

LETTERS TO THE EDITOR

ANOMALOUS PRESSURE DEPENDENCE OF T_c IN LANTHANIDES AND ACTINIDES AND THE MECHANISM OF SUPERCONDUCTIVITY

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SUPERCONDUCTIVITY of lanthanides and actinides under pressure has long since remained a problem which has not yet been understood. An anomalous pressure dependence of T_c of La and La:Pr has been reported by Wittig¹ who has explained the behaviour of $4f^2$ shell under pressure. These findings, (figure 1)

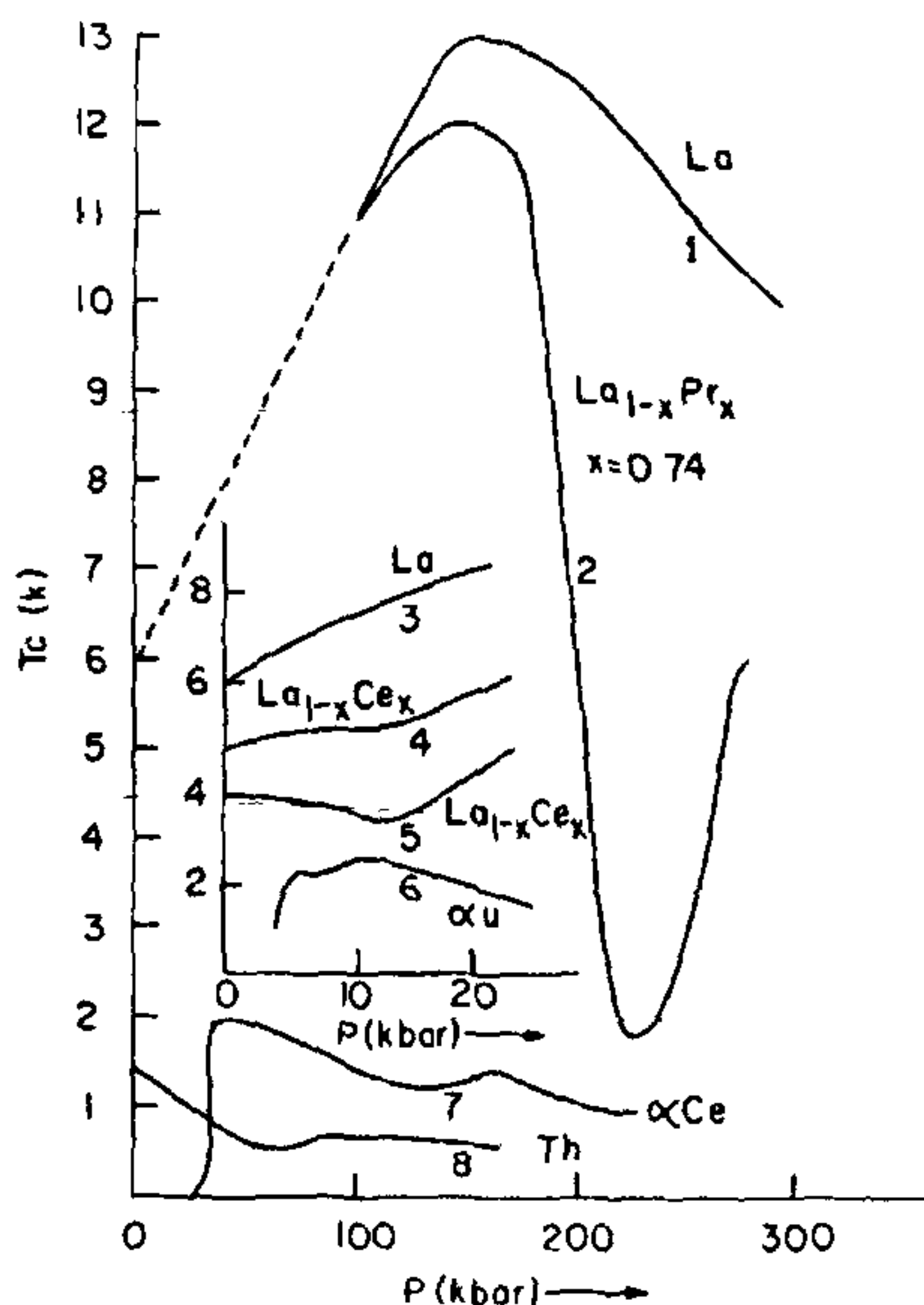


Figure 1. Pressure dependence of T_c , curves 1 and 2 (ref. 1) 3, 4 and 5 (ref. 5), 6 (ref. 4) 7 and 8 (ref. 2).

when compared with the reported data² on α Ce, Th, α U and various La alloys containing magnetic impurities, lead us to some striking contentions having immediate relevance to the question of the occurrence of superconductivity in lanthanides, actinides and their alloys. In fact despite several theoretical

attempts^{3,4} the observed pressure dependence of T_c of La and α U has to date remained unexplained. The observed behaviour is of a typical undulatory type where T_c initially rises with pressure and it subsequently undergoes a gradual depression. Matthias⁵ had suggested that this could indicate some alternative mechanism of superconductivity different from the phonon mechanism of the BCS theory⁶. It is surprising that none of the explanations put forth has envisaged the role of exchange interactions among conduction electrons which are expected to be pronounced when there is a sharp d band at E_F , and indeed exchange enhancement effects in La, α Ce, α U and Th under pressure have been completely ignored. These aspects turn out to be all the more important in the La alloys, such as La:Ce, La:Pr, La:Gd, etc, as they form the Kondo systems in which the imposed pressure can cause E_K or E_f to become equal to or even exceed E_F . Clearly, the possible positive role of exchange interactions among conduction electrons in the occurrence of superconductivity under pressure has been overlooked. The available experimental data suggest that the field of pressure dependent superconductivity of lanthanides and actinides needs to be examined in a different perspective.

There are several interesting features of the pressure dependence of T_c of La and La:Pr which have missed general consideration and they are given below.

- Under pressure, an initial rise in T_c is always observed in La, La-compounds α U and α Ce and this important aspect still remains to be understood². Obviously, the explanation of Appel³ does not apply as $4f$ level lies below E_F .
- The undulatory T_c behaviour has been observed in La, α U, α Ce, Th, and in La:Pr the behaviour is more pronounced. No convincing explanation for this has so far been reported. Moreover, the suggestion of magnetic to non-magnetic transition under pressure does not hold.
- As La and its alloys have a sharp d band at E_F the possible enhancement of exchange interactions among itinerant electrons has been overlooked. The same situation also exists for α Ce, α U and Th.
- La:Ce and La:Pr are known Kondo systems where effect of pressure is to shift and enhance the localised moments to the itinerant electrons. Schilling⁷ has argued that this would primarily lead to the enhancement of exchange interactions of antiferromagnetic type, *i.e.* $-J$. Clearly this cannot be ignored to explain the T_c behaviour under pressure.

It is evident that the creative role of exchange interactions among itinerant electrons in the above systems has been ignored. As previously suggested by us⁸ for Al, various A-15s, Chevral phases and ternary borides, if the exchange interactions among conduction electrons are responsible for electron pairing the above anomalies can be satisfactorily resolved. Accordingly if $T_c \propto -J_{d-d}$ it is expected that T_c will increase under pressure giving the observed initial rise. With further increase of pressure, the probable inclusion of $4f$ level⁵ will contribute $+J_{fvs}$ which should reduce T_c . This is supported by the fact that any addition of $4f$ impurity like Pr and Ce in La reduces T_c considerably after an initial rise. Thus,

$$T_c \propto -J(P)_{d-d} + J_{fvs} \pm J(P)$$

normal resonance
scattering scattering

where the effect of normal and resonance scattering parameters are as discussed by Coqblin and Ratto⁹.

Under pressure when $E_f \geq |E_f|$ the situation becomes a complicated Kondo problem¹⁰ which can lead to electron pairing that should give rise to a rise in T_c , as actually observed in La compounds. Here $J(P)$ can also change its sign which can lead to T_c enhancement. Similar situation is also expected in A-15 superconductors where high T_c results when $E \geq |E_f|$.

To conclude, superconductivity of lanthanides and actinides can be better explained in terms of our model⁸ where superconductivity is due to exchange interactions of $-J$ type in the conduction band.

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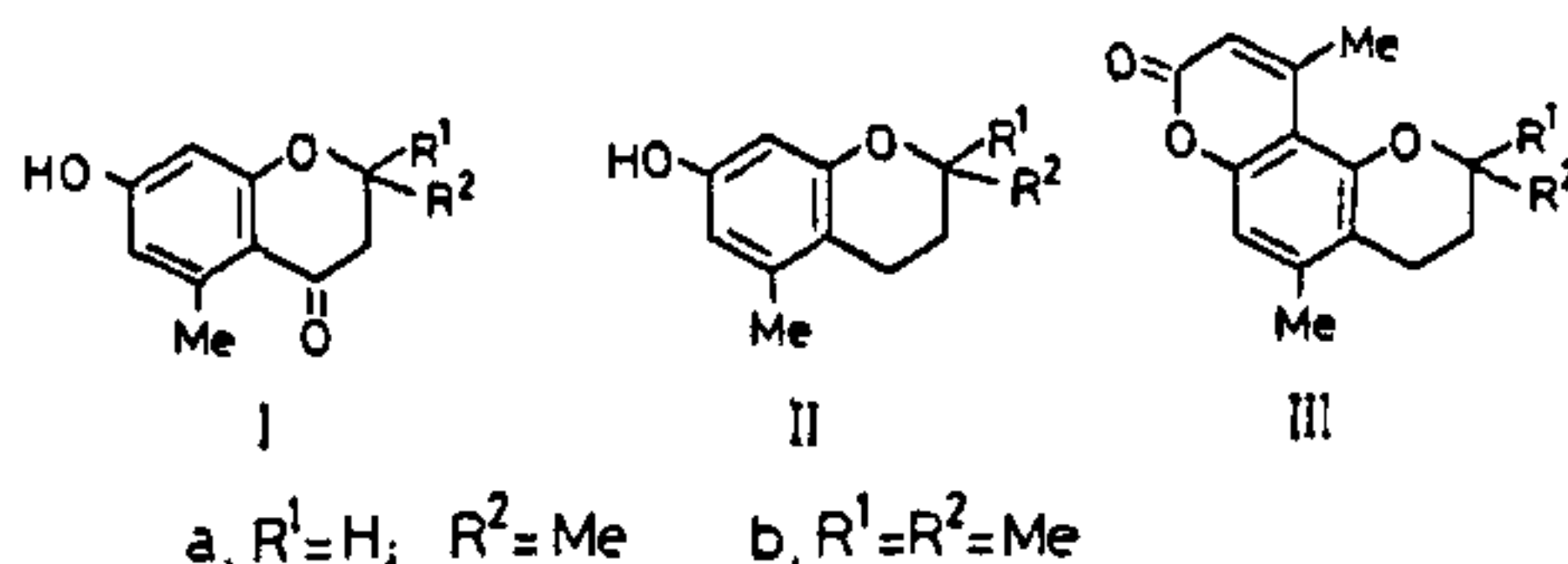
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PECHMANN CONDENSATION OF 7-HYDROXY-5-METHYLCHROMANS WITH ETHYL ACETOACETATE : SYNTHESIS OF 3,4-DIHYDRO-5,10-DIMETHYL-2H, 8H-BENZO (1,2-b:3,4-b') DIPYRAN-8-ONES

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PECHMANN condensation of 7-hydroxy-2,2-dimethylchroman with ethyl acetoacetate leads to the formation of a linear benzodipyrone — a xanthyletin derivative, was reported earlier¹. The condensation thus has taken place in position 6 in preference to 8 of the 7-hydroxy-chroman molecule. We report now our findings which show that a methyl substituent in position 5 of a 7-hydroxy-chroman molecule changes the site of the condensation from the position 6 to the position 8 to give an angular benzodipyrone (III).



Condensation of orcinol (3.5 g) with crotonic acid (6 g) by heating with fused zinc chloride (5 g) at 170–80° in an oil bath for 30 min, furnished 7-hydroxy-2,5-dimethyl-chromanone (I, pink needles from pet. ether-acetone, m.p. 170–71°, yield 1.5 g. Found C, 69.1; H, 6.4. $C_{11}H_{12}O_3$ requires C, 68.76; H, 6.2%; 2,4 DNP m.p. 265–66° Found N, 14.8; requires N, 15.0]. The sticky product that separated by adding water-HCl to the reaction mixture was extracted with ether, dried and triturated with cold toluene after removal of ether, when a solid was obtained. The condensation took place in the position β of orcinol was evident as the compound (I) gave no colouration with alc. ferric chloride eliminating the possibility of it to be a 5-hydroxychromanone derivative by condensing in position γ which would have given colouration due to proximity of OH to C=O for chelation. Clemmenson's reduction of I (2 g) by refluxing with zinc amalgam (5 g of zinc and 0.5 g of $HgCl_2$) and HCl (50 ml 1:1) for 6 hr with intermittent addition of more HCl (20 ml per hr) furnished 7-hydroxy-2,5-dimethylchroman (II, colourless oil