Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

Materials & Molecular Research Division

Submitted to Scripta Metallurgica

ON THE NATURE OF THE HYSTERETIC BEHAVIOR IN GdCu COMPOUND

Y. Gefen and M. Rosen

March 1980

RECEIVED
LAWRENCE
BERKELEY LABORATORY

APR 18 1980

LIBRARY AND
DOCUMENTS SECTION

TWO-WEEK LOAN COPY

*This is a Library Circulating Copy
which may be borrowed for two weeks.
For a personal retention copy, call
Tech. Info. Division, Ext. 6782.*

LBL 10608 C-2

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

ON THE NATURE OF THE HYSTERETIC BEHAVIOR IN GdCu COMPOUND

Y. Gefen

Nuclear Research Center Negev
P.O. Box 9001, Beer Sheva, Israel

and

M. Rosen*

Molecular and Materials Research Division
Lawrence Berkeley Laboratory,
University of California, Berkeley, CA 94720, USA

INTRODUCTION

The light rare earths-copper compounds (1:1) exhibit an orthorhombic FeB structure, whereas the heavy rare earths-copper compounds assume the CsCl structure (1). GdCu is the first of this series to be cubic. In the light rare earths-gold compounds that have a FeB symmetry, the CsCl structure can be obtained by quenching from the melt (2). The reason for this behavior is that the CsCl structure is unstable at low temperatures. Parthé et al. (3,4) explained the instability of the CsCl structure on the basis of the electron concentration, whereas Zener (5) related the instability of the CsCl structure at low temperatures as due to its large entropy at high temperatures.

Several 1:1 compounds with a CsCl type structure, e.g., Au-Cd, Ag-Cd, Cu-Zn, Cu-Sn, Ti-Ni, transform by a diffusionless thermoelastic martensitic transformation to an orthorhombic structure (6). This transformation is associated with superelasticity, shape memory effect, and rubberlike behavior. The CsCl $\rightarrow$ FeB phase transformation in the rare earths-gold (1:1) compounds was studied by X-ray diffraction and DTA (7). The thermal arrests were found to be weak and barely detectable. The metastable nature of the high temperature CsCl phase was mainly observed by the X-ray studies. Balster et al. (8) revealed a cubic to tetragonal phase change in YCu and LaAg doped with In. Electrical resistivity measurements showed a wide temperature hysteresis, characteristic of a martensitic phase transformation. A hysteresis of about 400 C was also observed in the CsCl $\rightarrow$ FeB phase change in YbAu compound employing magnetic susceptibility measurements (9).

Magnetic susceptibility measurements performed by de Wijn et al. (10) were interpreted as to indicate the occurrence of a phase transformation from CsCl to the FeB structure in GdCu compounds at 77 K. The CsCl structure was found to reappear after a high temperature heat treatment. However, Ross et al. (1) did not observe such a transformation by X-ray and Mössbauer effect measurements down to 4.2 K. A possible explanation for this disagreement was that the anomalous temperature dependence of the magnetic susceptibility (10) of GdCu might be strongly dependent on the previous heat treatments of the compound.

The objective of the present study was to investigate the behavior of the change in length and the electrical resistivity of GdCu over a wide temperature range in order to gain an insight into the reasons for the observed anomaly.

* On leave from the Materials Engineering Department, Ben Gurion University, Beer Sheva, Israel

EXPERIMENTAL

GdCu specimens were prepared by arc melting in a pure argon atmosphere at 250 Torr. The purity of the starting elements was 99.99% for Gd and 99.999% for Cu. The samples were remelted several times and homogenized at 600 C for 48 hours in vacuo. The stoichiometry and homogeneity was analyzed by the SEM-EDAX technique and found to be 42 ± 1 at.% Cu. Subsequent X-ray examination revealed a CsCl type structure. The lattice parameter ($a = 3.501$ Å) was in good agreement with the published value (12). Microphotography revealed small amounts of an unidentified second phase of a homogeneous distributions. This second phase was not detected by additional lines in the X-ray spectra. It was assumed to be free Gd.

For the electrical resistivity and the dilatometric measurements, cylinders of 3 mm in diameter and 20 mm long, were machined from the arc melted and homogenized bars. Electrical resistivity was measured during heating/cooling cycles employing the four probe potential method. A constant current of 0.5 A was supplied by a Kepko Model CK 50 Current Source. The voltage drop is determined by means of a Keithley 148 nV meter in conjunction with a Keithley 260 nV source in order to improve the resolution to 10 nV. The voltage drop against temperature change, between 77 and 700 K, was recorded on a HP 7001 AM Recorder. The electrical resistivity was determined to within 1% from the voltage drop, specimen geometry, and the values of the constant current. All measurements were carried out under a high vacuum in order to prevent oxidation of GdCu at high temperatures.

The temperature dependence of the change in the lengths of the samples was determined by means of two dilatometers. For the temperature interval between 77 and 400 K a capacitance dilatometer was used. The sample holder (13) was connected to a GR 1615A Capacitance Bridge and GR 1316 Oscillator. The change in capacitance against temperature was determined by measuring the deviation from balance with a PAR Lock-In Amplifier Model HR-8, and recorded on a HP 7001 AM Recorder. The accuracy of the calibrated dilatation measurement was 0.01%. In the temperature interval between 300 and 700 K a mechanical differential dilatometer was used. The samples were closed in evacuated quartz tubes. The dilatation was determined by means of a high precision LVDT. The estimated accuracy was 0.01%.

EXPERIMENTAL RESULTS

Figure 1 shows the temperature dependence of the electrical resistivity during a complete cooling/heating cycle. A temperature hysteresis of 370 K was observed. Upon cooling, a sharp increase in the electrical resistivity at 230 K marks the beginning of a possible crystallographic transformation. After the initial sharp rise a gradual increase is observed down to 140 K. The total increase in the electrical resistivity exceeds 100%. Upon heating, a fully reversible hysteresis loop is formed. The slope of the electrical resistivity versus temperature in both cooling and heating semicycles was found to be $0.11 \mu\Omega\text{cm K}^{-1}$, in the range of the whole hysteresis loop.

Figure 2 shows the change in length during the cooling and heating semicycles. The shape of the dilatometric curves is identical to that of the electrical resistivity (Fig. 1). The total change in length during a semicycle was found to be 0.6%. The total measured changes in volume was, therefore, 1.8%. Similar changes in volume were observed during the CsCl $\rightarrow$ FeB phase transformations in rare earths-gold (1:1) compounds (7) and in Yb-Ag (9).

Photomicrographs of the GdCu specimens while in the state of the heating and cooling semicycles, were prepared at room temperature. No difference in the microstructures of these two states of GdCu was observed.

XBL-803-8879

Fig. 1. The temperature variation of the electrical resistivity of GdCu compound in the temperature hysteresis region, upon cooling and heating.

XBL-803-8878

Fig. 2. The temperature variation of the length of GdCu compound in the temperature hysteresis region, upon cooling and heating.

DISCUSSION

DeWijn (10) interpreted the hysteresis loop in the magnetic susceptibility of GdCu as a crystallographic phase transformation from CsCl to FeB structure during the cooling semicycle. The present study revealed identical hysteresis loops in the electrical resistivity and volume change but could not substantiate the assumption of the occurrence of a crystallographic phase transformation (10) by X-ray and metallographic techniques.

Phase transitions in some rare earths-noble metal compounds have been identified as martensitic transformations (8,14). The definition was mainly based on the large temperature hysteresis accompanying the anomaly. However, a temperature hysteresis alone is not sufficient evidence for a martensitic transformation (15), characterized by a diffusionless, cooperative shear movement of atoms accompanied by a shape deformation of the transformed region.

The experimental results of the present study do not indicate, unambiguously, that the temperature hysteresis loops, in the volume change and electrical resistivity, are due to a crystallographic phase change. No corroborating evidence could be obtained from either X-ray diffraction or metallography. The microstructures of GdCu in the heating and cooling states, at room temperature, were identical. Moreover, total absence of any surface tilts or twinned structures, would preclude the operation of a martensitic mechanism. However, a small and continuous distortion of the cubic lattice accompanied by a pronounced elastic softening may be the cause of the observed anomaly as manifested by the temperature hysteresis loops in the magnetic susceptibility (10), and electrical resistivity and length changes in the present study.

ACKNOWLEDGMENT

The technical assistance of D. Kalir is gratefully acknowledged. The experiments were carried out in the Ultrasonics Laboratory, Physics Department of the Nuclear Research Center-Negev, Beer Sheva, Israel.

This work was supported by the U.S. Department of Energy under Contract W-7405-ENG-48.

REFERENCES

1. C. C. Chao and P. Duwez, J. Appl. Phys. 37, 2631 (1966).
2. C. C. Chao and H. L. Luo and P. Duwez, J. App. Phys. 34, 1971 (1963).
3. O. Schob and E. Parthé, Acta Cryst. 19, 214 (1965).
4. D. Hohnke and E. Parthé, Acta Cryst. 20, 572 (1965).
5. C. Zener, "Elasticity and Anelasticity in Metals," Univ. Chicago Press (1948).
6. L. Delaey, R. V. Krishnan, H. Tas and H. Warlimont, J. Mat. Sci. 9, 1521 (1974).
7. O. D. McMasters, K. A. Gschneidner, G. Bruzzone and A. Palenzona, J. Less Common Metals 25, 135 (1971).
8. H. Balster, H. Ihrig, A. Kockel and S. Methfessel, Z. Physik B 21, 241 (1975).
9. D. Debray, B. F. Wortmann, and S. Methfessel, Phys. Rev. 14, 4009 (1976).
10. H. W. DeWijn, K. H. J. Buschow and A. M. van Diepen, Phys. Stat. Solids 30, 759 (1968).
11. J. W. Ross and J. Siyalas, J. Phys. F 5, 1973 (1975).
12. E. Burzo, I. Ursu and J. Pierre, Phys. Stat. Solids 51, 463 (1972).
13. G. K. White, J. Phys. D 6, 2070 (1973).
14. C. Tannous, D. K. Ray and M. Belakhovsky, J. Phys. F 6, 2091 (1976).
15. M. Cohen, "The Martensitic Transformation" in Phase Transformations in Solids, editor R. Smoluchowski, John Wiley, New York, 1951, 538-560.