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Linewidth of crystal field transitions in doped superconductors

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Résumé. — Les transitions entre les états électroniques de Tb et Pr dans les supraconducteurs LaAl$_2$, LaAg, LaSn$_3$ et LaPb$_3$ ont été mesurées au moyen de la diffusion inélastique des neutrons. Les largeurs de raie peuvent être reliées aux processus de relaxation avec les électrons de conduction qui, à basse température, et pour des concentrations croissantes de terre rare sont dominés par des effets électrostatique et magnétique d’environnement local. Des moments induits dans des états fondamentaux non magnétiques du Tb expliquent des anomalies dans les dépendances avec la concentration des températures de transition vers l’état supraconducteur.

Abstract. — Transitions between the electronic states and their linewidths of Tb and Pr doped for La in the superconductors LaAl$_2$, LaAg, LaSn$_3$, and LaPb$_3$ have been measured applying inelastic neutron scattering. The line-widths can be correlated with relaxation processes to the conduction electrons, which at low temperatures and for increasing RE concentration are dominated by effects of the electrostatic and magnetic local environment. Selfinduced moments in the nonmagnetic groundstates of Tb are the reason for anomalies in the concentration dependence of the superconducting transition temperatures.

Recently we succeeded in resolving crystal field transitions in RE-doped La-compounds which become superconducting [1]. Using again the neutron TOF spectrometer D 7 at Grenoble ($E_t = 3.58$ meV) we now extended our investigation to even lower RE-concentrations and to La(Pr)Pb$_3$. As examples we have plotted in figures 1 and 2 TOF spectra of La(2 % Pr)Sn$_3$ and La(8 % Pr)Pb$_3$, respectively where the spectra of the corresponding hosts have been subtracted. The full lines are fitted TOF spectra based on the crystal field scattering law [2] where the $\delta$ functions $\delta(\omega - \omega_{mn})$ have been replaced by Lorentzians $L$ of width $2\gamma_{mn}$ as

$$L(\gamma_{mn}, \omega - \omega_{mn}) \propto \frac{\omega(1 - \exp(-\beta\omega_{mn}))}{\omega_{mn}(1 - \exp(-\beta\omega))}$$

Fig. 1. — Difference in the neutron TOF spectra of La$_{0.98}$Pr$_{0.02}$Sn$_3$ and LaSn$_3$ at 2 K in comparison to the fitted spectrum (18 counters summed).

Fig. 2. — Difference in the neutron TOF spectra of La$_{0.92}$Pr$_{0.08}$Pb$_3$ and LaPb$_3$ at 2 K in comparison to the fitted spectrum (12 counters summed).

to take account of relaxations consistent with Ref. [3]. In table I we have collected evaluated results on the transition energies $\omega_{mn}$, the exp. and calc. line intensities $I_{exp}$ and $I_{calc}$ at 2 K, the lowest crystal field states, the linewidths $\gamma_0$ (HWHM) of the lowest transition at 2 K and the slope of its temperature dependence in between 2 and 15 K.

\[\text{Counts per 15 s}\]

\[\text{Time of Flight}\]

\[\text{Neutron Energy Transfer [meV]}\]

\[\text{Counts per 15 s}\]

\[\text{Time of Flight}\]

\[\text{Neutron Energy Transfer [meV]}\]
Table I. — Results from the TOF spectroscopy of several Van Vleck paramagnets and superconductors at 2 K for the position $\omega_{\text{me}}$ of the observed inelastic lines, for the measured and calculated line intensity $I$ and for the linewidth (HWHM) at 2 K and its change with temperature up to 15 K.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$y$</th>
<th>$\omega_{\text{me}}$ [meV]</th>
<th>$I_{\text{exp}}$ [barn/ion]</th>
<th>$I_{\text{calc}}$ [barn/ion]</th>
<th>Level sequ.</th>
<th>$\gamma_0 \pm 0.04$ [meV]</th>
<th>$10 \delta \gamma / \delta T$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{La}_{1-x}\text{Tb}_x\text{Al}_2$</td>
<td>0.01</td>
<td>0.68</td>
<td>50</td>
<td>52.5</td>
<td>$\Gamma_3-\Gamma_5^1$</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>0.02</td>
<td>0.60</td>
<td>39</td>
<td>§ 37</td>
<td>$\Gamma_3-\Gamma_5^1$</td>
<td>0.15</td>
<td>0.08</td>
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<tr>
<td></td>
<td>0.04</td>
<td>0.57</td>
<td>24</td>
<td>$\Gamma_3-\Gamma_5^1$</td>
<td>0.24</td>
<td>0.09</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.06</td>
<td>0.69</td>
<td>15</td>
<td>$\Gamma_3-\Gamma_5^1$</td>
<td>0.32</td>
<td>0.09</td>
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<tr>
<td>$\text{La}_{1-x}\text{Tb}_x\text{Ag}$</td>
<td>0.02</td>
<td>0.6</td>
<td>32</td>
<td>53</td>
<td>$\Gamma_3-\Gamma_5^1$</td>
<td>0.17</td>
<td>0.14</td>
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<tr>
<td></td>
<td>0.04</td>
<td>0.58</td>
<td>22</td>
<td>$\Gamma_3-\Gamma_5^1$</td>
<td>0.27</td>
<td>0.15</td>
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<tr>
<td>$\text{La}_{1-x}\text{Tb}_x\text{Sn}_3$</td>
<td>0.02</td>
<td>0.66</td>
<td>38</td>
<td>57.6</td>
<td>$\Gamma_1-\Gamma_4$</td>
<td>0.06</td>
<td>0.10</td>
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<td>0.08</td>
<td>0.58</td>
<td>30</td>
<td>$\Gamma_1-\Gamma_4$</td>
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<tr>
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<td>0.15</td>
<td>0.50</td>
<td>20</td>
<td>§ 25</td>
<td>$\Gamma_1-\Gamma_4$</td>
<td>0.40</td>
<td>0.03</td>
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<tr>
<td>$\text{La}_{1-x}\text{Pr}_x\text{Sn}_3$</td>
<td>0.02</td>
<td>0.90</td>
<td>6.5</td>
<td>7.77</td>
<td>$\Gamma_1-\Gamma_4$</td>
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<td>0.08</td>
<td>0.80</td>
<td>5.4</td>
<td>$\Gamma_1-\Gamma_4$</td>
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<td>$\text{La}_{1-x}\text{Pr}_x\text{Pb}_3$</td>
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<td>1.02</td>
<td>6.8</td>
<td>5.4</td>
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<td>0.98</td>
<td>6.4</td>
<td>$\Gamma_3-\Gamma_4-\Gamma_5$</td>
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<td>1.96</td>
<td>2.2</td>
<td>$\Gamma_3-\Gamma_4-\Gamma_5$</td>
<td>0.14</td>
<td>0.02</td>
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<tr>
<td></td>
<td>0.15</td>
<td>0.95</td>
<td>7.0</td>
<td>$\Gamma_3-\Gamma_4-\Gamma_5$</td>
<td>0.21</td>
<td>0.08</td>
<td></td>
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<tr>
<td></td>
<td>2.03</td>
<td>2.4</td>
<td>$\Gamma_3-\Gamma_4-\Gamma_5$</td>
<td>0.14</td>
<td>0.01</td>
<td></td>
<td></td>
</tr>
<tr>
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<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>6</td>
<td>7</td>
<td></td>
</tr>
</tbody>
</table>

§, §§ Random magnetic fields of 1 T (§) resp. 2.5 T (§§) assumed.

We note that in the cases of $\text{La(Pr)Sn}_3$ and $\text{La(Pr)Pb}_3$ the observed level splittings differ markedly (40 %) from the corresponding values derived from specific heat [4] — and susceptibility measurements [5] for the same Pr concentrations and from the neutron scattering on $\text{PrPb}_3$ [6]. In the case of $\text{La(2 % Pr)Sn}_3$ the location of a $\Gamma_3$-state in between of $\Gamma_1$ and $\Gamma_4$ (important in Ref. [5]) is not compatible with the observed temperature dependence of the $\Gamma_1$-$\Gamma_4$-transition which has been measured now at 2, 4, and 8 K. Since we observe at 2 K two transitions for $\text{La(Pr)Pb}_3$ with intensities and an intensity ratio as expected for $(\Gamma_3-\Gamma_4)$/$(\Gamma_3-\Gamma_5)$ transitions, the crystal field parameters are unambiguously determined from this measurement alone

$x = +0.39$, $W = -0.03$ meV,

or

$C_4 = 0.27$ meV, $C_6 = -0.25$ meV.

All groundstates $|1\rangle$ are nonmagnetic $\Gamma_1$ or $\Gamma_3$ states connected by matrix elements of $J_x$ to the excited levels which in all cases are large compared to the diagonal matrix elements within the next higher level $|2\rangle$ (strong Van Vleck magnetism). The nonmagnetic groundstates do not prevent (indirect RKKY) magnetic interaction of the RE ions at low temperatures. Selfinduced moments take away intensity from the inelastic line (column 3 of table I) and move intensity to the elastic line. In two cases we managed to separate this quasielastic magnetic intensity from the nuclear elastic scattering. The ratio of the magnetic quasielastic scattering $I_{\text{QE}}$ to inelastic scattering $I_{\text{IN}}$ (= $I_{\text{exp}}$ table I) at 2 K expressed as the ratio of local susceptibilities

$\chi_{\text{QE}}^{\text{loc}} / \chi_{\text{IN}}^{\text{loc}} = (I_{\text{QE}} / I_{\text{IN}}) \beta \omega_{\text{me}} / (2(1 - \exp(-\beta \omega_{\text{me}})))$

is 0.95 and 2.53 for $\text{La(2 % Tb)Al}_3$ and $\text{La(4 % Tb)Al}_3$ resp. and 2.5 and 3.5 for $\text{La(8 % Tb)Sn}_3$ and $\text{La(15 % Tb)Sn}_3$ resp.

$\chi_{\text{QE}}^{\text{loc}}$ obeys Curie Weiss laws and is proportional to the square of the RE concentration as expected for pair correlations. $\chi_{\text{IN}}^{\text{loc}}$ is at the smallest concentration the same as the single ion Van Vleck susceptibility as has been measured with a SQUID magnetometer. It is interesting to note that the sum $\chi_{\text{QE}}^{\text{loc}} + \chi_{\text{IN}}^{\text{loc}}$ for the concentrations larger than 2 % gets close to the Curie law of the free $\text{ Tb}^{3+}$ ion.

The residual linewidth (at 2 K) given in column 6 is first of all dependent on effects of the local electrostatic (reason A) and magnetic environment (reason B) solely the smallest concentrations getting close to the single ion behaviour (column 4). Since concentrated $\text{PrPb}_3$ is paramagnetic at all temperatures we have to consider changes in the crystal field alone in this case. Assuming that the change in the level splitting from $\text{La(2 % Pr)Pb}_3$ to $\text{PrPb}_3$ scales with the number of nearest Pr neighbours the statistical average leads to a calculated halfwidth of 0.2 for the 1 meV transition of $\text{La(15 % Pr)Pb}_3$ explaining 2/3 of the effect. Reason B for the residual linewidth is
dominant in the cases of Tb-doping [1, 7]. For La(Tb)Sn, where the inelastic line already merges with the elastic line for a Tb concentration smaller than the critical concentration to destroy superconductivity, the increase in linewidth is accompanied by a strong reduction in $T_c$ relative to the crystal field calculation [1]. The fundamental reason for this additional suppression of $T_c$ is not an averaging over effective crystal field splittings due to an increasing linewidth but is the selfinduced moment which we detect as quasielastic scattering.

Reason C for the residual linewidth, dominant at smallest concentrations, are relaxations to conduction electrons. A calculation of the residual halfwidth of the inelastic line according to Ref. [3] using

$$\gamma_0 = 2 \pi (g_J - 1)^2 (N(0) J_{ex})^2 \left| \langle 2 \mid J_\sigma \mid 1 \rangle \right|^2 \omega_{min}$$

with

$$\gamma_0 (\text{La}(1\%\text{ Tb})\text{Al}_2) = 0.1$$

gives

$$N_0 J_{ex}(\text{La}(\text{Tb})\text{Al}_2) = 0.07$$

consistent with the results from pairbreaking and the specific heat. Comparing La(Tb)Al$_2$ and La(Tb)Sn$_3$ we conclude $N(0) J_{ex}$ to be the same for both compounds because the matrix elements scale as $2/1$. Since the pairbreaking in La(Tb)Al$_2$ ($2 N(0) J_{ex}^2$) is by a factor of 20 larger than for La(Tb)Sn$_3$ the effective local densities of states and the exchange integrals scale as $1/14$ and as $14/1$ respectively. Comparing La(Pr)Sn and La(Tb)Sn$_3$ we obtain $J_{ex}(\text{Pr}) = 4 J_{ex}(\text{Tb})$ assuming the same local density of states. The calculated ratio of pairbreaking becomes $3/1$ compared to the ratio of $9/1$ found experimentally. The results seem to be reasonable and consistent with other observations of a large exchange especially for La(Pr)Sn$_3$, which should be inspected again using now the proper level scheme.

The increase in linewidth with temperature is certainly due to the relaxations to the conduction electrons. Especially La(Tb)Al$_2$ justifies detailed calculations. In the other cases additional transitions superimpose with increasing temperature.

References