

## Magnetic Properties of the $Tb^{4+}$ Ion in $Li_2TbF_6$ : Particular Crystal Chemical Behavior within the $Li_2M^{IV}F_6$ Compounds

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Magnetic properties of polycrystalline samples of  $Li_2TbF_6$  were studied in high continuous magnetic fields up to 20 Teslas between 1.4 and 300 K. In this new structural type, all the results agree with the calculated  $Tb^{4+}$  free ion values ( $^8S_{7/2}$  ground state multiplet), and the 4+ oxidation state of the terbium ion was unambiguously inferred. The particular crystal chemical behavior of the  $Tb^{4+}$  ion is discussed using the phase relationship within the series of  $Li_2M^{IV}F_6$  compounds. © 1992 Academic Press, Inc.

### Introduction

In the course of study of the  $MF-M'F_4$  systems ( $M$  = alkaline metal,  $M'$  = rare-earth element in the tetravalent oxidation state, e.g., Ce, Pr, Tb) a compound corresponding to the molecular ratio  $LiF/TbF_4$  equal to 2, namely  $Li_2TbF_6$ , has been characterized (1) and focused on our attention because of its crystal chemical characteristics. The particular interest of this compound lies in the fact that it constitutes the only representative obtained under ambient pressure of a structure type, namely  $\alpha$ - $Li_2ZrF_6$ , known until now only through the high pressure form of  $Li_2ZrF_6$  (2). A coordination number greater than six for the  $Tb^{4+}$  ion expected from the structural relationship carried out by Demazeau *et al.* (2) within the  $Li_2MF_6$  compounds has been confirmed by the crystal structure determina-

tion recently performed from X-ray and neutron powder diffraction (3), showing this coordination number equal to 8 (Fig. 1). So this result perfectly corroborates the general rule in accordance with which the coordination increases with the ionic radius of the element. More surprising is the fact that the  $Li_2PrF_6$  compound characterized by K. Feldner and R. Hoppe (4) is of the  $\beta$ - $Li_2ZrF_6$  low pressure form, since the ionic radius of  $Pr^{4+}$  is greater than that of  $Tb^{4+}$  for a given coordination number and consequently an eight coordination number for  $Pr^{4+}$  could have been expected together with a structure of the  $\alpha$ - $Li_2ZrF_6$  high pressure type. In order to gain a better understanding this particular behavior of the  $Tb^{4+}$  ion, we use magnetic and optical measurements to confirm the oxidation state of this element, and then we suggest a possible explanation on the basis of the electronic configuration of

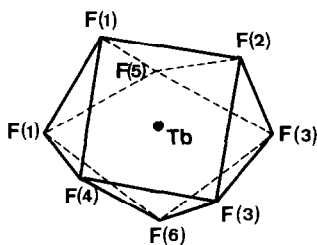


FIG. 1. The 8-coordination polyhedron of the  $\text{Tb}^{4+}$  ion in  $\text{Li}_2\text{TbF}_6$ , which may be described as related to a biccapped trigonal prism. Numbers in brackets correspond to the independent fluorine atoms in the asymmetrical unit as defined in Ref. (3).

the tetravalent cation and the size effect on the phases' stability.

### Experimental

Polycrystalline samples were prepared by reacting stoichiometric quantities of lithium chloride (Merck selectipur) and terbium oxide ( $\text{Tb}_4\text{O}_7$  Rhône Poulenc 99.9%) under pure fluorine gas flow. Samples were first heated at  $500^\circ\text{C}$  overnight, then allowed to cool to room temperature under fluorine atmosphere, ground, and annealed at  $550^\circ\text{C}$  for 12 h in a pure fluorine stream. Completion of reaction was checked by X-ray powder diffraction with a Siemens D500 diffractometer using a graphite monochromated  $\text{CuK}\alpha$  radiation.

Magnetic measurements over the temperature range 1.4–300 K were carried out using an automatic device provided with a cryostat associated to a calorimeter and described in detail elsewhere (5). The extraction technique was used to measure the magnetic moment in dc magnetic fields up to 20T produced by a Bitter magnet.

### Results and Discussion

Typical magnetization isotherm curves  $M(H)$  are reported in Fig. 2(a) for the studied polycrystalline  $\text{Li}_2\text{TbF}_6$  sample. At low

temperature and in magnetic fields higher than 15 Teslas, the magnetization was found to become field independent: the saturation magnetization equal to  $6.9 \pm 0.1$  Bohr magneton per formula unit is very close to the calculated  $\text{Tb}^{4+}$  free ion value, i.e.,  $7 \mu_B$ . It is worthwhile noting that the observed value is quite different from that ( $9 \mu_B$ ) associated to the ground state multiplet  ${}^7F_6$  of the trivalent terbium ion. Using the experimental  $M$  data, a unique dependence of  $M/M_0$  was brought to light (Fig. 2(b)); the results do not present any departure from the classical Brillouin function of the pure  ${}^8S_{7/2}$  state of the tetravalent terbium ion.

Above 100 K,  $M$  was found linear versus the applied magnetic field and the magnetic susceptibility was immediately deduced using a least-square refinement technique. Below 100 K, only the linear part of the  $M(H)$  curves was used. The reciprocal magnetic susceptibility,  $\chi^{-1} = f(T)$ , follows a Curie law (Fig. 3); the Curie constant is equal to 7.72 e.m.u.; this data corresponds to an effective moment of  $7.86 \pm 0.08 \mu_B$  per ion, which is in excellent agreement with the 7.94 theoretical value of the  ${}^8S_{7/2}$  multiplet. It is noticeable that no paramagnetic Curie temperature was observed: from this absence it is deduced that no exchange interactions between rare-earth ions are present and that no crystal field effects exist; this last point confirms the pure  $S$  state of the rare-earth.

The lack of any substantial traces of  $\text{Tb}^{3+}$  ions in our sample has also been checked and confirmed using selective excitations in both  ${}^5D_3$  and  ${}^5D_4$  levels of this ion. Indeed the emission spectrum of both  ${}^5D_3 \rightarrow {}^7F_J$  and  ${}^5D_4 \rightarrow {}^7F_J$  fluorescence recorded over the 380–630 nm wavelengths range exhibits no characteristic line of such emission transitions.

Figure 4 displays the particular role played by the  $\text{Tb}^{4+}$  ion among the large variety of  $\text{Li}_2\text{MF}_6$  compounds ( $M$  = tetravalent cation).

It is well known that some compounds

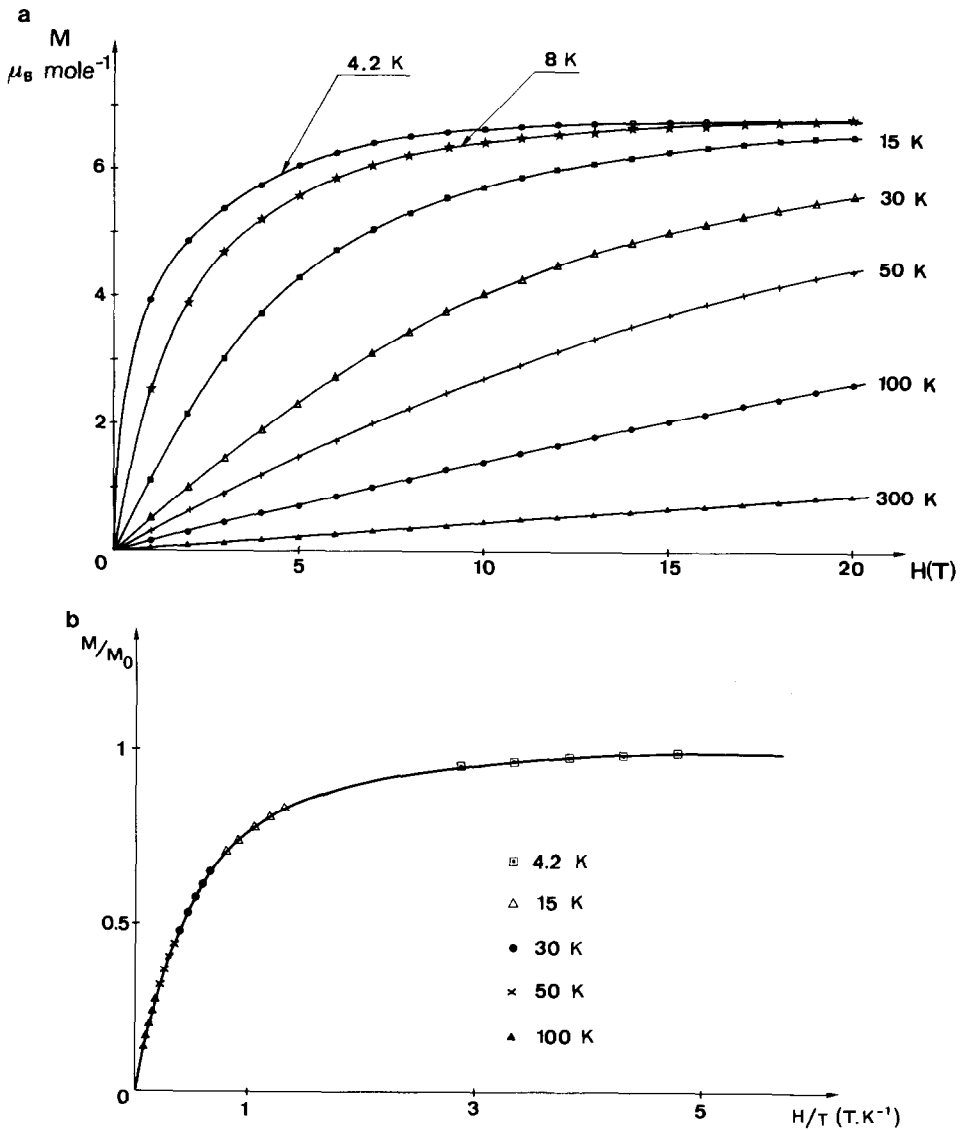


FIG. 2. (a) Magnetization versus external field at different temperatures. (b) Reduced magnetization  $M/M_0$  vs  $H/T$ , showing the excellent agreement with the Brillouin function associated to  $J = 7/2$ ,  $g = 2$ , and  $4f^n$  electronic configuration.

can undergo a polymorphic transformation under the pressure effect. This may occur in two ways.

In the first one, this can take place without change in the coordination number of the tetravalent cation and corresponds to a vertical transition labeled (I) in the diagram of

Fig. 4 and is exemplified by  $\text{Li}_2\text{GeF}_6$  and  $\text{Li}_2\text{SnF}_6$ . In this case the limit of the stability range of the different phases at ambient pressure and under high pressure can be correlated with the ionic radius of the involved tetravalent cation.

The other alternative in describing the ef-

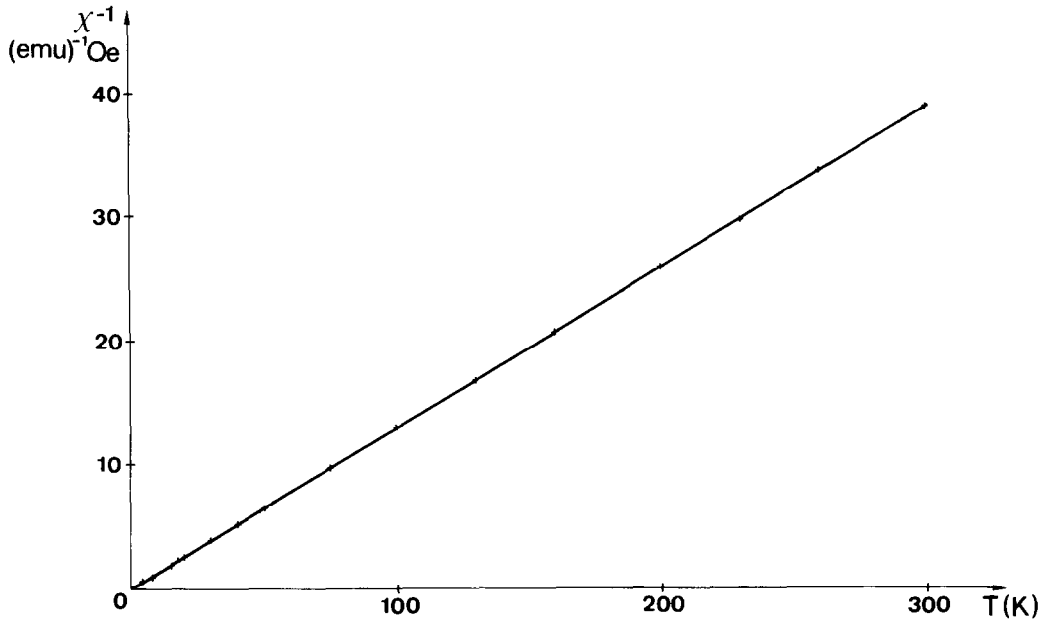


FIG. 3. Temperature dependence of the reciprocal magnetic susceptibility of  $\text{Li}_2\text{TbF}_6$ .

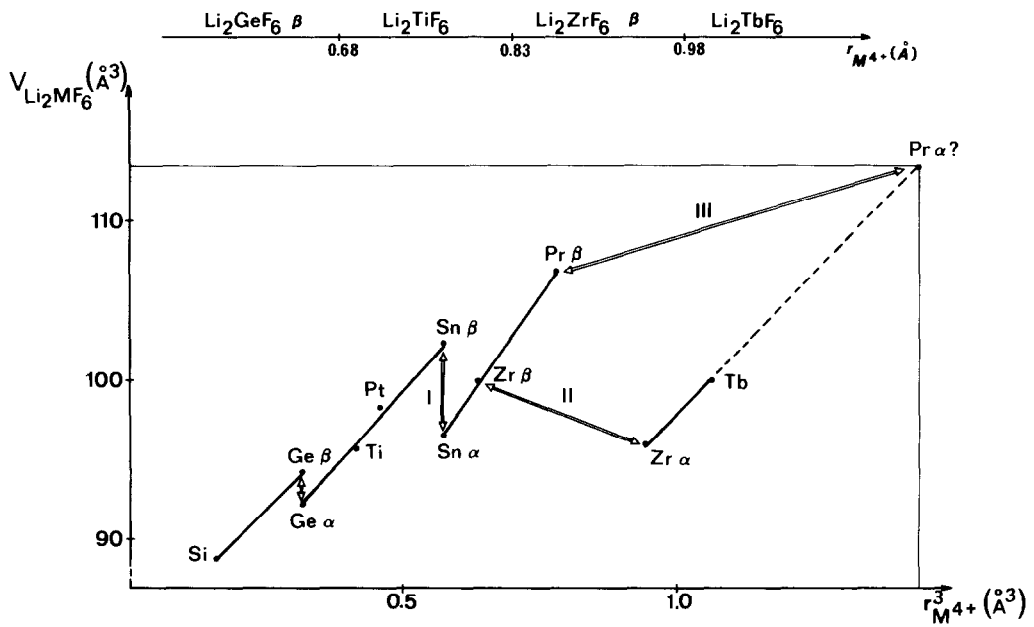


FIG. 4. Relationship between the molecular volume of  $\text{Li}_2\text{MF}_6$  and the cube of  $M^{4+}$  ionic radius showing the pressure-induced polymorphism and the stability domain of different structure within the  $\text{Li}_2\text{MF}_6$  compounds.

fect of the pressure on solid is the so-called "pressure coordination rule" (6), according to which the coordination number increases with pressure. This rule is illustrated by  $\text{Li}_2\text{ZrF}_6$  and corresponds to a lateral transition labelled (II) in Fig. 4. Thus, under a 70 kbar pressure,  $\text{Li}_2\text{ZrF}_6$  undergoes a polymorphic transformation which involves an increase of the coordination number of the  $\text{Zr}^{4+}$  ion from 6 to 8 leading to a crystal structure of the  $\text{Li}_2\text{TbF}_6$ -type (3).

In both (I) and (II) transition types the molecular volume of  $\text{Li}_2\text{MF}_6$  decreases under the pressure effect, even if the coordination number of the tetravalent cation is increased in the transition of the (II) type.

From this remark the non-existence of the  $\text{Li}_2\text{TbF}_6$  structure type isotypic form for the  $\text{Li}_2\text{PrF}_6$  compound can be understood. Thus, from the slope of the straight line relative to the  $\text{Li}_2\text{TbF}_6$  structure type and the value of the cubic ionic radius of the  $\text{Pr}^{4+}$  ion for an 8 coordination number, a molecular volume of  $112.9 \text{ \AA}^3$  could be predicted for  $\text{Li}_2\text{PrF}_6$ . So it seems very unlikely that a side transition from the low pressure  $\text{Li}_2\text{PrF}_6$  to a hypothetical high pressure form which corresponds to the (III) way and which involves an increase of the molecular volume could take place. It seems also very unlikely that further increase in pressure could produce a sufficient decrease of the molecular volume to stabilize the  $\text{Li}_2\text{PrF}_6$  compound in the  $\text{Li}_2\text{TbF}_6$  structure type form. The obtaining of  $\text{Li}_2\text{TbF}_6$ , as such, at ambient pressure, can be ascribed to the particularly stable  $f^7$  configuration of the  $\text{Tb}^{4+}$  ion. Let us mention that a similar feature is observed within the high pressure form of  $\text{LiTiMF}_6$  ( $M = \text{Mn, Fe, Co, Ni}$ ) compounds, since the Mn representative corresponding to a half-filled  $d^5$  shell exhibits a structure unlike the other one (7). On the contrary, the non-existence of the  $\beta\text{-Li}_2\text{ZrF}_6$  type form of

$\text{Li}_2\text{TbF}_6$  could be explained by the impossibility to induce the reverse transition to a less compact structure under the temperature effect due to the fact that the decomposition reaction  $\text{TbF}_4 \rightarrow \text{TbF}_3 + \frac{1}{2} \text{F}_2$  occurs above  $550^\circ\text{C}$ .

## Conclusion

In this work, the magnetic and crystal chemical properties of  $\text{Li}_2\text{TbF}_6$  have been studied and discussed. It should be noted first that the quality of the material used in our measurements was tested by X-ray diffraction. A very unusual crystal chemical behavior of the  $\text{Tb}^{4+}$  ion has been observed in this fluoride, which is to the best of our knowledge the first representative of this crystalline form obtained at ambient pressure. The so-found  $4f^7$  electronic configuration corresponds to the spherical electronic cloud which is the most compatible with the 8 coordination of this ion. Another important result of this work is the discussion of the relationship within the series  $\text{Li}_2\text{M}^{\text{IV}}\text{F}_6$  compounds to understand the influence of both electronic configuration and size effects on the different crystallographic phases.

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