



Journal of Alloys and Compounds 224 (1995) 249-252

# Superconductivity in LaCd<sub>2</sub>

J. Tang<sup>1</sup>, Q. Li<sup>2</sup>, K.A. Gschneidner Jr.<sup>3,\*</sup>

Ames Laboratory, Iowa State University, Ames, IA 50011, USA

Received 15 November 1994; in final form 13 December 1994

#### Abstract

Low temperature heat capacity and resistivity measurements indicated that LaCd<sub>2</sub> is a low temperature superconductor  $(T_c = 1.44 \text{ K})$ . It is a conventional weak-coupling superconductor with a coupling constant  $\lambda \approx 0.47$ . The electronic specific heat coefficient  $\gamma$  (8.0 mJ mol<sup>-1</sup> K<sup>-2</sup>) and Debye temperature  $\Theta_D$  (186 K) were determined from heat capacity data. The covalent bonding in LaCd<sub>2</sub> is probably responsible for preventing the softening of the phonon spectrum, which probably accounts for the low  $T_c$  value. LaCd<sub>2</sub> is the first superconducting intermetallic compound that has the CeCd<sub>2</sub>-type structure. However, compared with the lanthanum Laves phase compound superconductors, the structural difference may be insignificant in determining the superconducting properties.

Keywords: Superconductivity; Heat capacity; Resistivity

## 1. Introduction

In order to further understand the physics of 4f electrons in rare earth intermetallic compounds, a study of low temperature properties of Ce-Cd intermetallics was conducted [1]. Some of the corresponding La-Cd compounds were also examined because these lanthanum compounds can often be used as reference materials. The crystal structures of La and Ce compounds and their outer electronic configurations are usually the same and thus the differences in their behaviors will be due to the 4f electron of the Ce atom. Among the La-Cd compounds studied, LaCd<sub>2</sub> is the most interesting, because a superconducting transition was found at 1.44 K.

Superconductivity has been found in several cubic Laves phase La compounds, e.g. LaAl<sub>2</sub> ( $T_c = 3.2$  K [2]) and LaPt<sub>2</sub> ( $T_c = 0.46$  K [3]). LaCd<sub>2</sub> crystallizes in a different structure. It has the hexagonal CeCd<sub>2</sub> structure in which La atoms occupy 1(*a*) positions (0,0,0) and Cd atoms occupy 2(*d*) positions ( $\frac{1}{3}, \frac{2}{3}, x$ ), where  $x \approx 0.42$  [4-8]. The lattice parameters are a = 5.075 Å and c = 3.571 Å, although Iandelli and Ferro [4] reported a significantly lower c lattice parameter (3.458 Å).

### 2. Experimental details

The starting materials, La (99.8 at.% pure) and Cd (99.999 at.% pure) metals, were obtained from the Materials Preparation Center of the Ames Laboratory and Cominco Products Inc. respectively. The LaCd<sub>2</sub> sample was prepared by melting stoichiometric amounts of the constituents in a sealed tantalum crucible under a helium atmosphere using a resistance furnace. Owing to the high vapor pressure of Cd [9], it is important to seal the starting materials in a closed crucible in order to prevent the escape of Cd vapor at high temperatures. The La–Cd phase diagram indicates that LaCd<sub>2</sub> melts congruently at 953 °C [10] and therefore no further heat treatment was carried out. Optical metallography showed that the sample was single phase.

Low temperature heat capacity measurements (1.3-20 K) were carried out using an adiabatic heat pulse calorimeter [11]. Magnetic fields of 0, 0.1 and 0.2 T were applied during the heat capacity measurements. A conventional four-probe technique was used for making resistivity measurements between 0.5 and 2.4 K in a <sup>3</sup>He refrigerator.

<sup>\*</sup> Corresponding author.

<sup>&</sup>lt;sup>1</sup> Present address: Department of Physics, University of New Orleans, New Orleans, LA 70148, USA.

<sup>&</sup>lt;sup>2</sup> Present address: Department of Applied Science, Building 480, Brookhaven National Laboratory, Upton, NY 11973, USA.

<sup>&</sup>lt;sup>3</sup> Also Department of Materials Science and Engineering, Iowa State University, Ames, IA 50011, USA.

<sup>0925-8388/95/\$09.50 © 1995</sup> Elsevier Science S.A. All rights reserved SSDI 0925-8388(95)01529-9

## 3. Results

The original purpose of measuring the low temperature heat capacity of LaCd<sub>2</sub> was that it can serve as a reference material for CeCd<sub>2</sub>, which showed a rather complex magnetic behavior with two magnetic transitions at 18.5 and 22 K [1]. Without the complications brought about by the 4f electrons, LaCd<sub>2</sub> should behave as an ordinary metallic material, i.e. one would expect a linear electronic specific heat  $(\gamma T)$  and a  $T^3$  term from the lattice contribution. This was indeed the case above 1.5 K. However, its heat capacity exhibited a discontinuous jump at 1.4 K as shown in Fig. 1. The number of points below the transition was limited by the low temperature limit of our calorimeter. Although heat capacity data for LaCd<sub>2</sub> at lower temperatures are lacking, the nature of the transition associated with this jump can be clearly seen. The C/T vs.  $T^2$  plot (Fig. 2) showed a linear behavior down to the transition point, which indicated a non-magnetic nature of the transition. Heat capacity measurements in a magnetic



Fig. 1. Low temperature heat capacity of  $LaCd_2$  from 1.3 to 2.5 K.



Fig. 2. Low temperature heat capacity of LaCd<sub>2</sub> plotted as C/T vs.  $T^2$ . Magnetic fields of 0, 0.1 and 0.2 T were applied during the measurements.

field destroyed the peak observed at zero magnetic field (see Fig. 2) indicating that this is a superconducting transition. As a matter of fact, the value of  $(C_s - C_n)/\gamma T_c$  at  $T_c$  obtained from the heat capacity data is 1.46, which is close to the theoretical Bardeen– Cooper–Schrieffer. (BCS) value of 1.43 for a superconductor [12]. In calculating the above value, a  $\gamma$  of 8.0 mJ mol<sup>-1</sup> K<sup>-2</sup>, determined from the intercept of the straight line in Fig. 2, was used. The transition temperature  $T_c$  was found to be 1.44 K from the peak of the jump in the heat capacity.

A measurement of the field dependence of  $T_c$  was attempted by measuring the heat capacity under applied magnetic fields. As seen in Fig. 2, a field of 0.1 T is strong enough to shift  $T_c$  below 1.4 K, which is the lower limit of our calorimeter at that field.

In order to confirm this superconducting transition in LaCd<sub>2</sub>, electrical resistivity measurements were made from about 0.5 to 2.4 K (see Fig. 3). As seen, the superconducting transition is evident. The  $T_c$  value determined from the resistivity data (1.31 K) was somewhat lower than that noted above. The discrepancy between this value and the one obtained from heat capacity data is probably due to the fact that the resistivity of LaCd<sub>2</sub> in the normal state is small; thus a measuring current of 0.1 A was used in order to have a large enough voltage reading to overcome the background noise. Such a large current could cause Joule heating at the junctions between the sample and electrical leads. Another source of contact heating could be due to the fact that LaCd<sub>2</sub> is air sensitive, and during the time when the sample was taken out of the argon-filled glove-box to connect the electrical leads, a thin layer of oxide may have formed on the surface of the sample. As a result, the actual temperature of the sample was probably higher than the reading on the thermometer. We believe that the  $T_c$  value derived from the heat capacity measurements reflects the true transition temperature.



Fig. 3. Electrical resistivity as a function of temperature from 0.5 to 2.4 K.

Table 1

Compound	Structure type	Т <sub>с</sub> (К)	θ <sub>D</sub> (K)	$\gamma$ (mJ mol <sup>-1</sup> K <sup>-2</sup> )	λ
LaCd <sub>2</sub>	Hexagonal, CeCd <sub>2</sub>	1.44 *	186 *	8.0 *	0.47
LaAl <sub>2</sub>	Cubic, C15	3.2 [2]	352 [16]	10.95 [16]	0.49
LaPt <sub>2</sub>	Cubic, C15	0.46 [3]	236 [17]	3.51 [17]	0.36

Properties of some LaM<sub>2</sub> superconductors ( $T_c$ , superconducting transition temperature;  $\Theta_D$ , Debye temperature;  $\gamma$ , electronic specific heat constant;  $\lambda$ , electron-phonon coupling constant)

\* This study.

## 4. Discussion

The agreement between the measured value of  $(C_s - C_n)/\gamma T_c$  (1.46) and that from the BCS theory (1.43) implies that LaCd<sub>2</sub> is a conventional weak-coupling superconductor [13]. The magnitude of the electronic specific heat coefficient ( $\gamma = 8.0$  mJ mol<sup>-1</sup> K<sup>-2</sup>), which is about average for a low temperature superconductor, is consistent with this conclusion.

The phonon spectrum of LaCd<sub>2</sub> is moderately soft. The Debye temperature  $\Theta_D$  determined from the slope of the C/T vs.  $T^2$  plot is 186 K. The study by Mulokozi [8] indicated the formation of strong covalent bonds in RCd<sub>2</sub> (R≡rare earth) compounds. This covalent bonding might be responsible for preventing the softening of the phonon spectrum and therefore limiting the value of  $T_c$  to rather low temperature [14].

We now examine the superconducting behaviors of LaCd<sub>2</sub> and the two cubic Laves phase superconductors LaAl<sub>2</sub> and LaPt<sub>2</sub> to determine what factor(s) may play an important role in determining their  $T_c$ s. The important properties ( $T_c$ ,  $\Theta_D$  and  $\gamma$ ) are given in Table 1. It appears that the structure is not the predominant factor, nor do the  $T_c$ s scale with  $\Theta_D$ . There does appear to be a relation between the  $\gamma$  value and  $T_c$ . Since the electronic specific heat constant is dependent in part upon the electron-phonon enhancement factor (1+ $\lambda$ , where  $\lambda$  is the electron-phonon coupling constant), it would appear that the strength of the electron-phonon interaction is the most important parameter. We have calculated  $\lambda$  using the McMillan equation [15]

$$T_{\rm c} = \frac{\Theta_{\rm D}}{1.45} \exp\left(-\frac{1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)}\right)$$

where  $\mu^*$  is the electron-electron (Coulomb) coupling constant and generally has a value of about 0.10. Assuming that  $\mu^* = 0.10$  for the three LaM<sub>2</sub> compounds, one can calculate  $\lambda$  using the  $T_c$  and  $\Theta_D$  values listed in Table 1. The calculated  $\lambda$  values are also presented in Table 1. One notes that the  $T_c$ s follow the general trend in  $\lambda$  values, which parallel quite closely the  $\gamma$ values of the three LaM<sub>2</sub> phases. Since the scaling between  $T_c$  and  $\lambda$  (or  $\gamma$ ) is not perfect,  $\Theta_D$  also exerts some influence on the observed  $T_c$ . This is especially evident when one compares the  $T_c$  and  $\Theta_D$  values of  $LaCd_2$  with those of  $LaAl_2$ ; those of the latter are about twice as large as those of the former.

#### 5. Conclusions

LaCd<sub>2</sub> was found to be a superconductor with  $T_c = 1.44$ K. Both heat capacity and electrical resistivity experiments confirmed this result. The value of  $(C_s - C_n)/(C_s - C_n)$  $\gamma T_{\rm c}$  at  $T_{\rm c}$  (1.46) and the relatively small electronic specific heat coefficient  $\gamma$  (8.0 mJ mol<sup>-1</sup> K<sup>-2</sup>) suggested that LaCd<sub>2</sub> is a conventional weak-coupling superconductor. The electron-phonon coupling constant was estimated to be about 0.47, which indeed falls into the weak-coupling category. The Debye temperature was also determined from heat capacity data.  $\Theta_{\rm D} = 186$  K indicated a rather soft phonon spectrum; however, the covalent bonding in LaCd<sub>2</sub> probably prevented further softening of the phonon mode and thus resulted in the observed low  $T_c$ . LaCd<sub>2</sub> is a new member of the rare earth superconductor family. It is the first superconducting intermetallic compound with the CeCd<sub>2</sub>-type structure.

## Acknowledgments

The authors wish to thank B.J. Beaudry and N.M. Beymer for preparing the  $LaCd_2$  sample for us. The Ames Laboratory is operated for the US Department of Energy by Iowa State University under contract W-7405-ENG-82. This work was supported by the Office of Basic Energy Sciences.

#### References

- J. Tang and K.A. Gschneidner Jr., J. Less-Common Met., 149 (1989) 341.
- [2] M.B. Mapie, Appl. Phys., 9 (1976) 179.
- [3] T.H. Geballe, B.T. Matthias, V.B. Compton, E. Corenzwit, G.W. Hull Jr. and L.D. Longinotti, Phys. Rev., 137 (1965) A119.
- [4] A. Iandelli and R. Ferro, Gazz. Chim. Ital., 84 (1954) 463.
- [5] A. Iandelli and A. Palenzona, J. Less-Common Met., 15 (1968) 273.

- [6] G. Bruzzone, M.L. Fornasini and F. Merlo, J. Less-Common Met., 25 (1971) 295.
- [7] G. Bruzzone and F. Merlo, J. Less-Common Met., 30 (1973) 303.
- [8] A.M. Mulokozi, J. Less-Common Met., 53 (1977) 205.
- [9] R. Loebel, in R. Weast (ed.), CRC Handbook of Chemistry and Physics, CRC Press, Boca Raton, FL, 68th edn., 1987, p. D-215.
- [10] F. Canepa, G.A. Costa and E.A. Franceschi, Lanthanide Actinide Res., 1 (1985) 41.
- [11] K. Ikeda, K.A. Gschneidner Jr., B.J. Beaudry and U. Atzmony, *Phys. Rev. B*, 25 (1982) 4604.
- [12] N.W. Ashcroft and N.D. Mermin, Solid State Physics, Holt, Rinehart and Winston, New York, 1976, p. 747.
- [13] J.E. Crow and N.P. Ong, in J.W. Lynn (ed.), *High Temperature Superconductivity*, Springer, New York, 1990, p. 224.
- [14] C. Kittel, Introduction to Solid State Physics, Wiley, New York, 6th edn., 1986, p. 428.
- [15] W.L. McMillan, Phys. Rev., 167 (1968) 331.
- [16] R.E. Hungsberg and K.A. Gschneidner Jr., J. Phys. Chem. Solids, 33 (1972) 401.
- [17] R.R. Joseph, K.A. Gschneidner Jr. and R.E. Hungsberg, *Phys. Rev. B*, 5 (1972) 1878.