

Electrical Resistivity of Equiatomic Rare-Earth-Noble-Metal Compounds*

CHANG-CHIH CHAO

W. M. Keck Laboratory of Engineering Materials, California Institute of Technology, Pasadena, California

(Received 15 October 1965)

The electrical resistivity of twenty CsCl type intermediate phases of Gd, Tb, Dy, Ho, Er, and Tm with Cu, Ag, and Au and of Y and Nd with Ag were measured from 4.2°K to about 250°K. All of the resistivity-temperature curves, except that of YAg, show anomalies at temperatures which are in good agreement with the available antiferromagnetic-paramagnetic transition temperatures obtained by either neutron diffraction studies or magnetic susceptibility measurements. The spin disordering part of the resistivity of the CsCl phases were deduced and any attempt to apply the theory of de Gennes and Friedel which was used by Rocher for pure rare-earth elements, was not successful.

INTRODUCTION

THE electrical resistivity of rare-earth elements has been extensively studied during the last ten years.¹⁻⁴ For most of the pure rare-earth elements, there are very pronounced anomalies in the variation of electrical resistivity with temperature which have been attributed to the interaction between the conduction electrons and the 4*f* electrons. The same type of interaction was also used to explain the electrical resistivity of binary alloys containing rare-earth elements.^{5,6} In this investigation, the electrical resistivities of CsCl phases involving eight of the rare-earth metals with Cu, Ag, and Au were measured from 4.2° to 250°K. These intermediate phases constitute an interesting series of alloys for studying the role of the indirect exchange interaction between rare-earth ions because their crystal structure is simple and the electronic configuration of the alloying elements (Cu, Ag, or Au) is also relatively simple.

EXPERIMENTAL

Alloys were prepared by induction-melting stoichiometric amounts of elements in spot-welded tantalum tubes under argon atmosphere, and their crystal structure was checked by x-ray diffraction. The cylindrical bars required for resistivity measurements were prepared in the following manner: the alloys were powdered under argon atmosphere and the powder was tightly packed into a tantalum tube having a 2.8-mm inside diameter. The tube was sealed by spot welding and the alloys were remelted by slowly introducing the tube into the induction coil. This operation was repeated several times in order to eliminate gas bubbles during solidification. After the last melting, the bar

(including the tantalum tube) was machined to a final diameter smaller than the original inside diameter of the tantalum tubing (about 2 mm), in order to remove the outside layer that may have been contaminated by reaction with tantalum.

The resistance was measured by the standard four probe method with current reversal. Measurements were carried out from liquid-helium temperature to about 250°K. Temperatures were measured by means of copper-constantan thermocouples which were pressed against the specimen. In the temperature range from 4.2° to 100°K, the thermocouples were calibrated against a germanium cryogenic thermometer (Honeywell model MHSP 2406). Above 100°K, calibration tables of Pawell *et al.*⁷ were used.

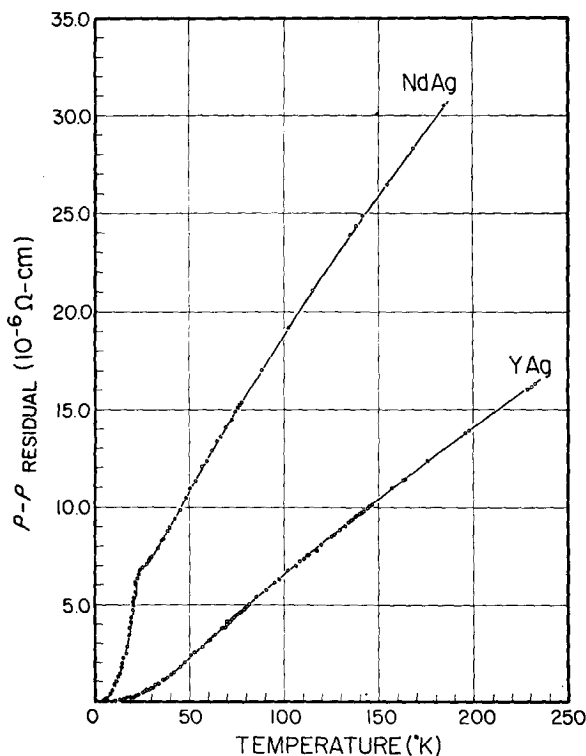


FIG. 1. Resistivity-temperature relationships for NdAg and YAg.

⁷ R. L. Pawell, M. D. Bunch, and R. J. Corruccini, *Cryogenics* **1**, 139 (1961).

* Work supported by the U. S. Atomic Energy Commission.

¹ M. A. Curry, S. Legvold, and F. H. Spedding, *Phys. Rev.* **117**, 953 (1960).

² R. V. Colvin, S. Legvold, and F. H. Spedding, *Phys. Rev.* **120**, 741 (1960).

³ J. K. Alstad, R. V. Colvin, S. Legvold, and F. H. Spedding, *Phys. Rev.* **121**, 1637 (1961).

⁴ F. H. Spedding, S. Legvold, A. H. Danne, and L. D. Jennings, in *Progress in Low-Temperature Physics*, edited by C. J. Gorter (North-Holland Publishing Company, Amsterdam, 1957), Vol. II.

⁵ F. A. Smidt, Jr., and A. H. Daane, *J. Phys. Chem. Solids* **24**, 361 (1963).

⁶ A. J. Dekker, *Phys. Status Solidi* **7**, 241 (1964).

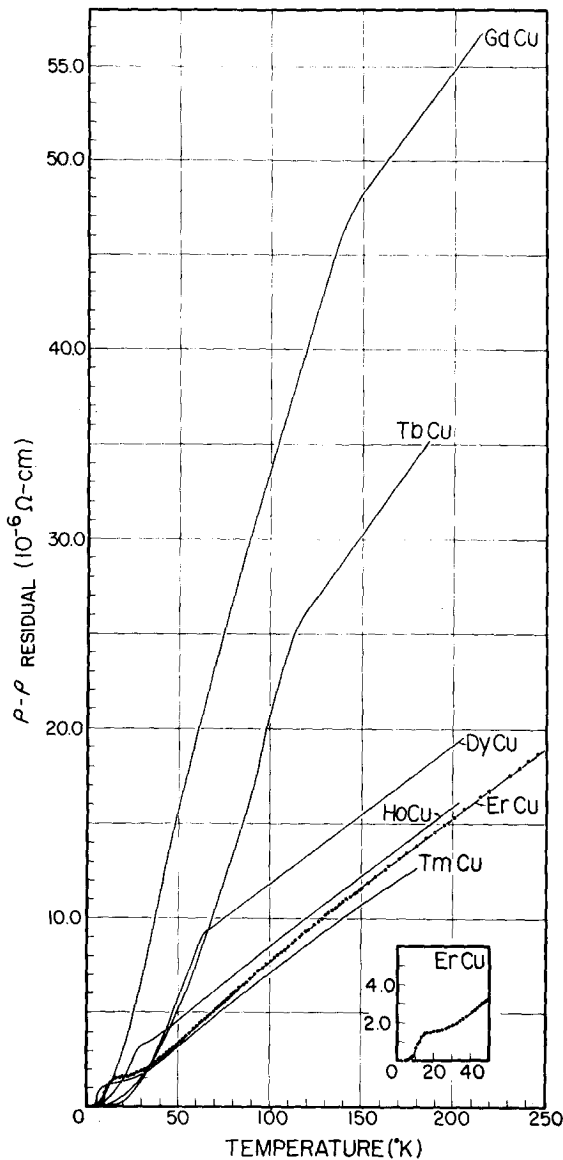


FIG. 2. Resistivity-temperature relationships for rare-earth-copper compounds.

The over-all uncertainties in the reported values of resistivity at a given temperature are estimated to be about $\pm 2.5\%$, the larger fraction of this probable error resulting from the difficulties in measuring the dimensions of the specimen.

RESULTS

The twenty CsCl phases of rare-earth elements with Cu, Ag, and Au studied in this investigation are listed in Table I. The resistivity-vs-temperature curves of these phases are shown in Fig. 1 to 4. In practically all these curves, changes in slopes around some critical temperature are present. The shape of the curves in the neighborhood of the transition temperature is not the same for all alloys, but the general features of the

TABLE I. CsCl phases used for electrical resistivity-temperature measurements.

...	...	AuGd ^a	AuTb	AuDy	AuHo	AuEr	AuTm
AgY	AgNd	AgGd	AgTb	AgDy	AgHo	AgEr	AgTm
...	...	CuGd	CuTb	CuDy	CuHo	CuEr	CuTm

^a A CsCl phase can be obtained in AuGd alloys by rapid quenching from the liquid state only [C. C. Chao, H. L. Luo, and P. Duwez, *J. Appl. Phys.* **34**, 1971 (1963)] but these specimens are not suitable for electrical resistivity measurements.

anomalous transition are of two different types. The first type (indicated as Type I in Table II) is a transition in which the slope of the curve has no extremum in the neighborhood of the transition. The second type (type I in Table II) is a transition with one or more extremum in the resistivity-temperature curve. These two types of curves have been previously observed for pure rare-earth elements.¹⁻³ The other important features of the resistivity-temperature curves of Figs. 1 to 4 are the residual resistivity and the slopes of the curves below and above the transition temperature. The residual resistivities are listed in Table II and are generally very low except for GdCu and NdAg and the phases containing gold. The presence of a second phase in these alloys could be the reason for the high residual resistivities. Metallographic examination of many of

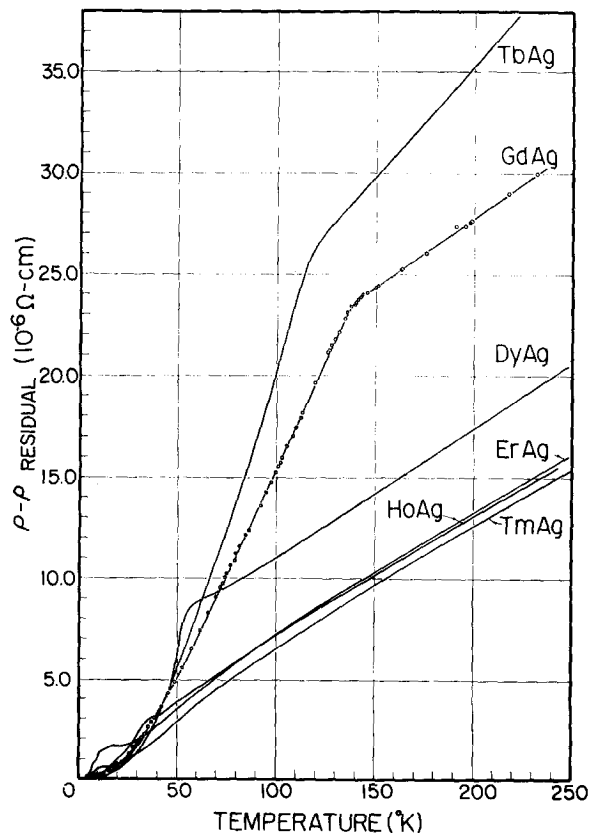


FIG. 3. Resistivity-temperature relationships for rare-earth-silver compounds.

the CsCl phases used in this study revealed the presence of a small amount of a second phase in the grain boundaries. The estimated amount of the second phase, however, was the same in all cases, including the TmAu, HoCu, and DyAg phases, for which the residual resistivities are very low (of the same order of magnitude as those reported by Colvin *et al.* for "pure" rare earths.) Hence, no clear explanation can be given at this time for the high residual resistivity in GdCu, NdAg, and the phases containing gold. Below the transition temperature, the resistivity-temperature curves are linear for only a limited number of alloys (see Table II). For all alloys, however, a well-defined slope (given in Table II) can be measured for temperatures above the transition temperature.

INTERPRETATION

A transition from a paramagnetic to an antiferromagnetic state in the CsCl phase in TbAg and TbCu alloys has been established by neutron diffraction.⁸ Magnetic susceptibility measurements carried out by Walline,^{9,10} also established similar transitions in CsCl

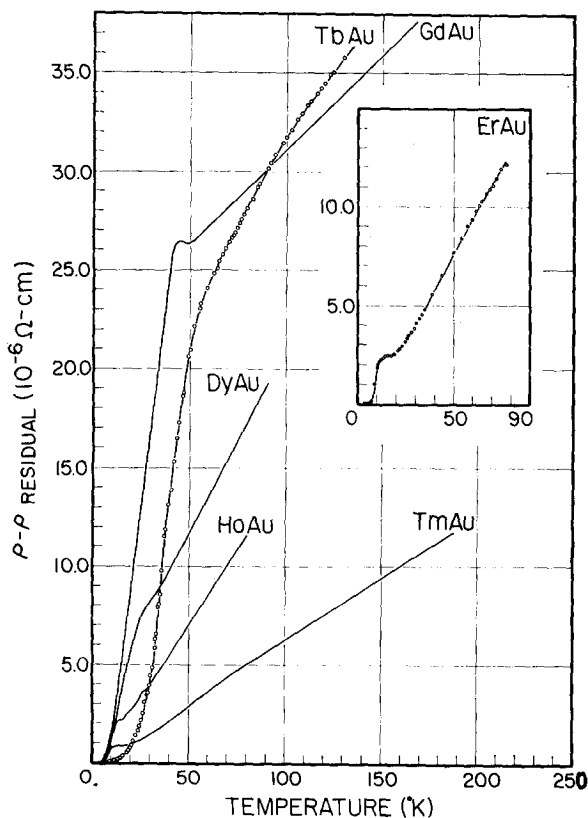


FIG. 4. Resistivity-temperature relationships for rare-earth-gold compounds.

⁸ J. W. Cable, W. C. Koehler, and E. O. Wollan, Phys. Rev. **136**, A240 (1964).

⁹ R. E. Walline and W. E. Wallace, J. Chem. Phys. **41**, 3285 (1964).

¹⁰ R. E. Walline and W. E. Wallace, J. Chem. Phys. **42**, 604 (1965).

TABLE II. Summary of results on the resistivity-temperature curves of CsCl phases.

CsCl phase	ρ_r ($\mu\Omega\text{-cm}$)	Rare-earth element (2)	ρ_s ($\mu\Omega\text{-cm}$)	CsCl phase	$(\partial\rho/\partial T)^a$ $\mu\Omega\text{-cm}/^\circ\text{K}$	$(\partial/\partial T)^b$ $\mu\Omega\text{-cm}/^\circ\text{K}$	Transition type
YAg	3.7
NdAg	7.8	0.5	0.15	II
GdCu	15.0	...	28.7	0.33	0.15	0.15	I
GdAg	2.6	106.4	14.2	0.22	0.07	0.07	I
GdAu	28.5	...	21.5	0.8	0.09	0.09	II
TbCu	3.4	...	9.9	...	0.14	0.14	I
TbAg	5.3	85.7	13.3	...	0.11	0.11	I
TbAu	23.3	...	16.7	I
DyCu	0.35	...	4.4	...	0.07	0.07	II
DyAg	1.2	57.6	4.6	...	0.06	0.06	II
DyAu	21.5	...	2.4	...	0.18	0.18	II
HoCu	1.6	...	0.6	...	0.08	0.08	II
HoAg	1.3	32.3	0.4	...	0.14	0.14	II
HoAu	17.5	...	0.6	...	0.15	0.15	II
ErCu	0.9	...	-0.7	...	0.03	0.03	II
ErAg	3.3	23.6	-0.4	...	0.06	0.06	II
ErAu	17.5	...	-1.6	...	0.17	0.17	II
TmCu	1.5	...	-1.0	...	0.07	0.07	II
TmAg	1.3	14.9	-1.4	...	0.07	0.07	II
	3.7	0.07	0.07	II
TmAu	1.7	...	-0.8	...	0.06	0.06	II

^a Slope of the $\rho(T)$ curve below transition temperature.

^b Slope of the $\rho(T)$ curve above transition temperature.

phases of rare earths with silver and copper. The anomalies in the resistivity-temperature curves observed in this investigation are most probably also related to a paramagnetic to antiferromagnetic transition. As shown in Table III, and excepting CuGd and CuTb, the transition temperatures deduced from the resistivity anomalies are in relatively good agreement with those obtained by either neutron diffraction or susceptibility.

The electrical resistivity $\rho(T)$ of the CsCl phases may be represented by the equation $\rho = \rho_r + \rho_p + \rho_s$, in which ρ_r represents the contribution of impurities and lattice imperfections ρ_p of phonon interaction and ρ_s is due to the spin disordering. If this is so, the term ρ_s can be obtained from the experimental data near 0°K. If the high-temperature part of the resistivity curve is reasonably linear (which is generally the case) the value of ρ_s can be obtained by extrapolating this linear portion of the curve to 0°K and subtracting the value of ρ_r . This procedure has been used by several investigators in the study of the electrical resistivity of pure rare-earth metals, and those deduced from the present study of CsCl phases are given in Table II. It is apparent that these values in the CsCl phases are much smaller than in the corresponding pure rare-earth elements.

It is also interesting to note that the analysis pro-

TABLE III. Transition temperature or temperature range of CsCl phases.

Phase	Transition temperature or range		
	This investigation (°K)	Neutron diffraction (°K)	Magnetic susceptibility (°K)
CuGd	135-145	...	41 ^c
CuTb	100-118	115 ^{a,b}	49 and 114 ^c
CuDy	62	62 ^a	61 ^c
CuHo	27	...	28 ^c
CuEr	10-15	33 ^a	17 ^c
CuTm	10-28	...	11 ^c
AgY	None	...	Pauli paramagnetic
AgNd	24-28	...	22 ^d
AgGd	137-140	...	138 ^d
AgTb	102-122	100 ^{a,b}	106 ^d
AgDy	53-65	64 ^a	55 ^d
AgHo	32-42	...	32 ^d
AgEr	10-24	34 ^a	15 ^d
AgTm	9-20	...	10 ^d
AuGd	42-50
AuTb	48-62
AuDy	24-34
AuHo	13-16
AuEr	13-19
AuTm	8-19

^a J. W. Cable, Oak Ridge National Laboratory (private communication, 24 Sept. 1964).

^b Reference 8.

^c Reference 10.

^d Reference 9.

posed by de Gennes and Friedel¹¹⁻¹³ for explaining the electrical resistivity of rare-earth metals is not applicable to CsCl phases. This analysis leads to the relation

$$\rho_s = \frac{3\pi m^*}{8 h e^2} \Gamma^2 \frac{(g-1)^2}{VE_f} j(j+1)$$

in which m^* is the effective mass of conduction electrons, e is the electron charge, Γ is the indirect interaction constant. V and E_f are the atomic volume and the Fermi energy, respectively. In the case of rare earths, Rocher¹³ has shown that a linear relationship exists between ρ_s

¹¹ P. G. de Gennes, *Compt. Rend.* **247**, 1836 (1958).

¹² P. G. de Gennes and J. Friedel, *J. Phys. Chem. Solids* **4**, 71 (1958).

¹³ Y. A. Rocher, *Advan. Phys.* **11**, 233 (1962).

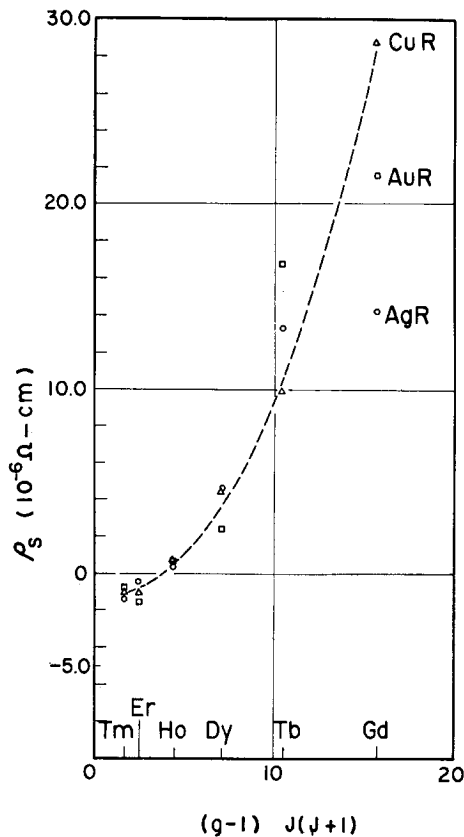


FIG. 5. The relationship between the resistivity due to the spin-disordering scattering and the value of $(g-1)^2 J(J+1)$ of tripositive rare-earth ions in rare-earth-noble-metal compounds.

and $(g-1)^2 j(j+1)$. As shown in Fig. 5, the results of this investigation clearly show that the model used for pure-earth elements is not applicable to the CsCl phases containing rare earths. This is not too surprising, since the effect of the presence of metallic ions (other than the rare-earth ions) in the lattice are not taken into account, and the rare-earth ions are supposed to form a simple cubic crystal with one atom per unit cell.

ACKNOWLEDGMENT

The author wants to thank Professor Pol Duwez for his encouragements and help throughout this investigation.