PARAMAGNETIC RESONANCE OF COBALT IN INTERMETALLIC COMPOUNDS*

R. G. Barnes, D. A. Cornell,† and D. R. Torgeson

Institute for Atomic Research and Department of Physics, Iowa State University, Ames, Iowa

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The detection and interpretation of the paramagnetic resonance of S-state ions in metallic substances has been the subject of a number of papers. These have dealt principally with the Mn^{2+} ion[1] and the Gd^{3+} ion[2] in very dilute concentrations (except for Gd^{3+}) in $GdAl_2$[2] and in gadolinium itself[3] and at low temperatures. By contrast, the case for experimental observation of the paramagnetic resonance of non-S-state ions has not been considered very promising.[2] We report here initial results on the paramagnetic resonance of a non-S-state ion—cobalt—in a series of intermetallic compounds, notably with the rare earths, yttrium and scandium, at temperatures ranging from 77 to 375°K.

The rare-earth–cobalt intermetallics investigated are of the cubic Laves phase structure, having the composition RCo_2 (R = rare earth), in which the cobalt occupies a site of trigonal symmetry ($\bar{3}m$). Specimens were prepared by arc melting, and although the buttons were turned and remelted several times to insure homogeneity, metallographic examination of the as-arc-cast samples showed them to be three-phase due to a peritectic reaction.[4] Subsequent heat treatment for one week at 920°C resulted in a single-phase microstructure. X-ray diffraction patterns of the freshly crushed powders were sharp with no extra lines present.

Resonance measurements were made at a nominal frequency of 9500 Mc/sec. Due to the fact that the sample particles (325 mesh) are somewhat larger than the skin depth, mode mixing occurs, and the resulting lines have been analyzed in a manner similar to that employed by Peter et al.[2] "Pure" absorption and dispersion signals, obtained by appropriate spectrometer balancing, are isotropic and closely Lorentzian in shape. The sample powder was either distributed thinly on plastic tape or mixed with a large quantity of talc and packed in a thin glass tube. Typical samples contained about 3-5 mg of compound, and did not measurably load the cavity.

The principal experimental results are summarized in Table I. Except in the case of $ScCo_2$, both the g value and width increase as the temperature decreases, with the widest lines occurring in those compounds containing magnetic rare earths. Some lines which are measurable at 300°K are so broad at 77°K that meaningful interpretation of the signal is impossible. Absorption intensitites were compared with a standard sample (pitch), with the spectrometer balance set to yield a pure absorption signal shape.

Demagnetizing factor corrections have not been applied to the entries in Table I; however, these are not large enough to influence the results significantly. Thus, at 300°K, the demagnetizing field is roughly 12 Oe in $ScCo_2$ and 0.5 Oe in $ZrCo_2$, smaller than the scatter in the raw data.

Magnetic susceptibility[5] and neutron diffraction[6] studies of the RCo_2 and RNi_2 series of compounds indicate that when R is trivalent and nonmagnetic (e.g., Lu, Y, Sc), RNi_2 exhibits only Pauli paramagnetism; the corresponding RCo_2 compounds exhibit Curie-type paramagnetism, but when R is tetravalent and nonmagnetic (e.g., Zr, Ce) RCo_2 is again Pauli paramagnetic. These observations lead to the

Table I. Representation g values, linewidths, and intensities of the cobalt paramagnetic resonance in RCo_2 intermetallics.

R	T (°K)	g	δH (Oe)[a]	spins/Co ion
Sc	300	4.81 ± 0.12	1095 ± 45	3.4
	77	4.65 ± 0.20	1325 ± 30	
Y	300	5.16 ± 0.11	590 ± 35	1.8
	77	5.44 ± 0.15	740 ± 30	
Ce	300	3.34 ± 0.06	1075 ± 60	27.2
	210	3.43 ± 0.08	1240 ± 70	
	152	3.57 ± 0.10	1410 ± 80	
	84	4.15 ± 0.12	2345 ± 100	
Pr	300	5.59 ± 0.25	2265 ± 60	
Nd	300	4.73 ± 0.06	1705 ± 50	3.5
Er	300	4.63 ± 0.13	2275 ± 100	2.4
Tm	300	4.24 ± 0.07	1355 ± 50	
Zr	300	4.20 ± 0.05	960 ± 40	0.3
	77	5.03 ± 0.15	1340 ± 40	
U	300	6.72 ± 0.15	825 ± 25	

[a] δH is the Lorentzian full width at half-maximum intensity.

plausible supposition that for trivalent R, the nickel ions are actually neutral atoms, with configuration d^{10}, and the cobalt ions are also neutral, with configuration d^9.[7] On this basis, we expect the cobalt paramagnetic resonance to be that of the d^9 ion, whereas no resonance would be expected in the nickel compounds. Indeed, in the pseudobinary system, $Sc(Co_xNi_{1-x})_2$,[8] the intensity of the cobalt paramagnetic resonance is directly proportional to the cobalt content. The intense resonance observed in $CeCo_2$, as well as the resonances found in $ZrCo_2$ and UCo_2, is difficult to interpret in view of the apparent Pauli paramagnetic nature of these compounds and the presumed d^{10} configuration for the cobalt.

The temperature dependence of the line broadening, a typical example of which is shown in Fig. 1, strongly suggests an activated distortion process with a thermal barrier on the order of 100°K in the case of $CeCo_2$. This result is very similar to that observed by Low and Suss[9] for the d^9 ions, Ni^{1+} and Cu^{2+}, in CaO, and also provides an argument favoring the d^9 configuration for the cobalt ion. In the present case, the point symmetry for the cobalt is nominally $\bar{3}m$, so that a dynamic Jahn-Teller distortion could be responsible for the line narrowing and perhaps also for the temperature dependence of g. However, it appears that an approach based on perturbation theory[10] would be unable to account for the large g values obtained.

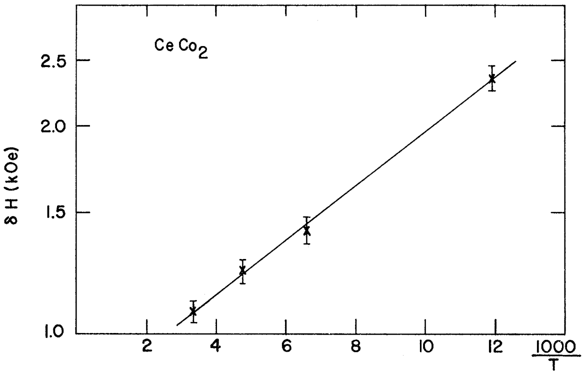

FIG. 1. Logarithm of the paramagnetic resonance linewidth (Lorentzian full width at half-maximum intensity) versus reciprocal temperature in the case of $CeCo_2$. The slope of the straight line reflects an energy of activation, $E_{act}/k \cong 100$°K.

Lanthanon-cobalt intermetallics of other compositions (principally with yttrium), as well as alloys, also yielded strong resonances at 300°K, suggesting that this phenomenon may be typical of cobalt in metallic systems with group II and III metals. Some further experiments with iron-containing intermetallics [e.g., in the $Sc(Fe_xNi_{1-x})_2$ system] have also yielded resonances.

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†Summer Faculty Participant; present address: Principia College, Elsah, Illinois.

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