104. *Rare-earth Carbides. Part II.* Magnetochemistry.*

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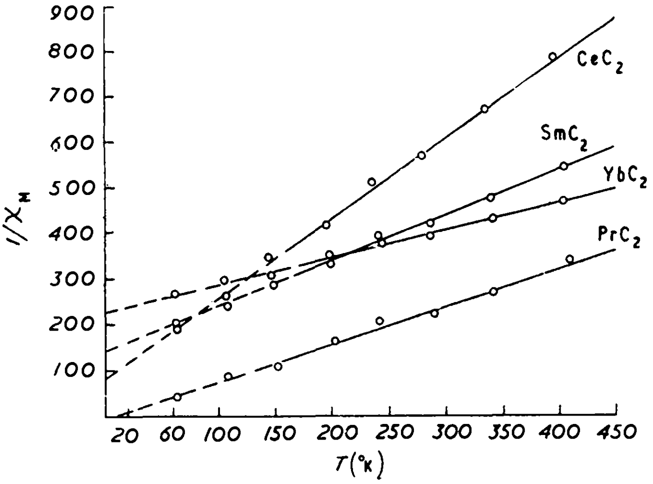
The intrinsic paramagnetism of tervalent rare-earth ions is affected only slightly by carbide formation. Except for samarium and ytterbium dicarbides, the small negative difference noted between the theoretical and the observed magnetism is attributed to partial spin coupling or quenching of the orbital angular moments. As carbides, samarium and ytterbium are considered to adopt their bivalent states. Bohr magneton numbers and Curie–Weiss constants are presented.

MAGNETIC susceptibilities for rare-earth metals agree[1,2] very well with the free gas susceptibility values of the tervalent ions. Within the limits indicated below, the rare-earth carbides are now found to have magnetic susceptibilities agreeing with those of the free ions and metals. There is some evidence, however, that in samarium and ytterbium dicarbides these lanthanons tend to be bivalent. This confirms to some extent our earlier structural considerations. Europium carbide was not studied.

FIG. 1. *Susceptibility of lanthanon dicarbides as a function of absolute temperature.*



Magnetochemical studies on carbides have been but little pursued, so data cannot be compared. We have, moreover, had to employ an empirical value of 0·3 × 10^{-6} c.g.s.

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* Part I, preceding paper.

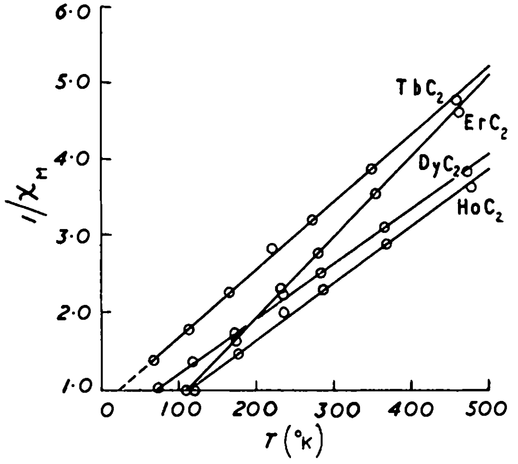
[1] Rhodes, Legvold, Elliott, Behrendt, and Spedding, USAEC-ISC-378, 1953; *Phys. Rev.*, 1958, **109**, 1544, 1547.

[2] LaBlanchetais, Thesis, Université de Paris, 1954; Selwood, "Magnetochemistry," 2nd edn., Interscience, New York, 1956.

unit for the diamagnetism of the $(C{\equiv}C)^{2-}$ entity based upon comparison of the susceptibilities of C–C and C=C and a tentative application of Slater's method of calculation.[3] The $(C{\equiv}C)^{2-}$ entity has been assumed to be present in the rare-earth carbides (preceding paper and ref. 2); and the fact that, after correction for its empirical value, values of $\mu_{\text{eff.}}$ have been obtained for the Ln^{3+} ions, agreeing with standard data, tends to confirm that the rare-earth dicarbides are, in effect, acetylide salts.

Figs. 1 and 2 show values of $1/\chi_M$ plotted against T° K, and the Table shows $\mu_{\text{eff.}}$, C, and θ values derived from the graphs through the Curie–Weiss formula, $\mu = 2{\cdot}839\sqrt{[\chi_M(T - \theta)]}$. Negative θ values are of no significance, serving merely to indicate the absence of potential ferromagnetism. Susceptibilities and field strength exhibit a simple horizontal linear relationship, again indicating absence of ferromagnetism. Although gadolinium metal has a ferromagnetic Curie temperature of 16° C,[1] this transition was not observed in the carbide; similarly, we did not observe the reported susceptibility minimum for samarium at 400° K.[4] Temperature–susceptibility curves for dysprosium carbide were not taken to temperatures low enough for observation of the antiferromagnetic anomaly observed in the metal by Trombe[5] at 150—200° K. Generally, although many points of resemblance to metallic paramagnetism have been observed, there remain some areas of distinction, particularly the differences in $\mu_{\text{eff.}}$. Although spin coupling was not observed in the rare-earth metals, we consider that some quenching of the orbital angular moment occurs in the carbides owing to proximity of the acetylide ion and the development of covalent bonding.

FIG. 2. *Susceptibility of lanthanon dicarbides as a function of lanthanon dicarbides.*



In samarium and ytterbium dicarbides we have previously indicated the attainment of bivalent states by these lanthanons, and this now appears confirmed by the Bohr magneton numbers for SmC_2 ($>Sm^{3+}$) and YbC_2 ($<Yb^{3+}$). Sm^{2+}, being isoelectronic with Eu^{3+}, will have $\mu_{\text{eff.}} \simeq 3{\cdot}0$—$3{\cdot}5$; Yb^{2+}, isoelectronic with Lu^{3+}, should have $\mu_{\text{eff.}} \simeq 1{\cdot}0$. A proportion of bivalent ions in the carbides of these elements is to be compared with their metallic constitutions, which are also considered[6] to contain 2^+ ions.

Carbide	$\mu_{\text{calc.}}$	$\mu_{\text{obs.}}$	C	θ	Carbide	$\mu_{\text{calc.}}$	$\mu_{\text{obs.}}$	C	θ
Ce	2·56	2·19	0·59	−61°	Tb	9·70	9·57	11·36	−91·2°
Pr	3·62	3·15	1·35	+5·2	Dy	10·60	10·53	13·75	−68·9
Nd	3·68	3·53	1·55	+40	Ho	10·60	10·47	13·59	−25·6
Sm	1·65	2·85	1·01	−139	Er	9·6	8·75	9·49	+14·7
Gd	7·94	7·59	7·14	+41·3	Yb	4·6	3·69	1·69	−388

[3] Slater, *Phys. Rev.*, 1928, **32**, 349; 1930, **36**, 57.

[4] Van Vleck, " Theory of Electrical and Magnetic Susceptibilities," Oxford, 1932.

[5] Trombe, *Compt. rend.*, 1945, **221**, 19; **1953**, 236, 591; *J. Phys. Radium*, 1951, **12**, 22.

[6] Klemm and Bommer, *Z. anorg. Chem.*, 1937, **231**, 138.

Experimental. Carbides were prepared as in the preceding paper. After removal of excess of carbon, crushing to 100 mesh, and drying, the carbides were sealed in individual capillary tubes and magnetic susceptibilities were measured on a Gouy-type balance as previously described,[5] from the temperature of liquid nitrogen up to 500° K.

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