

cuvette. Thus, the site of binding of Gd(III)-MP-IX is the heme pocket in the Gd(III)-Mb.

TABLE I
Visible absorption maxima of Gd(III)-MP-IX, Eu(III)-MP-IX, Gd(III)-Mb and Eu(III)-Mb^a

Compound	Solvent	Soret (nm)	α (nm)	β (nm)
Gd(III)-MP-IX	Pyridine	410.5 (269) ^b	577 (19.6)	540 (18.4)
"	Methanol	404.5 (251)	574 (19.4)	537 (16.0)
"	Tris-HCl ^c	401.5 (277)	571 (14.4)	534.5 (12.2)
Gd(III)-Mb	"	405.5 (310)	572.5 (19.1)	535 (14.7)
Eu(III)-MP-IX	Pyridine	409 (208)	577 (15.8)	541 (14.8)
"	Methanol	405 (176)	574.5 (14.1)	538 (13.7)
"	Tris-HCl	401 (181)	572 (10.0)	535.5 (8.6)
Eu(III)-Mb	"	405.5 (254)	573.5 (17.1)	537 (14.4)

^a Concentrations of metal porphyrin and metal protein complex are in the range 3 to 8 μ M.

^b The values in parenthesis are millimolar extinction coefficients ϵ_{mM} ($\text{mM}^{-1} \text{cm}^{-1}$).

^c Tris-HCl is 0.1 M buffer of pH 8.

The electron paramagnetic resonance (EPR) spectrum of Gd(III)-Mb was recorded in Fig. 1 at liquid nitrogen

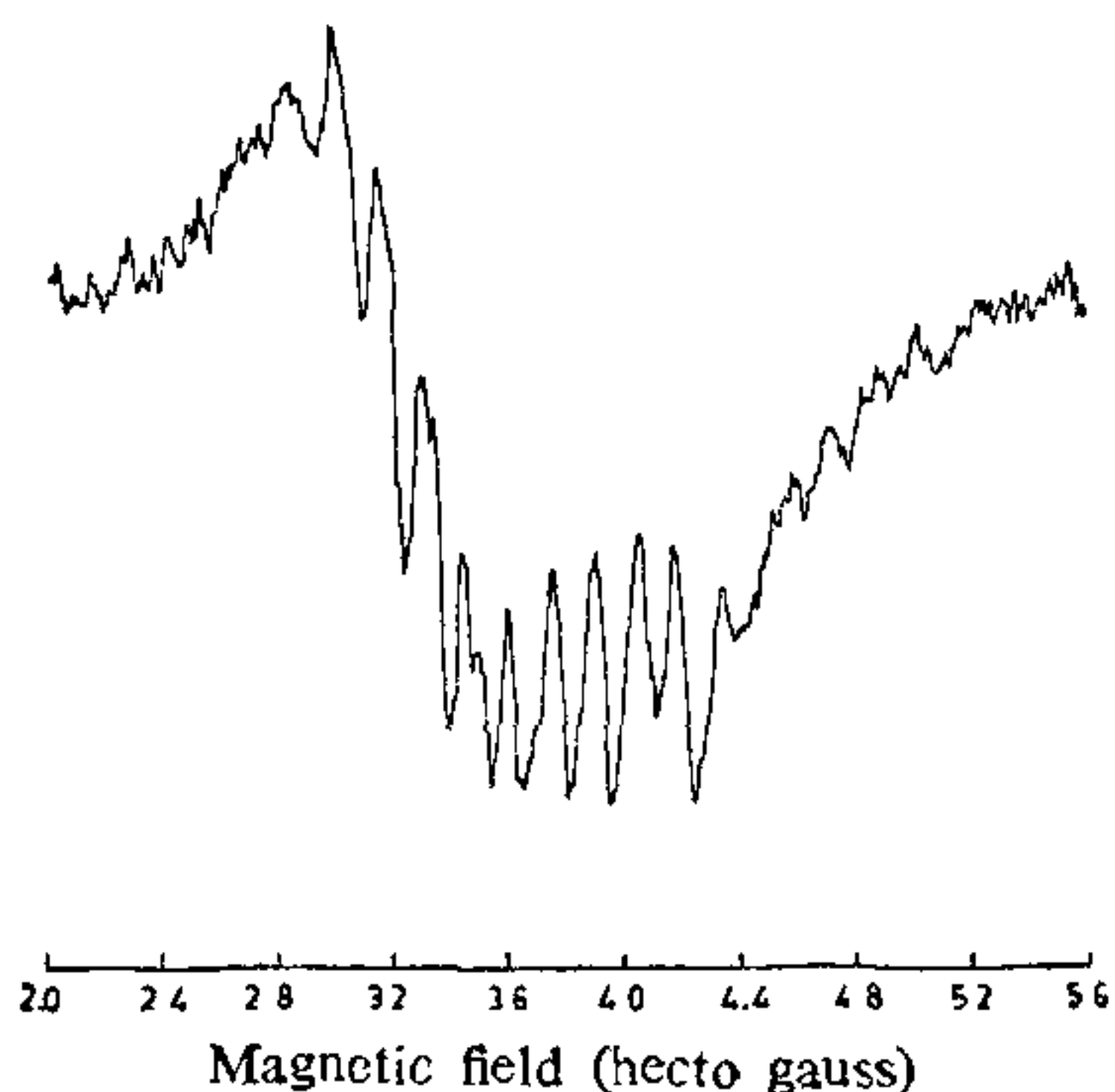


FIG. 1. Electron paramagnetic resonance spectrum of gadolinium(III) myoglobin in 0.1 M potassium phosphate buffer of pH 8 at 77° K. Concentration of Gd(III)-Mb was 1 mM.

temperature. The signal of Gd(III) in the Gd(III)-Mb shows nitrogen hyperfine structure with about 14 peaks (hyperfine splitting ≈ 15 gauss). These 14 peaks of nitrogen hyperfine structure are interpreted in terms of Gd(III)-MP-IX in the heme pocket where the four nitrogen atoms of the porphyrin and fifth nitrogen atom of proximal histidine⁶ are coordinated to gadolinium(III). Thus, the EPR spectrum of Gd(III)-Mb further supports the site of binding of Gd(III)-MP-IX in the heme pocket of the Gd(III)-Mb. The splitting of the nitrogen hyperfine structure in the Gd(III)-Mb is expected to vary with change in structure of Gd(III)-Mb and, thus, these structural changes can be probed using Gd(III) in the Gd(III)-Mb.

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CRYSTALLOGRAPHIC STUDY OF SOME MIXED PYROCHLORES

ANALYSIS¹ of natural pyrochlore minerals suggest that wide variety of both cationic and anionic substitutions are possible; however, literature survey revealed that very little work is reported²⁻⁴ on pyrochlore compounds where substitution of cations is carried out at A as well as B sites. In the present studies, mixed pyrochlores containing cations of different oxidation states at A and B sites have been prepared. Pyrochlore structure has the general formula $A_2B_2O_7$, where A is a larger cation coordinated by eight oxygen ions while B is a smaller cation octahedrally surrounded by six oxygen ions. The space group is $Fd3\overline{m}$.

All the compositions mentioned in Table I were prepared by using standard ceramic technique and X-ray diffractometer patterns were taken on Philips machine using $\text{CuK}\alpha$ radiation with Ni filter.

From Table I it is observed that the compound PbXTiNbO_7 , where X = Sm, Gd, Dy, Y and Bi possess pyrochlore structure while the compound containing neodymium is outside the limit of pyrochlore formation. If the compounds mentioned in Table I are considered on the basis of radius ratio,

TABLE I

Compound	Average radius of cations at A site	Average radius of cations at B site	Radius ratio rA/rB	Phases present
PbYTiNbO ₇	1.165	0.625	1.864	Pyrochlore, a = 10.25A
PbDyTiNbO ₇	1.170	0.625	1.872	Pyrochlore, a = 10.26A
PbGdTiNbO ₇	1.185	0.625	1.896	Pyrochlore, a = 10.30A
PbSmTiNbO ₇	1.200	0.625	1.920	Pyrochlore, a = 10.36A
PbBiTiNbO ₇	1.210	0.625	1.936	Pyrochlore, a = 10.44A
PbNdTiNbO ₇	1.215	0.625	1.944	Pyrochlore, a = 10.39 + Nd ₂ Ti ₂ O ₇ (monoclinic)

it is observed that the stability region of the pyrochlore compounds extends from Shannon and Prewitt's⁵ radius ratio, $[r(A^{2+}A^{3+})/r(B^{4+}B^{5+})]$, of 1.864 to 1.936 and when it is 1.944 (PbNdTiNbO₇) a trace of monoclinic (Nd₂Ti₂O₇) phase is observed along with pyrochlore. Except the compound containing Bi³⁺ the lattice parameters gave a satisfactory straight line when plotted against ionic radii of A³⁺ ions (Fig. 1).

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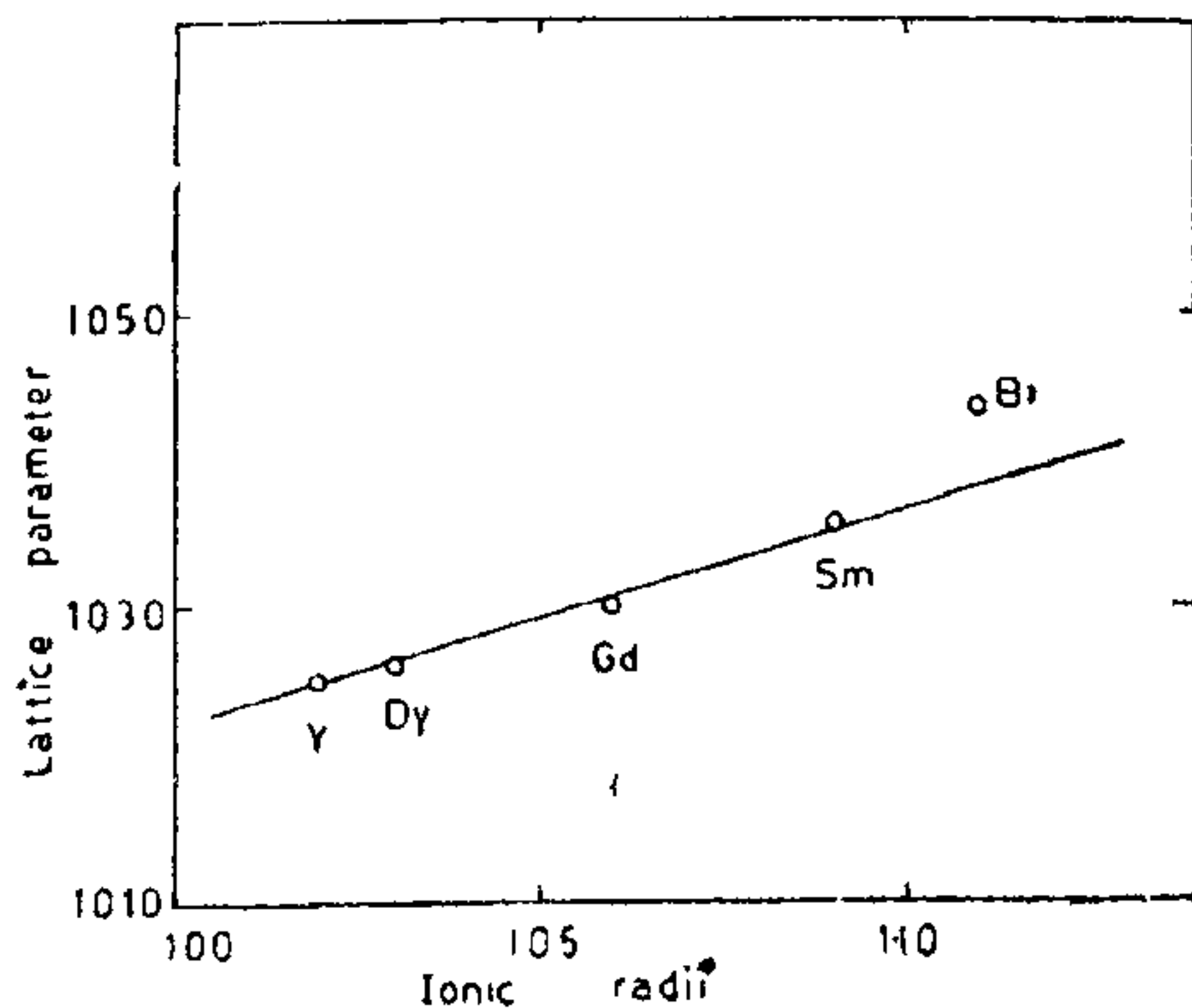


FIG. 1. Lattice parameter vs. ionic radii of A³⁺ ions.

Higher lattice parameter value of PbBiTiNbO₇ and its deviation from a linear plot may be due to wider difference in electronegativity between lanthanons and bismuth.

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HABIT MODIFICATION CAUSED BY MONOTHIO ETHYLENE GLYCOL DURING THE ELECTRODEPOSITION OF CADMIUM

ADDITION agents are often added in small quantities to electroplating baths for the purpose of reducing the overvoltage required for electrodeposition, improve the quality of the deposit and to produce a bright and adherent deposit. On a polycrystalline substrate of cadmium the effect of thiourea glue, gelatin, glycole, etc., has been studied^{1,2}. However, the influence of monothio ethylene glycol on the growth habit has not been reported. The present experimental work was carried out to study the habit modification of cadmium electrodeposits deposited on polycrystalline cadmium from