

Specific Heat of CeCo_2 at Temperatures
Between 1.5 and 300°K^*

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Abstract

The heat capacity of CeCo_2 has been measured in the ranges 1.5 to 13°K and 8 to 300°K. Results in the liquid helium range show a marked deviation from the usual relation $C/T = \gamma + \beta T^2$, giving a minimum at $T^2 \approx 5^\circ\text{K}^2$ when C/T is plotted against T^2 . The results are discussed in terms of spin fluctuation effects, suggested by the work of Doniach and Engelsberg, and of the magnetic cluster effect described by Schröder. An approximate enhancement factor λ_t involving electron-phonon and electron-electron interactions is given. The large heat capacity near room temperature may be accounted for by an electronic contribution. The heat capacity behavior of CeCo_2 is similar in all respects to that previously observed for CeNi_2 .

Introduction

In recent publications from this laboratory low temperature heat capacity results have been presented for intermetallic compounds involving the lanthanide elements in chemical union with Al^{1,2}, Sb and Bi^{1,3}, Ni¹, Co⁴ and In⁵. Results for CeNi₂ were found to be anomalous. Plots of C_p/T versus T^2 were not linear below 4°K but instead exhibited an upturn for $T < 2.3^\circ\text{K}$. In addition, C_p exceeds the Dulong-Petit limit for $T > 200^\circ\text{K}$ and it continues to increase with rising temperature in an approximately linear fashion near room temperature. Measurements were undertaken on CeCo₂ partly to ascertain if it behaves similarly. Studies of the kind reported in this communication are also of use in stimulating theoretical work on the band structure of rare earth intermetallics.

Experimental Details

Two sets of heat capacity measurements on CeCo₂ were carried out. The first set was made in the temperature range of 8 to 300°K using the intermittent heating technique in the adiabatic calorimeter previously described³. The second set was made over the 1.5 to 13°K range using a pulse technique which will be described in detail elsewhere⁶. In order to make the comparison between CeCo₂ and CeNi₂ more meaningful, measurements on the latter compound were repeated in the 1.5 to 13°K range, using the pulse technique and a newly prepared sample. The pulse calorimeter was under on-line computer control, which considerably enhanced the precision of the results and the speed with which the measurements could be made.

The sample used in the calorimeter for the 8 to 300°K measurements was prepared by levitation melting and consisted of a number of small pieces (about 5 g. each) having a total mass of 115.13 g. The sample for the pulse calorimeter consists of a single piece of about 5 g. mass. Specimens of CeCo_2 and CeNi_2 for this calorimeter were prepared by induction heating in a water-cooled copper boat. The cobalt and nickel were of the Johnson-Matthey Spectrographically Standardized grade and the cerium was of 99.9% purity. After the samples had annealed for two weeks at approximately 800°C under an argon atmosphere, the x-ray pattern showed only lines characteristic of the MgCu_2 structure with lattice parameters in good agreement with the reported values⁷.

Results and Discussion

Results obtained on CeCo_2 and CeNi_2 in the low temperature range are shown in Fig. 1. The data on CeCo_2 covering the range 1.5 to 300°K are given as smoothed values of the heat capacity at regular temperature intervals in Table 1. The precision of the original data, expressed as the average of the absolute values of the deviations from a smooth curve is about 1% in the range below 13°K. Between 13 and 200°K the average deviation is $\pm 0.2\%$, while between 200 and 300°K the average deviation is $\pm 0.4\%$.

The upturns shown in the data plotted in Figure 1 are of considerable interest. They cannot be ascribed to hyperfine interactions since none of the stable cerium isotopes has magnetic or quadrupole moments. However, CeNi_2 has been examined in considerable detail; the earlier concept of Ce as a quadripesitive entity in CeNi_2 proved to be

untenable⁸. It appears that it is in the tripositive state but with the spin strongly compensated by interaction with the conduction electrons. It is possible that this also holds for Ce in CeCo₂. If this is correct, there may be a contribution to the heat capacity from the breakup of the spin-compensated state (the Kondo heat capacity). The temperature dependence of the Kondo heat capacity is unknown in concentrated systems, although the groundwork for its ultimate clarification may already have been laid^{9,10, 11}. In any case, in this system we may also expect to see the effects of spin fluctuations, to which attention has been drawn by Doniach and Engelsberg^{12, 13}. These authors have shown that in "nearly ferromagnetic" systems spin fluctuations can give a contribution to the heat capacity which is proportional to $T^3 \ln T$. An expression for the total heat capacity including lattice, conventional electronic and spin fluctuation contributions is:

$$C = \gamma T + \beta T^3 + b T^3 \ln T/T_s . \quad (1)$$

The first two terms represent the electronic (enhanced by electron-phonon interactions and spin fluctuation effects) and the lattice contributions. The third is a consequence of spin fluctuations. T_s is the characteristic spin fluctuation temperature and b is a constant. Equation (1) may be rewritten as:

$$C = \gamma T + a T^3 + b T^3 \ln T . \quad (2)$$

where $a = \beta - b \ln T_s$. It is clear that the constant a may be zero or negative for sufficiently large values of b and T_s .

Another possible contribution to the low temperature upturns shown in Fig. 1 is the "magnetic cluster" effect discussed by Schröder¹⁴. When

a system contains clusters of magnetic atoms which are sufficiently large, the alignment of moments within a cluster leads to a large net moment which can oscillate about an orientation determined by the energy of crystal anisotropy. This can lead to a constant term C' in the specific heat as shown in equation (3).

$$C = \gamma T + \beta T^3 + C' \quad (3)$$

Such clusters can be readily formed in CeCo_2 because of the Laves phase (MgCu_2 type) structure. A stoichiometric excess of cobalt will result in the substitution of a cobalt atom for a cerium atom at various sites in the lattice, and each such site will consist of a cluster of 17 cobalt atoms. Properties dependent upon the concentration of clusters are expected to be very sensitive to slight stoichiometric excesses of Co (or Ni) in these compounds.

Since clusters can affect the heat capacity either directly, through the mechanism described by Schröder¹⁴, or indirectly through the production of spin fluctuations, we consider it probable that both effects will occur simultaneously in these compounds. Equation (4) has terms (C' and $bT^3 \ln T$) corresponding to both effects.

$$C = \gamma T + aT^3 + C' + bT^3 \ln T \quad (4)$$

The fit of this equation to the CeCo_2 and CeNi_2 data may be seen in Fig. 1. Only data between 1.5 and 5°K were used to determine the values of the constants, since above this range increasing divergence of the curve from the data is observed. In this regard the fit of the present data is consistent with cases previously studied^{15, 16} and with the uncertainties concerning the expected range of validity of the $T^3 \ln T$ terms¹³.

After the present measurements were completed and the results were being prepared for publication, Machado da Silva and Hill¹⁷ published their results on the low temperature behavior of both CeCo_2 and CeNi_2 . Their curves, covering the temperature range from 1 to 10°K, differ significantly from those obtained in this study. They report λ type anomalies in both CeCo_2 and CeNi_2 , peaking at about 5.9°K, which they ascribe to the presence of unreacted cerium. Their plots of C/T versus T^2 , on the other hand, show no evidence for the minima which we observed. The absence, in the results of Machado da Silva and Hill, of the effects which we have attributed to cobalt (or nickel) clusters is to be expected in samples with excess cerium. By extrapolation from the temperature region above the λ type anomalies they were able to obtain values of γ . Values of γ were also obtained in the present study by fitting the data to equation (4), using a least squares procedure. The results are shown in Table 2. The precision indices shown in the table are the standard deviations obtained in the least squares treatment.

In view of the approximate agreement with the results of Machado da Silva and Hill, we conclude that since equation (4) involves both magnetic clusters and spin fluctuations, the two effects are probably both present in these systems. In assessing the validity of the values of γ obtained here we note that the results are sensitive to the temperature range over which the data are fitted. This is perhaps not surprising since the temperature range over which the $T^3 \ln T$ relation is expected to hold is uncertain¹³. These facts, together with the experimental uncertainties in the data, make it clear that the values of γ obtained are expected to be only approximate. It should be emphasized that the value

of γ obtained in these studies does not reflect the bare density of states at the Fermi level, but includes an enhancement factor proportional to the increase in the effective mass resulting from electron-phonon and electron-electron interactions¹⁵.

CeCo₂ has been found to be a superconductor with a transition temperature of about 1.4°K^{18,19}. It has been shown that T_c is very sensitive to changes in composition; a variation of the order of 0.1% on either side of a critical stoichiometric ratio causes T_c to drop below 0.5°K. This dependence upon composition is inferred from the observed variation of T_c with lattice parameter¹⁹. CeNi₂, in contrast to CeCo₂, has been shown to remain in the normal state¹⁸ down to 0.015°K. In view of the fact that the anomalies in CeCo₂ and CeNi₂ occur at the same temperature and are similar in form, it is not likely that the effect in CeCo₂ (i.e. the upturn in Fig. 1) is related to its superconductivity. The strong composition dependency of T_c in CeCo₂, however, may be due to magnetic effects²⁰, e.g. magnetic clusters and/or spin fluctuations, which are also responsible for the observed heat capacity anomalies.

Collings and Ho²¹ and Collings, Ho and Jaffee²² have derived an empirical method based on the BCS²³-Morel²⁴ expression to determine an enhancement factor λ_t involving both electron-phonon and electron-electron interactions. This is applicable for an alloy series, making use of the superconducting transition temperature T_c and the calorimetrically determined values of the Debye temperature θ_D and the γ . (See Appendix) The modified BCS-Morel relationship between the quantities T_c , θ_D and γ shows that a semilog plot of T_c/θ versus $(0.212 \gamma)^{-1}$ will be linear for a series of alloys if the apparent pairing potential V_{app} is

constant. The data for CeRu_2 , LaRu_2 and LaAl_2 ^{25,26} plotted in such a manner are shown in Figure 2. It is seen that the points lie close to a straight line whose slope yields $V_{\text{app.}} = 0.24$ eV-formula unit. The total enhancement factors $\lambda_t = 0.212 V_{\text{app.}} \gamma$ are therefore 1.19, 0.69 and 0.56 for CeRu_2 , LaRu_2 and LaAl_2 respectively. When data for CeCo_2 are plotted it is seen that the point lies far below the line. This, we believe, is a consequence of the depression of T_c by the spin fluctuations, an effect not present in CeRu_2 , LaRu_2 and LaAl_2 . We expect, however, that the electron-phonon interactions in CeCo_2 will be characterized by the same value of $V_{\text{app.}}$ as in the other members of the same series plotted in Fig. 2. It is possible that, although the spin fluctuations have a very profound effect upon the superconducting transition temperature, the spin fluctuation enhancement of γ in CeCo_2 may be much less than the phonon enhancement²⁰. If the enhancement of the experimental γ is essentially all due to electron-phonon and electron-electron interactions we can calculate a value of λ_t by substituting the measured value of γ into the expression $\lambda_t = 0.212 V_{\text{app.}} \gamma$. Taking γ to be 33.4 mj/mol. deg.² we find that $\lambda_t = 1.70$.

CeCo_2 exhibits unusual behavior in many respects. One puzzling question concerns the relative values of T_c in YCo_2 , LuCo_2 and CeCo_2 . Although all three compounds are non-ferromagnetic and would be expected to exhibit superconductivity, LuCo_2 has been shown to remain normal down to 0.32°K ²⁷ while YCo_2 has not been reported to be a superconductor. T_c for CeCo_2 , on the other hand, is about 1.4°K ^{18,19}. The first two

compounds are "nearly ferromagnetic"* and the spin fluctuations are undoubtedly responsible for the suppression of T_c . On the other hand, if Ce in CeCo_2 exists largely as Ce^{++++} , the extra electron donated by Ce^{+++} results in a greater filling of the 3d band, making the Co less polarizable than in the other compounds. Thus, although spin fluctuations are present in CeCo_2 , they are probably weaker than in YCo_2 and LuCo_2 , and hence do not completely suppress the superconductivity.

The room temperature (300°K) value for C_p of CeCo_2 is 80.5 joules/mol.deg. We may note that this quantity can be accounted for by a combination of reasonable values for the contributions of the vibrational, dilatational and electronic heat capacity terms. According to Machado da Silva and Hill¹⁷ θ_D for CeCo_2 is 186°K . Although this value is expected to apply strictly only to the low temperature region, we will, in view of the lack of other data, assume that it holds approximately at room temperature also. From this we find that the vibrational contribution to C_v is 73.4 joules/mol.deg. at 300°K . In estimating the electronic contribution we note that the electron-phonon enhancement factor becomes negligible at temperatures approaching $2\theta_D$ ²⁸ and it is assumed that the same applies to the spin fluctuation enhancement. We therefore use the γ value of 12.4 mj/mol.deg.², which is our measured value of 33.4 reduced by the factor $1/(1 + \lambda_t)$. This gives an electronic contribution of 3.7 j/mol.deg. at 300°K , making the total C_v equal to 77.1 j/mol.deg. The difference, $C_p - C_v$, is then 3.4 j/mol. deg. or about 4% of C_p . This is in the expected range for the magnitude of the dilatation term.

* This is evidenced by the fact that if a magnetic rare earth is substituted for the Y or Lu, the cobalt develops a moment.

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APPENDIX

In the following development we review the steps leading to the derivation of an electron-phonon enhancement factor applicable to both an alloy series and an homologous series of compounds. For non-interacting electrons, the electronic specific heat coefficient is a function only of the band structure and is related to the Fermi density-of-states by:

$$\gamma_{BS} = (1/3) \pi^2 k^2 [2N(E_F)] \quad (5)$$

where k is the Boltzmann constant, and $N(E_F)$ is the electronic density of states at the Fermi surface for a single spin orientation, expressed here in terms of a formula unit of CeCo₂. If the units of γ_{BS} and $N(E_F)$ are respectively, $\text{mj mole}^{-1} \text{ deg}^{-2}$ and $(\text{eV formula unit})^{-1}$ then

$$N(E_F) = 0.212 \gamma_{BS} \quad (6)$$

The experimentally measured γ can be expressed in terms of a total enhancement factor: λt

$$\gamma = \gamma_{BS}(1+\lambda t) \quad (7)$$

According to Morin and Maita, plots of $\ln(T_c/\theta_D)$ versus $1/N(E_F)$ for various families of transition metal alloys and compounds are fairly linear in the form,

$$T_c/\theta_D \sim \exp [-1/N(E_F)V] \quad (8)$$

They concluded that for the alloy and compound system studied, the V of equation (8) was essentially constant. Collings and Ho²¹ proceeded to show that an apparent pairing potential V_{app} is just the quantity required to obtain λt from the experimentally measures γ . Let $V_{app} = V/(1+\lambda t)$, then using equations (6), (7) and (8).

$$\ln(T_c/\theta_D) + \text{const} = -[0.212\gamma_{BS} V_{app} (1 + \lambda t)]^{-1} = -[0.212\gamma V_{app}]^{-1} \quad (9)$$

The slope of $\ln(T_c/\theta_D)$ versus $(0.212 \gamma)^{-1}$ is therefore $-1/V_{app}$. It is then possible to express γ_{BS} explicitly in terms of the measured γ and the slope parameter, V_{app} .

$$\gamma_{BS} = \gamma / (1 + 0.212 \gamma V_{app}) \quad (10)$$

TABLE I

Heat Capacity of CeCo_2 at Selected Temperatures

T deg K	Cp j/mol. deg	T deg K	Cp j/mol. deg
1.5	0.0587	80	47.46
2	0.0762	90	51.82
3	0.117	100	55.46
4	0.174	110	58.50
5	0.255	120	61.05
6	0.358	130	63.24
7	0.508	140	65.13
8	0.722	150	66.78
9	0.995	160	68.25
10	1.316	170	69.56
12	2.07	180	70.73
14	2.96	190	71.77
16	3.99	200	72.71
18	5.10	210	73.55
20	6.30	220	74.34
25	9.73	230	75.10
30	13.65	240	75.85
35	17.66	250	76.63
40	21.62	260	77.45
45	25.51	270	78.30
50	29.26	280	79.15
55	32.82	290	79.91
60	36.19	298.15	80.38
70	42.27	300.0	80.46

TABLE 2

Constants in equation 4, evaluated from
experimental data between 1.5 and 5°K

	constants in equation 4				M. da S. and Hill
	c mj/mol. deg	a mj/mol. deg ⁴	b mj/mol. deg ⁴	γ mj/mol. deg ²	γ
CoCo ₂	9.15 ±1.10	-0.42 ±0.14	0.651 ±0.070	33.4 ± 0.9	38.2
CeNi ₂	4.15 ±0.58	-0.213 ±0.068	0.322 ±0.034	24.2 ± 0.5	24.9

Captions for Figures

- Fig. 1 Plot of C/T versus T^2 for $CeCo_2$ and $CeNi_2$. The line in each case was obtained by fitting Eq. 4 to the data.
- Fig. 2 Semilog plot of T_c/θ_D versus $(0.212\gamma)^{-1}$ (see appendix).

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