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Crystalline Field Effects in Superconducting $La_{1-x}Tb_xAl_2$ under Pressure

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Abstract. The pressure dependence of the superconducting transition temperature of $LaAl_2$ and alloys with Tb and Gd impurities has been measured. The results are compared with a theoretical calculation of the pressure dependence of T_c, which is based on the variation by pressure of the crystalline field experienced by the Tb ions. Measurements on LaGdAl$_2$ where crystal field effects are absent have been used to study the influence of pressure on the scattering rate.

1. Introduction

In the presence of a crystalline field the $(2J+1)$-fold degenerate groundstate of a rare earth impurity with angular momentum J splits into a sequence of crystalline field levels. This has important consequences on the properties of superconductors containing rare earth impurities, expecially in the case when the groundstate in the presence of crystalline field is nonmagnetic. The influence of crystalline fields has been demonstrated by experiments on the depression of the superconducting transition temperature as function of the impurity concentration [1, 2], the jump in the specific heat at the phase transition [3], and the upper critical magnetic field [2]. These experiments can be interpreted by a theory which takes into account the pairbreaking effect of inelastic scattering of conduction electrons on the magnetic impurities [4–7].

In this paper we present measurements and a theoretical analysis of the pressure dependence of the superconducting transition temperature T_c of

$La_{1-x}Tb_xAl_2$ and $La_{1-x}Gd_xAl_2$.

The dependence of T_c on the impurity concentration x measured previously [2] indicates that the groundstate of Tb^{3+} ions is nonmagnetic and separated from the first excited magnetic state by the energy $\delta = 5-7$ K. These results are supported by measurements of the susceptibility [8], the Schottky anomaly in the specific heat [9] and the thermoelectric power [10]. The alloy $La_{1-x}Gd_xAl_2$ does not show any crystal field effects because of the vanishing orbital momentum of Gd^{3+} ions. This is demonstrated by the good agreement of the measurements [11] T_c versus x with the theory of Abrikosov and Gorkov [12].

By applying pressure, the strength of the crystalline field is changed because of its dependence on the lattice parameter. The resulting change of the level splitting leads to a variation of the pairbreaking effect and hence to a change in T_c. This effect has been measured recently on $La_{1-x}Tb_xAl_2$ by Guertin *et al.* [13]. Our experiments on $La_{1-x}Tb_xAl_2$ give similar results.

We compare our experimental results with a theoretical calculation of the pressure dependence of T_c using the complete level scheme of Tb ions as calculated by Lea, Leask and Wolf (LLW) [14] for different values of the crystalline field parameters. Though it is not possible to determine the crystalline field parameters from these measurements uniquely, we can show that the pressure dependence of T_c is consistent with the depression of T_c as function of the impurity concentration. Thus, pressure experiments are an additional test of the model underlying the theory of superconductors containing magnetic impurities with crystalline field split energy levels.

Our experiments on $La_{1-x}Gd_xAl_2$ show that contrary to previous assumptions [15] the change of the scattering rate of conduction electrons under pressure cannot be neglected. This effect can be ascribed to a variation of the exchange interaction or the density of states at the Fermi surface.

2. Influence of Pressure on the Pairbreaking Effect of Magnetic Impurities

The strength of the effective crystal field acting on a rare earth impurity at a lattice site of cubic symmetry can be characterized by two expansion coefficients B_4 and B_6. The level system of rare earth ions has been calculated by LLW using the parameters, W, X_L which are related to B_4 and B_6 by

$$B_4 F(4) = W \cdot X_L, \tag{1a}$$

$$B_6 F(6) = W(1-|X_L|) \tag{1b}$$

$F(4)$ and $F(6)$ are numerical factors depending on the total angular momentum J. The energy separation of any two levels μ, ν is given by:

$$\delta_{\mu,\nu} = W \cdot E_{\mu,\nu} \tag{2}$$

where $E_{\mu\nu} = E_\mu(X_L) - E_\nu(X_L)$ is the difference of the corresponding eigenvalues of the reduced Hamiltonian, tabulated by LLW. The strength of the crystal field depends on the lattice parameter R. On applying a hydrostatic pressure p the relative change of R is given by:

$$\Delta R/R = -\tfrac{1}{3}\kappa p \tag{3}$$

where κ is the compressibility of the material. Assuming

$$B_4 \sim R^{-5}; \quad B_6 \sim R^{-7} \tag{4}$$

which is valid under rather general conditions (especially for the point charge model), the variation of the parameters W and X_L is given by

$$\Delta W/W = -(7-2|X_L|)\Delta R/R, \tag{5a}$$

$$\Delta X_L/X_L = 2(1-|X_L|)\Delta R/R. \tag{5b}$$

The relative change of the energy separation of the impurity levels contains two contributions:

$$\frac{\Delta\delta}{\delta} = \frac{\Delta W}{W} + \frac{\Delta E}{E}. \tag{6}$$

The first term reflects the general increase of the strength of the crystal field due to pressure and is always positive. The second term is proportional to ΔX_L and is related to the change of the level scheme by the change of the relative magnitude of B_4 and B_6. This term is important near crossing points of energy levels.

Concerning the pairbreaking of magnetic impurities with crystalline field split impurities the principal effect of pressure is the change of the ratio δ/T_{c0}, where δ is the energy separation between the ground state and the first excited state with a transition, allowed by the exchange interaction, and T_{c0} is the transition temperature of the host material. Thus a decrease of T_{c0} under pressure enhances the variation of the pairbreaking effect of the magnetic impurities.

There are secondary effects resulting from a change of the crystal field, which are proportional to ΔX_L: 1. the change of the relative position of higher energy levels compared to the ground state separation, 2. the change of transition matrix elements.

Furthermore we have to consider the influence of pressure on the exchange interaction J_{ex} between conduction electrons and magnetic impurities and on the density of states $N(0)$ at the Fermi surface, which both enter the scattering rate of conduction electrons on magnetic impurities:

$$\tau^{-1} = x \cdot 2\pi \cdot J_{ex}^2 N(0)(\Lambda-1)^2. \tag{7}$$

Here x and Λ are the concentration and the Landé factor of the magnetic impurities. As in Ref. 5 the transition matrix elements have been separated from the definition of τ^{-1}, because they depend on the particular level system. In the following discussion of the data, the change of the scattering rate due to pressure will be determined from experiments on <u>La</u>GdAl$_2$.

3. Experiments

The $La_{1-x}Tb_xAl_2$ samples have been prepared from 4 *N* pure La, 3 *N* pure Tb (both supplied from Rare Earth Products Limited) and 5 *N* pure Al by induction melting the constituents in a water cooled copper crucible in a high purity argon atmosphere. First, $LaAl_2$ and $TbAl_2$ were fabricated. Then a master alloy containing 10% Tb was prepared, portions of which were diluted with $LaAl_2$ in two further steps to get the final concentrations. Each alloy was melted 5 times. The weight loss, controlled after each melting process, was negligible. The samples were heat treated in vacuum of 10^{-7} torr at 850 °C for 16 hours. The Gd alloy was prepared in the same way.
The experiments were carried out with the usual fluid-cell method, the samples and a coil for an inductive measurement of T_c being immersed in the fluid [16]. The given values of T_c are defined by the mid-point of the transition curve. The corresponding transition widths were 40, 22, 180 and 46 mK for the samples $LaAl_2$, $La_{0.998}Tb_{0.002}Al_2$, $La_{0.994}Tb_{0.006}Al_2$ and $La_{0.998}Gd_{0.002}Al_2$, respectively. The pressure was determined from the transition temperature of tin using the relation between T_c and p given in Ref. 17. All samples were placed within the same pressure cell and measured in the same run. Approximately 10 mg were used of each sample.

Experimental values of T_c versus pressure are shown in Fig. 1 for all samples. They have been fitted with parabolic curves. Maximum deviations of the experimental points from the fit curve amount to 5 mK. The initial slope of $LaAl_2$ is 179 mK/kbar.
In Fig. 2a the difference $T_c(p)-T_c(0)$ is plotted with the values taken from the fit. In this plot the different pressure dependences of the transition temperatures of the Tb and Gd-alloys are demonstrated. This becomes clearer in Fig. 2b where the relative change of the pairbreaking effect of a single impurity is plotted on the same pressure scale.

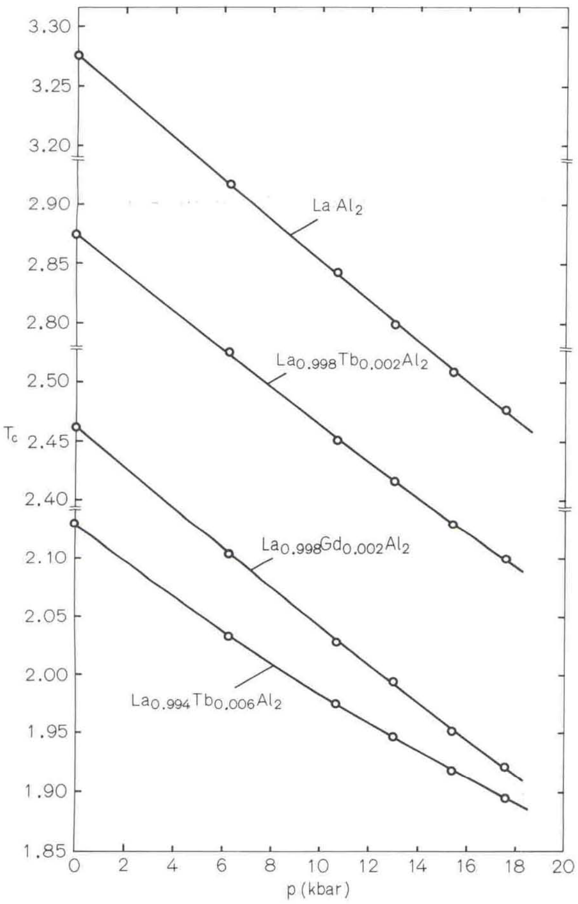

Fig. 1. The transition temperatures T_c of pure $LaAl_2$ and of the alloys $\underline{La}TbAl_2$ and $\underline{La}GdAl_2$ as function of the hydrostatic pressure p

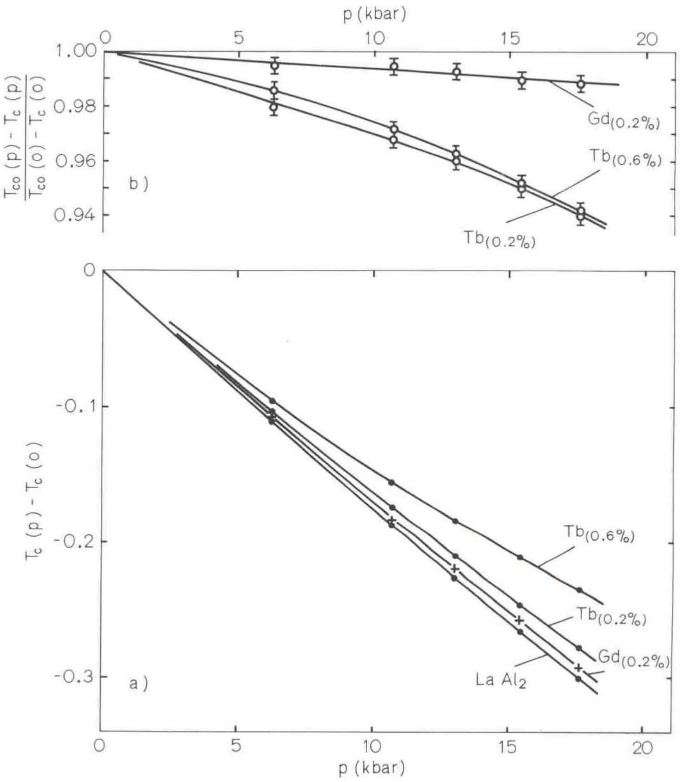

Fig. 2. a) The differences between the transition temperatures under pressure and at zero pressure, $T_c(p)-T_c(0)$, of $LaAl_2$ and the alloys with La substituted by Tb and Gd. b) The relative change of the pair-breaking effect of the Tb- and Gd-impurities $\frac{T_c(p)-T_{c0}(p)}{T_c(0)-T_{c0}(0)}$ versus pressure, T_c and T_{c0} denoting the transition temperatures of the magnetic alloys and of pure $LaAl_2$, respectively

Within the uncertainties, the corresponding values of the two Tb alloys coincide and are essentially larger than the small effect shown by the Gd alloy.

It must be noted that the effect of pressure on the pair breaking effect of Gd impurities was not detected in earlier experiments [15]. It is supposed, that in those experiments the superconducting transition of the alloys did not permit a separation of this small effect.

4. Analysis of Experimental Results

The following analysis of the pressure dependence of T_c is based on a theoretical investigation of the dependence of T_c on the level scheme and the concentration of magnetic impurities outlined in Ref. 5, combined with experimental results on the concentration dependence of T_c [2]. The transition temperature T_c of an alloy containing impurities with crystalline field split energy levels can be written quite generally:

$$T_c/T_{c0} = F(Z, Y, X_L) \tag{8}$$

T_{c0} is the transition temperature of the pure sample. $Y = \delta/T_{c0}$, where δ is the energy separation of the two lowest levels (provided that the transition is allowed) and is used as a scale of the whole level scheme. The explicit dependence of F on X_L is used to fix the position of the higher energy levels and the transition matrix elements. $Z = (\tau \cdot T_{c0})^{-1} \cdot f$ is proportional to the impurity concentration, contained in the scattering rate τ^{-1}. It is normalized through the function $f(Y, X_L)$ in such a way that $dT_c/dZ = -1$ for $T_c = T_{c0}$.

If we denote the change of T_c under pressure by $\Delta T_c = T_c(p) - T_c(0)$ and use similar abbreviations for the other pressure dependent quantities, the change of the difference between the transition temperature of the alloy and the pure sample can be written as

$$\Delta T_c - \Delta T_{c0} = (F-1)\Delta T_{c0} + T_{c0}\Delta F. \tag{9}$$

Using the explicit and implicit dependence of F on Z, Y and X_L this quantity can be decomposed into four contributions

$$\begin{aligned}\Delta T_c - \Delta T_{c0} = {} & \left(F - 1 - Z\frac{\partial F}{\partial Z}\right)\Delta T_{c0} \\ & + T_{c0} Z \frac{\partial F}{\partial Z} \tau \Delta(1/\tau) \\ & + T_{c0}\left(Z\frac{\partial F}{\partial Z}\cdot\frac{1}{f}\cdot\frac{\partial f}{\partial Y} + \frac{\partial F}{\partial Y}\right)\Delta Y \\ & + T_{c0}\left(Z\frac{\partial F}{\partial Z}\cdot\frac{1}{f}\cdot\frac{\partial f}{\partial X_L} + \frac{\partial F}{\partial X_L}\right)\Delta X_L.\end{aligned} \tag{10}$$

The last two terms of the r.h.s. of Eq. (10) contain the influence of pressure on the level system of the magnetic impurities. The derivatives of f and F have to be calculated numerically; they correspond to the change of the initial slope and the curvature of T_c vs x, respectively, for a variation of the crystalline field parameters. The variation of $Y = \delta/T_{c0}$ is given by

$$\Delta Y = Y(\Delta\delta/\delta - \Delta T_{c0}/T_{c0}). \tag{11}$$

The variation of δ can be calculated from Eq. (6) using the results of LLW and the compressibility of $LaAl_2$, given in Ref. 13. As ΔT_{c0} is negative for $LaAl_2$, the total effect of pressure on the pairbreaking effect of magnetic impurities in $LaAl_2$ is enhanced. The contribution of the term proportional to ΔX_L is small in most cases. However, the dependence of δ on X_L (Eq. (6)) is important near crossing points of the two lowest energy levels.

The first term of Eq. (10) is due to a change of the scale of the pairbreaking effect of magnetic impurities for a variation of T_{c0}. It is related to the deviation from linearity of T_c vs x. It can be calculated theoretically for a given sequence of crystalline field levels. But according to the relation

$$F - 1 - Z\frac{\partial F}{\partial Z} = T_c/T_{c0} - 1 - x\frac{\partial(T_c/T_{c0})}{\partial x} \tag{12}$$

this terms can *also* be determined completely from experiments on the concentration dependence of T_c.

The term proportional to $\Delta(1/\tau)$ can be determined from the experiments with <u>La</u>$GdAl_2$ in the following way: As the crystal field has no influence on the magnetic states of Gd ions the pressure dependence is given by the first two terms of Eq. (10). Using the known values of T_c vs x and the experimental result on the pressure dependence of T_c we can evaluate $\tau \cdot \Delta(1/\tau)$. Assuming that the relative change of the scattering rate under pressure is equal for Gd and Tb ions imbedded in the same host material we can use this value in our analysis of Tb alloys.

We concentrate our analysis of the pressure dependence of T_c on the samples

$La_{0.998}Gd_{0.002}Al_2$ and $La_{0.994}Tb_{0.006}Al_2$.

The experimental data for these samples are (variations due to pressure are given for $p = 10$ kbar):

<u>$LaAl_2$</u>

$T_{c0} = 3.276$ K, $\Delta T_{c0} = -0.174$ K,

<u>$La_{0.998}Gd_{0.002}Al_2$</u>

$T_c = 2.451$ K, $Z = 0.24$, $\Delta T_c = -0.170$ K,

$$\left(T_c/T_{c0} - x\frac{\partial(T_c/T_{c0})}{\partial x}\right)\cdot\Delta T_{c0} = -1\ \text{mK}.$$

From these data we obtain:

$$\tau \cdot \Delta(1/\tau) = 6 \cdot 10^{-3},$$

$\underline{La_{0.994}Tb_{0.006}Al_2}$

$$T_c = 2.130\ \mathrm{K}; \quad Z = 0.35; \quad \Delta T_c = -0.145\ \mathrm{K};$$

$$\left(T_c/T_{c0} - x\frac{\partial (T_c/T_{c0})}{\partial x}\right) \cdot \Delta T_{c0} = +4\ \mathrm{mK};$$

$$x\frac{\partial T_c}{\partial x} \cdot \tau \Delta(1/\tau) = 7\ \mathrm{mK}.$$

In the table we have listed our theoretical result of T_c/T_{c0} and $T_c - T_{c0}$ for $La_{0.994}Tb_{0.006}Al_2$ for two values of the groundstate separation and different values of the LLW parameter X_L. The experimentally determined value of 11 mK for the first two terms of the r.h.s. of Eq. (10) has been added. These results have to be compared with the experimental values of $T_c/T_{c0} = 0.650$ and $\Delta T_c - \Delta T_{c0} = 29$ mK. It can be noticed that for a large number of level schemes, characterized by the parameter X_L, both the experimental values of T_c/T_{c0} and $\Delta T_c - \Delta T_{c0}$ are in agreement with the assumption of a groundstate separation between 1 and 2 T_{c0}. This is true even in the case when the groundstate of Tb ions is magnetic ($\Gamma_5^{(1)}$). A magnetic groundstate, however, can be ruled out from measurements of the susceptibility [8] and also from measurements of the concentration dependence of T_c for samples with higher concentrations of Tb ions [2]. Large deviations of the calculated values from the experimental values of ($\Delta T_c - \Delta T_{c0}$) occur near crossing points of the lowest energy levels, for example at $X_L = 0.6$ ($W > 0$) and $X_L = 0.8$ ($W < 0$).

Table 1. Calculated values of T_c/T_{c0} and $\Delta T_c - \Delta T_{c0}$ at 10 kbar for two values of the ground-state separation δ. The uncertainty in the values of $\Delta T_c - \Delta T_{c0}$ amounts to ± 2 mK

	Ground State	T_c/T_{c0}		$\Delta T_c - \Delta T_{c0}$ [mK] at $p = 10$ kbar	
		$\delta/T_{c0} = 1$	$\delta/T_{c0} = 2$	$\delta/T_{c0} = 1$	$\delta/T_{c0} = 2$
$W < 0$					
$X_L = 1$	Γ_3	0.645	0.664	26	36
0.8	Γ_2	0.646	0.672	42	74
0.6	Γ_2	0.647	0.667	26	48
0.4	Γ_2	0.648	0.666	26	51
0.2	Γ_2	0.648	0.666	25	40
0	Γ_2	0.648	0.667	25	40
−0.2	Γ_2	0.650	0.665	29	36
−0.4	Γ_2	0.644	0.669	32	57
−0.6	Γ_1	0.643	0.665	25	38
−0.8	Γ_1	0.644	0.664	24	36
$W > 0$					
$X_L = 1$	Γ_1	0.644	0.664	23	36
0.8	Γ_1	0.641	0.665	23	35
0.6	Γ_1	0.650	0.654	1	−6
0.4	$\Gamma_5^{(1)}$	0.641	0.649	22	29
0.2	$\Gamma_5^{(1)}$	0.641	0.649	19	25
0	$\Gamma_5^{(1)}$	0.642	0.650	21	28
−0.2	$\Gamma_5^{(1)}$	0.644	0.648	23	30
−0.4	$\Gamma_5^{(1)}$	0.642	0.650	27	32
−0.6	Γ_3	0.644	0.665	21	26
−0.8	Γ_3	0.644	0.664	26	37

5. Conclusions

We have shown that the pressure dependence of the superconducting transition temperature of $La_{1-x}Tb_xAl_2$ can be described quantitatively by a theory which takes into account the crystal field splitting of magnetic impurities. The results are consistent with earlier experiments on the concentration dependence $T_c(x)$. The variation of T_c under pressure depends essentially on the change of the energy splitting δ between ground state and first excited state. The results turned out to be rather insensitive to the details of the level scheme, as in the case of the concentration dependence $T_c(x)$. Therefore, the original idea to determine the crystal field parameters from these experiments, could not be realized.

For a quantitative analysis of the experimental results, not only the change in the crystal field splitting is essential but also the following points are important and must be taken into account:

1. As the pairbreaking effect depends on the ratio δ/T_{c0}, the large decrease of the superconducting transition temperature T_{c0} of $LaAl_2$ with pressure enhances the effect due to the crystal field splitting.
2. From the experiments with $\underline{La}GdAl_2$, where crystal field splitting is absent, it can be concluded, that also the scattering rate of the conduction electrons τ^{-1} is changed under pressure. The value of $\Delta\tau^{-1}/\tau^{-1}$ was used for the analysis of the results on $\underline{La}TbAl_2$ and can be useful for similar experiments with other crystal field split impurities in $LaAl_2$.

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