

[Eq. (2) with $\theta=40.9^\circ$] to show that the angular distribution of the electron charge density is proportional to $x^2y^2z^2$ plus other terms like $z^2(x^4+y^4)$, etc. This distribution points along the body diagonals of the Cs cube and gives rise to the Pa⁴⁺—Cs¹³³ hfs observed in Fig. 7. We note in passing that the resolution is very high, splitting (presumably quadrupolar) as small as 10 kc/sec being resolved in some cases.

ACKNOWLEDGMENTS

We wish to acknowledge with much thanks the stimulating advice and help of Professor B. B. Cunningham on the preparation of Pa⁴⁺ in a solid matrix; the assistance of Professor Roy Anderson on the design and construction of the paramagnetic resonance apparatus; and the helpful collaboration of Dr. Ru-tao Kyi on preliminary resonance experiments.

Electrical Resistivity of Lanthanum, Praseodymium, Neodymium, and Samarium*

J. K. ALSTAD, R. V. COLVIN,[†] S. LEGVOLD, AND F. H. SPEDDING*Institute for Atomic Research and Department of Physics, Iowa State University, Ames, Iowa*

(Received November 9, 1960)

The electrical resistivities of polycrystalline samples of La, Pr, Nd, and Sm are reported in the temperature range 1.3°K to 300°K. La exhibits a superconducting transition at 5.8°K. The curve for Pr has slope changes at 61°K and 95°K. The Nd curve shows small jumps at 5°K and 20°K. Sm shows slope changes at 14°K and 106°K.

MEASUREMENTS on the resistivities of the light rare earths were reported by James *et al.*¹ in 1952. Improved techniques for producing metals of higher purity have led to the measurements on La, Pr, Nd, and Sm reported here. Some improvement has also been made in the experimental procedure and apparatus. The present work is an extension of the results of Colvin *et al.*² and Curry *et al.*³ on the electrical resistivity of the

other polycrystalline rare-earth metals, and completes the work.

The samples were prepared from arc-melted buttons of the metals. These were turned to cylinders approximately $\frac{3}{16}$ inch in diameter by 2 inches long. The results of analyses for impurities are shown in Table I. The resistivities of the samples were measured in the cryo-

TABLE I. Analysis (in %).

Element	Impurities (determined from spectrographic and vacuum fusion analysis)
Lanthanum	Ce \leq 0.03, Pr \leq 0.03, Nd \leq 0.02, Ca \leq 0.01, Fe \leq 0.15, Si \leq 0.01, Mg \leq 0.01, Ta \leq 0.2, Cu, Ni, Sm, trace present.
Praseodymium	Nd \leq 0.02, Ce \leq 0.1, La \leq 0.005, Ca \leq 0.1, Fe \leq 0.02, Mg \leq 0.01, Si \leq 0.025, Ta \leq 0.2, Cr \leq 0.01, O \leq 0.094, H \leq 0.0005, N \leq 0.0920, Ca, Cu, Mn, Ni, Ti, Y, trace present.
Neodymium	Sm \leq 0.06, Pr \leq 0.08, Ca \leq 0.05, Mg \leq 0.01, Fe \leq 0.005, Si \leq 0.025, Ta \leq 0.1, Cr \leq 0.01, O \leq 0.035, B, Mn, Ni, trace present.
Samarium	Ca \leq 0.03, Fe \leq 0.005, Mg \leq 0.01, Si \leq 0.01, Cu \leq 0.05, Gd \leq 0.02, Nd \leq 0.02, Eu \leq 0.005.

* Contribution No. 951. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

[†] Now at the Edgar C. Bain Laboratory of the U. S. Steel Corporation, Monroeville, Pennsylvania.

¹ N. R. James, S. Legvold, and F. H. Spedding, Phys. Rev. **88**, 1092 (1952).

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

³ M. A. Curry, S. Legvold, and F. H. Spedding, Phys. Rev. **117**, 953 (1960).

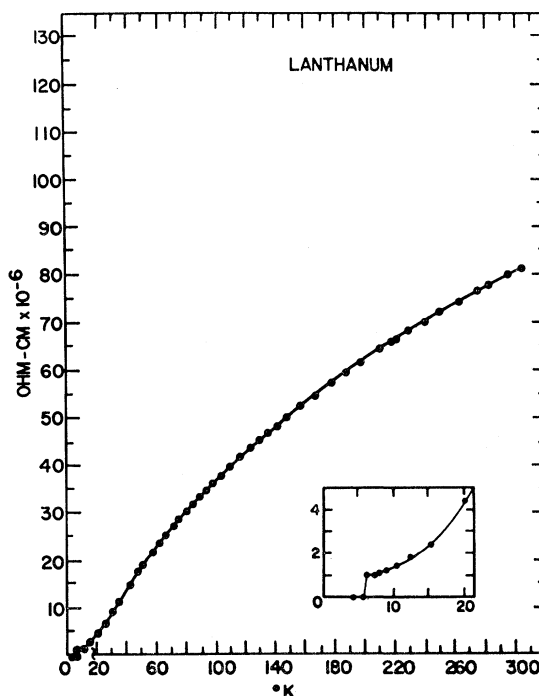


FIG. 1. The electrical resistivity of La vs temperature.

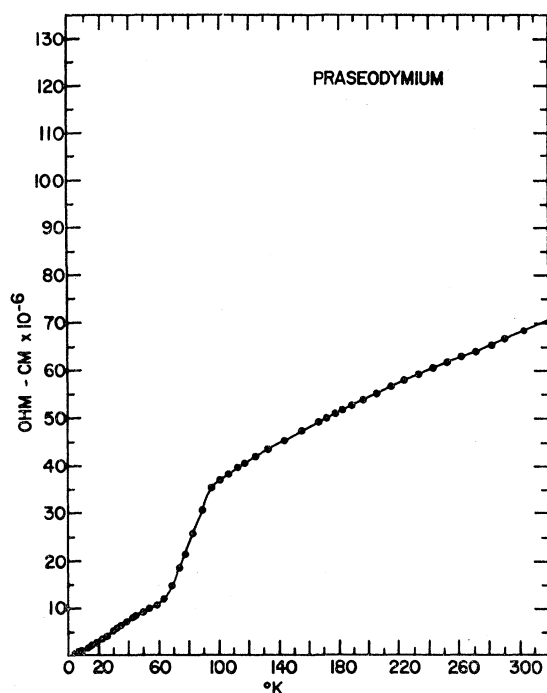


FIG. 2. The electrical resistivity of Pr vs temperature.

stat described by Colvin *et al.*² The standard four-probe method was used; the potential contacts were 2.5 cm apart. Temperatures were measured with a copper-constantan thermocouple; any temperature in the range from 4.2°K to 300°K could be maintained by

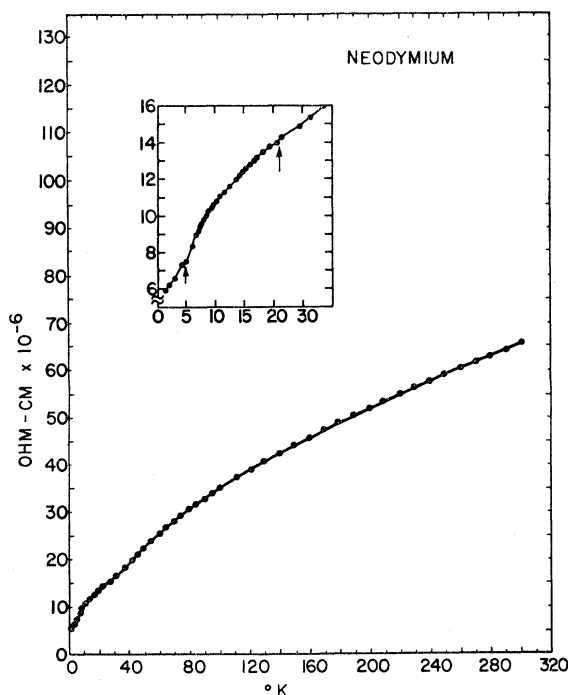


FIG. 3. The electrical resistivity of Nd vs temperature.

means of an automatic temperature controller. The probable error in the resistivity of a given sample varied from 1.5% at room temperature to 0.1 microhm-cm at 4.2°K. The temperature was known to within one-half degree throughout the range.

The resistivity of lanthanum is shown in Fig. 1. Aside from the superconducting transition, the curve is well behaved over the temperature region investigated. The transition temperature was found to be $5.8 \pm 0.3^\circ\text{K}$, as shown in the inset. This is in agreement with Anderson *et al.*⁴ It is likely that both the face-centered cubic structure, which is stable above 300°C, and the hexagonal close-packed structure were present in this sample. The residual resistivity (1.0×10^{-6} ohm-cm) of the

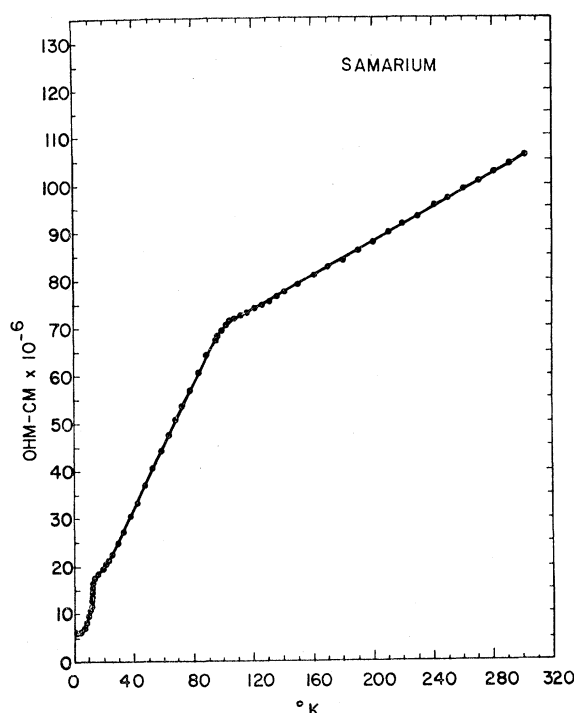


FIG. 4. The electrical resistivity of Sm vs temperature.

present sample was significantly lower than the 10×10^{-6} ohm-cm reported by James *et al.*¹ for their sample.

The praseodymium data (Fig. 2) show an abrupt slope increase at 61°K and a slope decrease at 95°K. This is in contrast with earlier work¹ which indicated no abnormal behavior in the electrical resistivity in the low-temperature region. Lock⁵ reports no indication of anomalous behavior in the magnetic susceptibility. The specific heat data,⁶ however, show a broad peak covering the 60°K to 100°K temperature region. Since the more distinct slope discontinuities displayed by the present sample (together with the lower residual re-

⁴ G. S. Anderson, S. Legvold, and F. H. Spedding, Phys. Rev. **109**, 243 (1958).

⁵ J. M. Lock, Proc. Phys. Soc. (London) **B70**, 566 (1957).

⁶ D. H. Parkinson, F. E. Simon, and F. H. Spedding, Proc. Roy. Soc. (London) **A207**, 137 (1951).

sistivity) are thought to be consequences of improved sample purity, it would seem advisable to investigate the magnetic susceptibility of this sample over the temperature region in question. A temperature hysteresis effect was noted in the resistivity; that is, later runs on the same sample gave lower resistivity values at the same temperatures.

Figure 3 shows the behavior of the low-temperature resistivity of neodymium. The inset is a blow-up of the region from 0°K to 30°K showing more clearly the two jumps in the resistivity at 5°K and 20°K. Measurements of magnetic susceptibility,^{5,7} thermoelectric power⁸ and heat capacity⁶ also indicate abnormal behavior near these temperatures. Lock⁵ suggests that neodymium undergoes a magnetic transition near 7°K, being antiferromagnetic below this temperature.

The resistivity of samarium (Fig. 4) shows a knee at 14°K and a sharp change in slope at 106°K. Measure-

ments of specific heat⁹ and thermoelectric power⁸ show abnormal behavior near the higher temperature; maxima have been reported in the specific heat¹⁰ and magnetic susceptibility⁵ curves near 14°K. The suggestion has been made⁵ that samarium is also antiferromagnetic below 14°K.

From a comparison of the results reported here with those reported earlier, it appears that the low-temperature resistivity of a rare-earth metal is very sensitive to the presence of impurities. The rare earths are very effective "getters" for negative impurities such as oxygen, carbon, nitrogen, and hydrogen; it is believed that very small amounts of these materials in the earlier samples drastically affected their resistivities.

ACKNOWLEDGMENTS

The authors wish to thank Mr. R. Johnson, Mr. C. Haberman, and Mr. G. Wakefield for preparing the metals.

⁷ D. R. Behrendt, S. Legvold, and F. H. Spedding, *Phys. Rev.* **106**, 723 (1957).

⁸ H. J. Born, thesis, Iowa State University, Ames, Iowa, 1960 (unpublished).

⁹ L. D. Jennings, E. D. Hill, and F. H. Spedding, *J. Chem. Phys.* **31**, 1240 (1959).

¹⁰ L. M. Roberts, *Proc. Phys. Soc. (London)* **B70**, 434 (1957).

Visible Luminescence of Rare-Earth Yttrium Gallium Garnets

S. P. KELLER AND G. D. PETTIT

International Business Machines Research Center, Yorktown Heights, New York

(Received October 3, 1960)

Yttrium gallium garnet ($\text{Y}_3\text{Ga}_5\text{O}_{12}$) has been prepared with small percentages of different rare earths substituted for yttrium. Garnets activated with Pr, Sm, Eu, Tb, Dy, Ho, Er, and Tm are all luminescent. The emission and excitation spectra of the samples have been measured at 77°K. The data have been analyzed in terms of the atomic energy levels of the impurity ions and the effects of crystalline field and of phonon interactions. Wherever possible, comments are made about whether the crystal field can be treated as possessing cubic or lower symmetry.

I. INTRODUCTION

IN previous works^{1,2} we have reported on visible fluorescent emissions of SrS and BaTiO₃ singly activated with rare-earth ions. We analyzed the data in terms of the energy levels of the rare earths and the perturbations effected by the crystalline field potential. Because of the present widespread interest in garnet materials and because of the possibility of observing interesting magnetic interactions in iron garnets, we undertook a similar fluorescent investigation of these materials.

Previous data indicate that the rare earth has a free ion structure and that the crystal field potential effects a small perturbation on it. This is indicated by the similarity of optical data for different materials containing the same rare earth species. The similarity is especially

evident for short wavelength data involving transitions of 4f electrons, which are well shielded from the lattice by filled 5s and 5p orbitals. Lest it be thought that all materials containing rare earths possess the same optical properties, it must be pointed out that excitation spectra³ can be very different for different materials.

In order to measure emissions from rare earth sites, there must be an energetic excitation of the site. There are two simple and important mechanisms for getting energy to the site. One mechanism involves an excitation of the host lattice by means of the creation of an electron hole pair. The free electron and hole can then recombine at a rare-earth site thus imparting energy to the rare earth, exciting it, and causing fluorescent emissions. For such a mechanism the excitation spectrum should be indicative of the host lattice and should

¹ S. P. Keller and G. D. Pettit, *J. Chem. Phys.* **30**, 434 (1959).

² S. P. Keller and G. D. Pettit, *J. Chem. Phys.* **31**, 1272 (1959).

³ An excitation spectrum is defined as the dependence of the intensity of emitted light on the wavelength of the incident light.