(g - 1)J$:

$$G = F_d - g\mu_B hm = (K/2)(r - r_0)^2 + am^2 + bm^4 + cm^6 - g\mu_B hm \quad (3)$$

where

$$h = -[g_J - 1)J/g\mu_B]I_0 \quad (4)$$

and I_0 represents the 3d–4f exchange interaction, still to be determined. We have used these expressions to predict the stable itinerant-electron moment as a function of rare earth constituent (spin) shown in figure 3. For these predictions we have held I_0 constant at the value that gives the observed moment for $GdCo_2$. (I_0 is expected to vary with
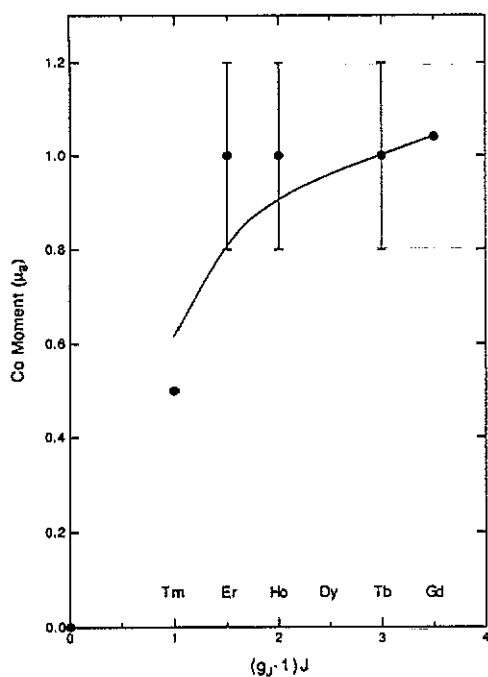
Figure 3. The itinerant-electron moment for heavy rare earth RCo_2 compounds versus rare earth spin. Solid circles: experimental results from [1, 10, 11]. Solid line: molecular field theory using the FSM calculations for YCo_2.
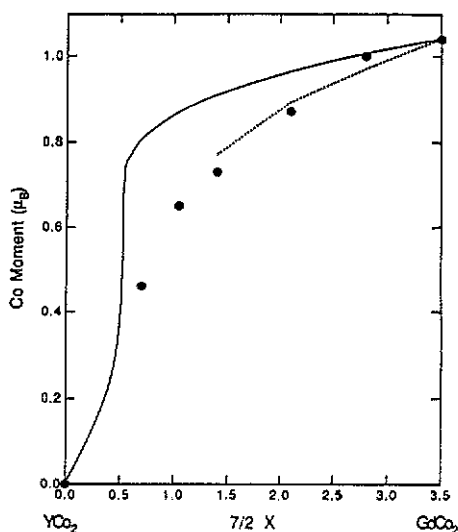
Figure 4. The itinerant-electron moment for $Y_{1-x}Gd_xCo_2$ versus the net Gd spin ($\frac{1}{2}x$). The data points (solid circles) are those of Lemaire and Schweizer [1]. The solid line is the result of a constant-volume molecular field calculation based on FSM calculations for YCo_2. The dashed line is the result of including the effects of composition fluctuations.

volume as discussed below but the small variation does not affect the predictions in figure 3 significantly.) The volume enters these predictions because we evaluate a, b, and c at the observed lattice constant for each compound; thus each rare earth compound is located at different (m, V) coordinates on the energy surface in figure 2. (The experimental lattice constants were adjusted by the ratio between the observed and calculated lattice constant of YCo_2 in order to normalize them to the energies obtained from the local density band structure calculation [6].) The experimental data for $GdCo_2$ and $TmCo_2$ in figure 3 are taken from magnetization measurements [1, 10] (total moment per formula unit minus the theoretical moment of the rare earth) which should reflect the moment of the entire itinerant-electron system as determined by the calculations. Experimental moments for the Co ions in $TbCo_2$, $HoCo_2$, and $ErCo_2$ are from neutron diffraction [11], which gives the rare earth and Co moments separately. (For simplicity we will use the designation 'Co moment' hereafter to represent the entire itinerant-electron system.) Note that the predicted Co moments for the heavy rare earth compounds include the effects of the monotonic increase in lattice constant with rare earth

spin. All of the heavy rare earth compounds have lattice constants smaller than YCo_2 so their $E(m)$ curves are similar to that shown for 13.3 au in figure 1. Conversely for the light rare earths, where the lattice constant *decreases* with increasing rare earth spin, the predicted Co moments lie on a higher curve, with the two curves meeting at $GdCo_2$. For the larger lattice constants of the light rare earth compounds the predicted Co moment curve is sharper as a function of rare earth spin, reflecting the development of a high-spin energy minimum. Our predicted Co moments for $PrCo_2$ and $NdCo_2$ are 0.88 μ_B and 0.92 μ_B, respectively, compared with experimental results $0.50 + 0.25$ μ_B [12] and $0.8 + 0.2$ μ_B [10], respectively. Of all the experimental Co moments, only that of $PrCo_2$ does not lie within the experimental error of the theoretical prediction. This anomaly in $PrCo_2$ may well reflect the large crystal field experienced by the 4f electrons in this compound [3].

We have also calculated the itinerant moments as a function of x for the pseudobinary alloy $Gd_xY_{1-x}Co_2$ studied in [1]. In this case, since the equilibrium volumes of $GdCo_2$ and YCo_2 are nearly the same, volume effects are negligible (the energy curve is the one shown for 13.3 au in figure 1) and the predicted Co moments arise only from the metamagnetic behaviour induced by the Gd 4f moment. We have used the virtual crystal approximation for the field from the Gd, namely

$$h = -(1/g\mu_B)I_0 \tfrac{7}{2}x \tag{5}$$

and we have taken I_0 to fit the data for $x = 1$ ($GdCo_2$). Results are shown in figure 4. The data in this case were obtained from magnetization measurements with the effective moment of the Gd subtracted [1]. As figure 4 clearly indicates, the molecular field theory overestimates the itinerant-electron magnetization in the alloy. This is most probably due to the fluctuations in h caused by the random distribution of Gd and Y atoms on the rare earth sites. It is possible to maintain the band-theory-plus-rare-earth-molecular-field approach in this case by including the fluctuations in molecular field. Thus, h is a random function of position, and so also is the Co magnetization. We have extended the band structure model in a phenomenological way, by including an exchange stiffness term proportional to the gradient squared of the magnitude of the spatially varying magnetization. The constant of proportionality is one half the longitudinal exchange stiffnesss. By treating the fluctuations in h as a perturbation, we have developed an equation of state for the magnetization identical in form to equation (3) but with a and b replaced by effective parameters that are magnetization dependent. After so generalizing, we have recalculated m versus x for the $Y_{1-x}Gd_xCo_2$ alloy. A good fit to the experimental data was obtained assuming an exchange stiffness of 6.7×10^{-6} erg cm^{-1}. (See the dashed line in figure 4.) The fluctuating molecular field was calculated assuming that the probabilities of Gd site occupation were spatially uncorrelated and given by the binomial distribution.

We turn now to the calculation of the magnetovolume effect in the RCo_2 compounds, that is, the spontaneous increase in volume due to the onset of the magnetization. From the condition that the Gibbs free energy (equation (3)) be a minimum under variations in lattice parameter r, we find

$$\delta V/V = 3(r - r_0)/r = -(3/Kr_0)(a'm^2 + b'm^4 + c'm^6 + (g_J - 1)JI_0'm) \tag{6}$$

where the primes on a, b, c, and I_0 indicate derivatives with respect to r. $\delta V/V$ depends explicitly on rare earth spin through the last term in (6), and implicitly through the spin dependence of m. The experimental *variation with heavy rare earth* of $\delta V/V$ [13] is well reproduced by (6) using experimental m-values [10, 11] and our expressions for a, b, c,

and K, if we take $I'_0 = -0.1$ mRyd au^{-1}. Using this estimate, we can confirm that the volume dependence of I_0 has little effect on the moment calculation, as we had assumed earlier. The *absolute values* of $\delta V/V$ calculated from (6) are, however, significantly larger than the experimentally observed values.

3. Summary

We have outlined a theory for the magnetic and volume magnetoelastic properties of the RCo$_2$ compounds utilizing the fixed-spin-moment band calculations for YCo$_2$ of Schwartz and Mohn [6]. The calculations we have performed, when compared with experiment, may be considered as a test of the idea that the itinerant-electron systems in the RCo$_2$ are adequately described by the YCo$_2$ band structure and by a molecular field from the R spins. We conclude that this is a reasonable picture, provided modifications like rare earth crystal-field effects and composition fluctuations are included where appropriate. (The perturbational approach to fluctuations described above is appropriate only for alloy compositions with high concentrations of the magnetic rare earth.) The extension of this idea to calculating the magnetovolume effect apparently is not as straightforward. The calculated volume dependences of the Landau coefficients are too large to account for the experimental results, although the variation in volume with rare earth constituent in the RCo$_2$ compounds is reproduced in the calculations.

Acknowledgments

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