Magnetic Properties of Rare Earth—Lead Intermetallics*

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Magnetic susceptibilities of the series of intermetallics represented by the formula RPb_3 (R = Ce, Pr, Nd, Sm, Eu and Gd) are reported for temperatures ranging from 2.8 to 300°K. Curie–Weiss behavior is noted for all compounds except SmPb₃ with slopes in good agreement with that expected for assemblages of free tripositive ions (dipositive for EuPb₃). The behavior of SmPb₃ is in accordance with the behavior usually observed for Sm compounds and is due to the narrowness of the multiplet spacing in the tripositive samarium ion. PrPb₃ exhibits Van Vleck paramagnetism below 15°K; its susceptibility-temperature behavior is analyzed in terms of an overall crystal field splitting of 80°K. Results indicate the possible onset of antiferromagnetism at 17 and 22°K for GdPb₃ and EuPb₃, respectively. The other compounds give no indication of forming a cooperative magnetic phase at temperatures down to 2.8°K.

Introduction

Magnetic characteristics of intermetallic compounds containing the rare earths have been the subject of numerous studies carried out in this laboratory in recent years (1). The present work dealing with the rare earth-lead compounds represents a continuation of these studies. Phase diagram determinations and crystallographic work carried out by Gschneidner and his associates (2, 3) have revealed a series of intermetallics of composition RPb_3 (R = a rare earth) occurring in the Cu_3Au structure. Magnetic susceptibilities of six RPb_3 compounds (with R = Ce, Pr, Nd, Sm, Eu and Gd) have been determined over the temperature range extending from 2.8 to 300°K and are reported in this communication.

Experimental Details and Results

The compounds were made by fusing together stoichiometric proportions of the components. The compounds were then annealed at 800°C for 1-2 weeks. Magnetic measurements were made by the Faraday method using technique and equipment which is standard in this laboratory (4).

Results are summarized in Table I and Figs. 1-3.

Curie-Weiss behavior is noted at higher temperatures for all compounds except $SmPb_3$ with effective moments in reasonable agreement with those expected for free tripositive ions (the dipositive ion in case of EuPb₃). Predominance of antiferromagnetic exchange is indicated by the negative values of θ . Results obtained for CePb₃ are in good agreement with those reported in an earlier study from this laboratory (5). Only the Eu and Gd compounds give evidence of magnetic ordering; they seem to order antiferromagnetically near 20°K. The others give no evidence of the formation of a cooperative magnetic phase down to 2.8°K, despite their large negative Weiss Constants.

TABLE I

 $\begin{array}{c} \mbox{Magnetic Characteristics of } RPb_{3} \\ \mbox{Compounds} \end{array}$

	μ_{eff}			
	Meas	Calcd*	<i>θ</i> (° K)	T_{N}
CePb ₃	2.3	2.56	-20	
PrPb3	3.7	3.62	-10	
NdPb ₃	3.5	3.68	-25	
SmPb₃	—	_	_	_
EuPb3	7.5	7.94	47	22°
GdPb ₃	7.6	7.94	-60	17°

* $g\sqrt{J(J+1)}$.

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FIG. 1. Temperature dependence of inverse susceptibility of SmPb3 and PrPb3 in an applied field of 19 kOe.

As seen in Fig. 1, the $\chi_{\rm M}^{-1}$ versus-*T* curve for PrPb₃ deviates from Curie–Weiss behavior below 10°K. This deviation can be attributed to the influence of the cubic crystal field on the Pr³⁺ (5*f*², *J* = 4) ions. The cubic crystal field splits the lowest *J* multiplet of Pr³⁺ into a singlet, two triplets and a doublet as shown in the inset of Fig. 2. From the values of $\chi_{\rm M}^{-1}$ the crystal field energy splitting was estimated considering the crystal field potential to be pure fourth order (6, 7). The influence of exchange was also taken into account using the expression $1/\chi = 1/\chi_0 - \lambda$, where χ_0 is the susceptibility in the absence of exchange and λ is the molecular field constant. The best agreement

between the experimental and theoretical curves was obtained for a total crystal field splitting of about 80°K and $\lambda_{\rm M} = -5.5$ (See Fig. 2). This leads to a Γ_1 , Γ_4 separation of about 20°K.

Figure 1 also reveals the nonlinear behavior of χ_{M}^{-1} -versus-*T* curve for SmPb₃. The deviation from Curie–Weiss behavior is due to the existence of low lying multiplet (J = 7/2) lying about 1500°K above the ground multiplet (J = 5/2) (8).

The $\chi_{\rm M}^{-1}$ -versus-*T* curves for EuPb₃ and GdPb₃ are presented in Fig. 3 together with the magnetization temperature curves for temperatures below 30°K. Weak maxima are observed at 17 and 22°K



FIG. 2. Inverse susceptibility versus temperature for PrPb₃. The solid line indicates calculated values (see text); points represent experimental values.



FIG. 3. Temperature dependence of inverse susceptibility and magnetization of EuPb₃ and GdPb₃ in an applied field of 19 kOe.

for GdPb₃ and EuPb₃, respectively, suggesting the formation of antiferromagnetic phases at these temperatures. The χ versus T behavior of GdPb₃ below the weak maximum closely resembles that of GdIn₃ observed by Buschow *et al.* (9).

- 3. O. D. McMasters and K. A. GSCHNEIDNER, J. Less Common Metals 13, 193 (1967).
- 4. R. A. BUTERA, R. S. CRAIG AND L. V. CHERRY, *Rev. Sci. Instr.* 32, 708 (1961).
- 5. T. TSUCHIDA AND W. E. WALLACE, J. Chem. Phys. 43, 3811 (1965).
- D. P. SCHUMACHER AND C. A. HOLLINGSWORTH, J. Phys. Chem. Solids 27, 749 (1966).
- W. G. PENNEY AND R. SCHLAPP, *Phys. Rev.* 41, 194 (1932).
- J. H. VAN VLECK, "The Theory of Electronic and Magnetic Susceptibilities," p. 245, Oxford University Press, London and New York, 1932.
- K. H. J. BUSCHOW, H. W. DE WIJN, AND A. M. VAN DIEPEN, J. Chem. Phys. 50, 137 (1969).

- References
- Summaries of the earlier work is included in two recent reviews from this laboratory by W. E. Wallace, "Progress in Rare Earth Science and Technology" (L. Eyring, Ed.), Vol. 3, p. 1, 1968 and "Progress in Solid State Chemistry," Vol. 6, 1971, in press.
- 2. J. T. DEMEL AND K. A. GSCHNEIDNER, J. Nucl. Materials 29, 111 (1969).