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Paramagnetic Behavior of Some Rare-Earth Cobalt Compounds

E. Burzo

Institute for Atomic Physics, P.O. Box 35, Bucharest, Romania

In the ferrimagnetic rare-earth cobalt compounds, the reciprocal susceptibility obeys a Néel-type law. As a function of rare-earth content, the paramagnetic moments of cobalt atoms vary similarly with those deduced from saturation measurements. Particularly, for $R\mathrm{Co}_2$ (R = Gd, Tb, Dy, Ho, or Er) compounds the cobalt effective moment is $(2.00 \pm 0.50)\mu_B$, twice the value obtained in the ordered state.

I. INTRODUCTION

The study of magnetic properties of rare-earth cobalt intermetallic compounds has been a subject of great interest. The $4f$ electrons, responsible for the magnetism of rare earths, are well localized. This cannot be asserted about the cobalt $3d$ magnetic shell. Thus, depending on the modification of the valence-electron concentration as a consequence of the increase of rare-earth content in compound, a decrease of the cobalt magnetic moment, determined from saturation measurements, is evidenced.[1,2] Generally, we refer to mean magnetic moments since the magnetic contribution of cobalt atoms in compounds with complex crystalline structure differs according to position.[3]

This paper shall present an experimental study of magnetic behavior of two classes of compounds: (i) the $R\mathrm{Co}_2$ (R = Gd, Tb, Dy, Ho, or Er) Laves-phase compounds. The special interest in these compounds is associated with the crystalline structure. The punctual symmetry of the cobalt and rare-earth atoms is $\overline{3}m$ and cubic, respectively. In this case the determined magnetic moments correspond to the real values, since the Co and R atoms occupy equivalent positions in the lattice; (ii) the gadolinium cobalt compounds. Since gadolinium is in the S state, its magnetic moment, unlike the other rare earths, is influenced very little by the crystalline field. Consequently, from the saturation measurements the real cobalt mean contribution may be obtained.

The studies previously performed generally had in view only measurements below the Curie temper-

ature. By paramagnetic investigations we intend to emphasize the existence and the values of the cobalt moment outside the magnetically ordered domain.

Previous investigations on the paramagnetic range were made by Farrell and Wallace[4] on some $R\mathrm{Co}_2$ compounds. They supposed that the reciprocal susceptibility for TbCo_2, DyCo_2, and ErCo_2 obeys a Curie-Weiss law. Recently, based on the paramagnetic measurements,[5] Bloch and Lemaire[6] have proposed a phenomenological model for the interpretation of magnetic characteristics of these compounds. These authors consider a two-component alloy, in which one component R possesses a permanent magnetic moment and the other, Co, has an exchange-enhanced paramagnetic susceptibility.

It is our purpose to present a different interpretation of the magnetic behavior of these systems. As a result of the present study we conclude that the paramagnetic moment of cobalt atoms $\mathfrak{M}^p_{\mathrm{Co}}$, deduced from the Curie constants is approximately twice the $\mathfrak{M}^0_{\mathrm{Co}}$ value obtained from saturation measurements. The variation of cobalt magnetic moment as function of the molar fraction of R atoms characterizes the two temperature ranges, the ratio $\mathfrak{M}^p_{\mathrm{Co}}/\mathfrak{M}^0_{\mathrm{Co}}$ being approximately constant. This behavior is similar to that observed in metallic cobalt, where $\mathfrak{M}^p_{\mathrm{Co}} \approx 3.30\,\mu_B$ is twice the value $\mathfrak{M}^0_{\mathrm{Co}} = 1.70\,\mu_B$ determined in the ordered state.[7]

II. EXPERIMENTAL

The samples were prepared by the melting method previously described.[1] After a fast quenching, to block the possible peritectic transformations,

TABLE I. Magnetic properties of $R\mathrm{Co}_2$ compounds.

Compound	GdCo_2	TbCo_2	DyCo_2	HoCo_2	ErCo_2
Saturation magnetic moment per formula unit (μ_B)	4.96	6.30	6.80	7.30	6.20
Magnetic moment of cobalt atom (μ_B)	1.02[a]	1.00[b]	1.00[b]	1.00[b]	1.00[b]
Magnetic moment of rare-earth atoms (μ_B)	7.00	8.30	8.80	9.30	8.20
Curie temperature (°K)	395	228	135	74	33
Volume dependence of Curie temperature $\dfrac{d\log_{10}T_C}{d\log_{10}V}$ [c]	6	5	6	9	13

[a]Determined supposing $\mathfrak{M}_{\mathrm{Gd}}=7\ \mu_B$.
[b]Determined by neutron diffraction (Ref. 8).
[c]Reference 5.

the samples were annealed at 800 °C for 24 h under vacuum of 10^{-6} Torr. Control of sample purity was checked by x-ray analysis.

The magnetic measurements below the Curie temperature were performed with an axial extraction method in a variable magnetic field up to 26 kOe. The Curie temperatures T_C were determined from thermal variation of magnetization in the remanent field of the electromagnet.

The paramagnetic studies were performed with a translation balance, the samples being sealed in quartz ampoules under vacuum. The experimental points were obtained both by heating and cooling the samples in a magnetic field of 4 and 8 kOe. In all these cases the results were the same, showing absence of any ferromagnetic impurities or oxidation phenomena.

III. MAGNETIC PROPERTIES OF $R\mathrm{Co}_2$ (R = Gd, Tb, Dy, Ho, OR Er) COMPOUNDS

The neutron-diffraction studies[8] evidenced that the cobalt moments $\mathfrak{M}_{\mathrm{Co}}^0 = (1.00\pm0.20)\mu_B$ are antiparallel oriented as compared with those of rare earths. The saturation magnetic moments per formula unit are presented in Table I. Taking into account the above values of the cobalt moments, the magnetic contributions of rare-earth elements were determined. These are smaller than the theoretical $g_J J$ values, probably a consequence of the crystalline-field effects.[9] Assuming that the magnetic moment of gadolinium atoms is $7\mu_B$, we determined a magnetic contribution of $1.02\mu_B$ per cobalt atom in GdCo_2 from saturation measurements.

One notes a constant magnetic contribution of cobalt atoms in these systems and consequently a similar electronic configuration.

In HoCo_2[1] and ErCo_2[10] first-order magnetic transitions are observed. These seem to be essentially determined by the rare earths. The Curie temperatures are greater than those of rare-earth metals and vary significantly with pressure.[5] This behavior may be correlated with the presence of cobalt magnetic atoms having a modified electronic configuration as compared to pure metal. For the isomorphous compound GdNi_2, where nickel is nonmagnetic, the Curie temperature is pressure independent.

Above the Curie point the reciprocal susceptibility $1/\chi$ obeys a Néel-type relation,[11] characteristic for ferrimagnetic ordering:

$$\frac{1}{\chi}=\frac{1}{\chi_0'}+\frac{T}{C'}-\frac{\sigma'}{T-\theta}\ . \tag{1}$$

This law is valid starting with $\sim 80\ °\mathrm{K}$ above the Curie temperature. Except for this discrepancy which was ascribed by Néel[11] to molecular-field fluctuations, a good agreement between the experimental points and theoretical predictions (plotted by solid line) is observed in Fig. 1. In Table II we present the C', $1/\chi_0'$, σ', and θ' parameters used for plotting the theoretical curves.

The Curie constants C' deduced from the asymptotic region of the hyperbolas [Eq. (1)] are greater than those real C's, as a consequence of the thermal variation of the molecular field coefficients.[12] The real Curie constant C is[12,13]

$$1/C=1/C'-\gamma(1/\chi_0')\ . \tag{2}$$

Making use of the pressure studies[5] we have estimated $\gamma=4\times10^4$ to 10×10^{-4} (see the Appendix). Adopting $\gamma=7\times10^{-4}$, the real Curie constants C were obtained (Table III).

The measurements carried out on $R\mathrm{Ni}_2$ compounds[4,14] where nickel is nonmagnetic, pointed out that the Curie constants are identical with those of rare-earth ions. Thus, in agreement with the additional law of susceptibilities, we obtained the magnetic contribution of cobalt atoms (Table III).

It is reasonable to attribute an effective moment $\mathfrak{M}_{\mathrm{Co}}^p = (2.00\pm0.50)\mu_B$ to all the studied compounds. The minus deviation may be a consequence of (i) the presence of the temperature-independent pa-

TABLE II. The C', $1/\chi_0'$, σ', and θ' parameters used for plotting theoretical curves.

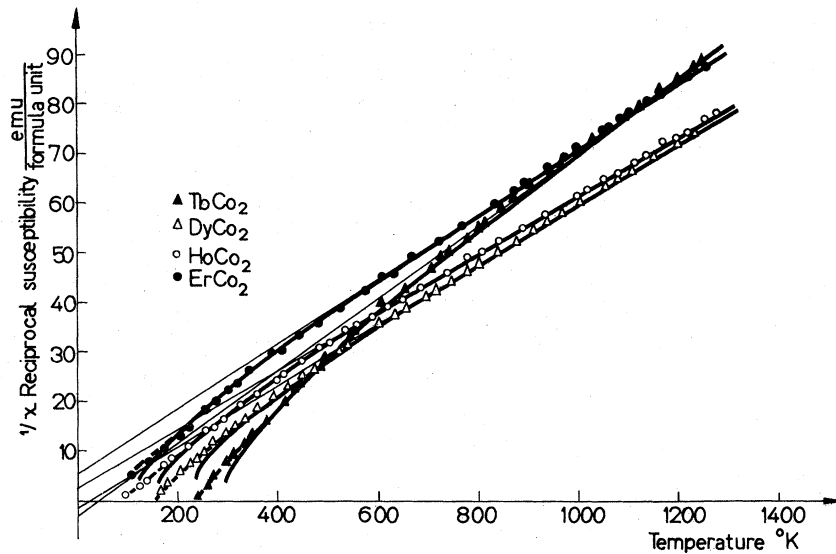| Compound	C' (emu)	$\dfrac{1}{\chi_0'}$	σ'	θ'
GdCo_2	9.60	-8.44	1653	425
TbCo_2	13.26	-3.50	1178	260
DyCo_2	16.28	-1.40	505	180
HoCo_2	16.40	2.40	490	120
ErCo_2	14.84	5.60	405	80

FIG. 1. Temperature dependence of reciprocal susceptibility for $TbCo_2$, $DyCo_2$, $HoCo_2$, and $ErCo_2$ compounds.

ramagnetic term due to conduction electrons, which may increase the Curie constants up to 1%, or (ii) the estimation of γ value being too low.

As in the case of saturation measurements, the cobalt electronic configuration is similar for the studied compounds. The effective moment of cobalt atoms is twice the value obtained by saturation measurements.

Finally, it is interesting to point out that for RCo_2 compounds the exchange-interaction coefficients J_{R-R} and J_{R-Co}, defined by

$$J_{R-Co} = g_J N_{R-Co}/(g_J - 1) ,$$
$$J_{R-R} = g_J^2 N_{R-R}/(g_J - 1)^2 ,$$

(3)

have approximate constant values; $J_{R-Co} = 105 \pm 15$ and $J_{R-R} = 50 \pm 10$, close to those calculated in the model proposed by Bloch and Lemaire. In the relation (3) we noted by g_J the spectroscopic splitting factor of the rare-earth ion and N_{R-Co}, N_{R-R} the molecular-field coefficients, describing the interactions between rare-earth cobalt and rare-earth–rare-earth, respectively.

IV. MAGNETIC PROPERTIES OF GADOLINIUM COBALT INTERMETALLIC COMPOUNDS

In order to confirm the generality of the above results concerning the magnetic behavior of cobalt atoms, we have extended the magnetic studies on the gadolinium-cobalt compounds.

Generally, these compounds may be classified from a crystallographic point of view into two groups: (i) compounds with a high cobalt content: Gd_2Co_{17}, $GdCO_5$, Gd_2CO_7, $GdCo_3$, and $GdCo_2$. They present a crystalline structure derived by ordered substitutions[15] from the $CaCu_5$ fundamental type in which $GdCo_5$ crystallizes; (ii) compounds

with a rich gadolinium content: Gd_4Co_3 and Gd_3Co. The crystalline structure consists of trigonal gadolinium prisms, including cobalt atoms.

We present in Fig. 2 a synthesis of the measurements below the Curie points. In order to compare the results we plotted in Fig. 2 the variation of reduced spontaneous magnetization M/M_0 as function of reduced temperature T/T_C.

In an analysis of the magnetic properties of these systems we admit a model with two magnetic sublattices antiparallel oriented, corresponding to the cobalt and gadolinium atoms. One observes that, depending on the magnetic contribution of the two sublattices, various magnetization curves characteristic of ferrimagnetic ordering are evident. We notice, according to Néel's classification,[11] that for the Gd_2Co_{17} compound this variation is of P type, for $GdCo_5$ is of M type, for Gd_2Co_7 is of N type, and for other intermetallic compounds with a richer gadolinium content the spontaneous magnetization obeys a Q-type variation.

Gd_3Co is metamagnetic, exhibiting an antiferro-

TABLE III. Corrected Curie constant, the contribution of cobalt atom at Curie constant, and the magnetic moment per cobalt atom for $\gamma = 7 \times 10^{-4}$.

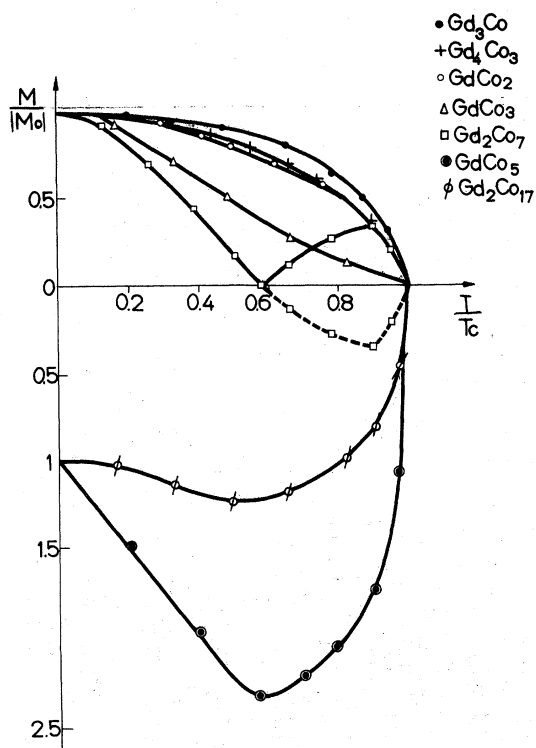| Compound	$GdCo_2$	$TbCo_2$ ($\gamma = 7 \times 10^{-4}$)	$DyCo_2$
Corrected Curie constant (emu) per formula unit	9.15	12.90	15.90
Contribution of cobalt atom at Curie constant (emu)	0.62	0.56	0.82
Magnetic moment per cobalt atom (μ_B) determined	2.16	2.05	2.50
supposed		2.00 ± 0.50	

FIG. 2. Reduced spontaneous magnetization $\mathfrak{M}/\mathfrak{M}_0$ as a function of reduced temperature T/T_C for gadolinum-cobalt compounds.

ferromagnetic transition even in a weak field. The magnetic contribution of cobalt atoms in this compound is null.

Using the above magnetic model we determined the mean magnetic value of cobalt atoms (Table IV). This contribution decreases with the increase of gadolinium molar fraction in compound.

Paramagnetic measurements were performed on the following compounds: Gd_2Co_7, $GdCo_3$, $GdCo_2$, Gd_4Co_3, and Gd_3Co. The Gd_3Co obeys a Curie–Weiss behavior. The effective magnetic moment per gadolinium atom, $8.04\mu_B$, is close to the theoretical value. Cobalt has no paramagnetic mo-

ment. The temperature dependence of reciprocal susceptibility in compounds where a magnetic contribution of cobalt atom in ordered state is evidenced obeys a Néel-type law (1). In accordance with the adopted magnetic model, the values of $1/\chi_0$, C, σ, and θ constants implicated in relation (1) were determined (Table V). A good agreement between the experimental points and theoretical curves plotted with these parameters is observed (Fig. 3).

The Curie constant for Gd_4Co_3 was corrected using $\gamma = 4 \times 10^{-4}$. In compounds with a richer cobalt content than $GdCo_2$, corrections for the Curie constants were not made. The absence of pressure studies and dilatation measurements did not permit us to estimate γ. We consider that these corrections are not significant, being in the limit of experimental errors.

As in the case of RCo_2 compounds we determined the mean magnetic contribution of cobalt atoms in the paramagnetic state (Table V). The cobalt mean magnetic moments as a function of gadolinium content are represented in Fig. 4. A continuous decrease of the determined values with the increase of molar fraction of gadolinium is observed. Similar behavior was found both for iron[16,17] and nickel[18] in rare-earth compounds.

V. CONCLUSIONS

The experimental measurements show an interesting magnetic behavior of cobalt atoms in rare-earth compounds. In addition to a localized character evidenced both by saturation and paramagnetic studies, we noticed a sensibility of these moments to rare-earth content, the valence-electron concentration, respectively. Such behavior can be justified in the model proposed by Friedel.[19]

The conduction electrons contributed by rare earths fill the $3d$ band, modifying its configuration. Thus, with the increase of the rare-earth content the electronic configuration of cobalt is gradually changed from that characteristic of metallic cobalt up to a complete $3d$ shell.

Of course, superposed on this general tendency,

TABLE IV. Magnetic properties of gadolinium cobalt intermetallic compounds.

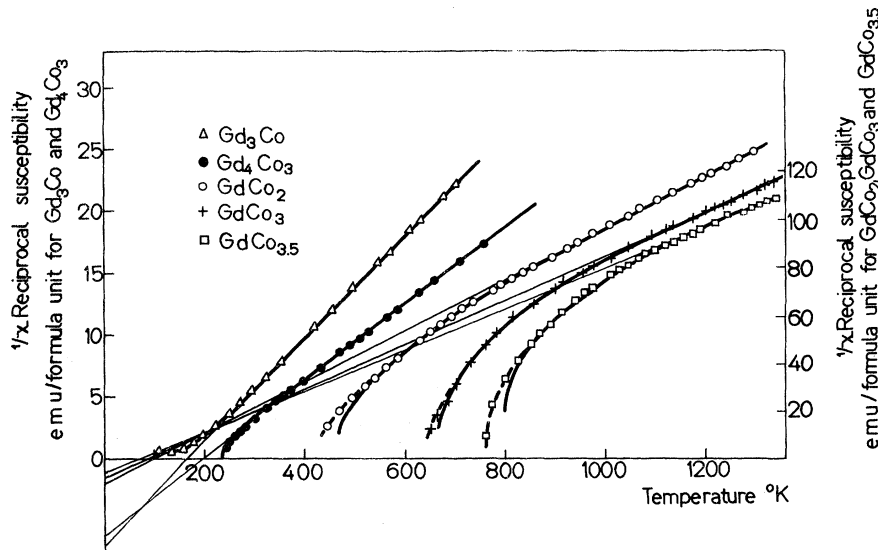| Compound	Gd_2Co_{17}	$GdCo_5$	Gd_2Co_7	$GdCo_3$	$GdCo_2$	Gd_4Co_3	Gd_3Co
Magnetic moment per formula unit (μ_B)	14.1	1.4	2.6	2.3	4.95	26.0	21.5
Mean magnetic moment per cobalt atom (μ_B)	1.66	1.67	1.63	1.57	1.02	0.66	0
Curie temperature (°K)	1222	1020	767	611	395	233	130

FIG. 3. Temperature dependence of reciprocal susceptibility for $GdCo_{3.5}$, $GdCo_2$, $GdCo_3$, Gd_4Co_3, and Gd_3Co compounds. To compare the results for the first three compounds we plotted the susceptibility for a formula unit having one gadolinium atom.

other factors may also influence the cobalt magnetic moments.

(i) The magnetic interactions between rare-earth atoms modify the state density at the Fermi level and, consequently, induce supplementary magnetic moments at cobalt atoms. This explains the smaller cobalt magnetic moment in compounds with nonmagnetic rare earths.[1]

(ii) The particularities of crystalline structure may also influence cobalt magnetic moments. As for Gd_4Co_3 one observes $\mathfrak{M}_{Co}$ values greater than those supposed by extrapolation (Fig. 4). This may be correlated with the modification of interaction energy between the cobalt atoms, a consequence of extremely small distances among these atoms.[20] In Y_4Co_3 cobalt exhibits magnetic moments, though YCo_2 with a richer cobalt content is a Pauli paramagnet, confirming our supposition.

The variation of magnetic moment of cobalt atoms with rare-earth content characterizes the two temperature ranges, the $\mathfrak{M}_{Co}^p/\mathfrak{M}_{Co}^0$ ratio being approximately constant. Particularly for RCo_2 studied compounds $\mathfrak{M}_{Co}^p = (2.00 \pm 0.50)\mu_B$, while $\mathfrak{M}_{Co}^0$ $= (1.00 \pm 0.20)\mu_B$. This behavior is also characteristic of iron and nickel in rare-earth compounds, being similar to that observed for $3d$ transition elements.

ACKNOWLEDGMENT

APPENDIX: ESTIMATION OF γ VALUE

The large variation of the Curie temperature with pressure seems to indicate a significant thermal variation of the molecular-field coefficients N[12,13]:

$$N = N_0(1 + \gamma T),$$

where N_0 is the molecular-field coefficient at 0 °K

TABLE V. C, $1/\chi_0$, θ, and σ constants implicated in relation (1).

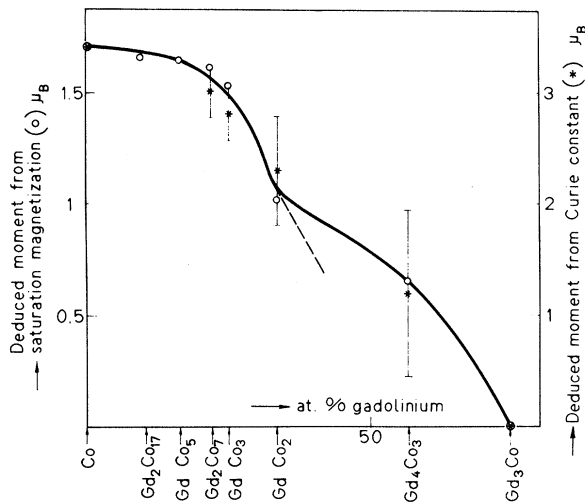| Compound	Curie constant (emu) per formula unit	$\dfrac{1}{\chi_0}$	θ	σ	Effective moment per cobalt atom (μ_B)	$\dfrac{\mathfrak{M}_{Co}^p}{\mathfrak{M}_{Co}^0}$	Curie paramagnetic temperature (°K)
$GdCo_{3.5}$	11.72	−5.80	790	1152	3.00 ± 0.10	1.84	⋯
$GdCo_3$	10.95	−8.00	640	1650	2.90 ± 0.10	1.85	⋯
$GdCo_2$	9.15[a]	−8.44	425	1653	2.16 ± 0.50	2.09	⋯
Gd_4Co_3	32.10[a]	−5.50	240	3	1.20 ± 0.80	1.82	⋯
Gd_3Co	24.15	⋯	⋯	⋯	0		160

[a]Corrected values.

FIG. 4. Variation of cobalt magnetic moment values
with gadolinium content.

and γ is a characteristic constant of the system:

$$\gamma = 3\alpha \frac{d\log_{10}N}{d\log_{10}V}.$$

The α thermal dilatation coefficients for RCo_2 compounds were previously determined.[21]

Under the conditions resulting from the relative magnitude of molecular-field coefficients we approximate

$$\frac{d\log_{10}N}{d\log_{10}V} \approx \frac{d\log_{10}T_C}{d\log_{10}V} - 2\frac{d\log_{10}M_0}{d\log_{10}V}.$$

We noted by $d\log_{10}T_C/d\log_{10}V$ and $d\log_{10}M_0/d\log_{10}V$ the variation with the volume of the Curie temperature and saturation magnetization, respectively.

We estimated the γ constant for $GdCo_2$, $TbCo_2$, and $DyCo_2$, where the $d\log_{10}T_C/d\log_{10}V$ values have about the same magnitude (Table I). Since $d\log_{10}M_0/d\log_{10}V$ are not known, we consider in a first approximation

$$\left|\frac{d\log_{10}T_C}{d\log_{10}V}\right| \approx \left|\frac{d\log_{10}M_0}{d\log_{10}V}\right|.$$

The Bloch's pressure studies for $3d$ transition alloys[13] confirm that this assumption is acceptable. It results under such conditions that $\gamma = (4-10) \times 10^{-4}$. The values thus obtained are greater, but of same order of magnitude as those determined for rare-earth garnets[22] and ferrites.[13]

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ERRATA

Effect of Exchange with Local Moments and Hyperfine Interactions on the Electron-Spin-Resonance Line Shape in Metals, J. H. Pifer and R. T. Longo [Phys. Rev. B 4, 3797 (1971)]. The manner in which we have extended the Langreth-Cowan-Wilkins equations to unequal g values is incorrect.[1] The cross-relaxation terms in Eqs. (3) and (4) are written so that total magnetization rather than an-