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Effect of pressure on the crystal field splitting in rare earth pnictides and chalcogenides (*)

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Résumé. — On fait le point sur la situation expérimentale concernant la variation avec la pression du champ cristallin des pnictides et des chalcogénures de praséodyme. Cette situation expérimentale est comparée aux prédicitions du modèle des charges ponctuelles. On discute de la séparation des contributions de l'échange et du champ cristallin à partir des décalages de fréquence RMN ou des mesures de susceptibilité ; on considère les problèmes associés à l'explication de ces effets par des modèles mettant en jeu les électrons de conduction.

Abstract. — The experimental situation for the pressure dependence of the crystal field of praseodymium pnictides and chalcogenides is reviewed and compared with the predictions of the point charge model. The problem of separating exchange and crystal field contributions from the measured NMR frequency shift or susceptibility measurements is discussed as well as problems with explaining these effects with conduction electron related models.

There has been a good deal of interest and an accompanying degree of controversy in the interpretation of various data related to the variation with interatomic spacing of the crystal field splitting in singlet ground state materials. The point charge model (PCM) has been remarkably successful in treating neutron diffraction [1] determined crystal fields across the rare earth pnictide series. Therefore, it was quite surprising that pressure dependence of the Knight shift in Pr and Tm pnictides indicated the opposite volume dependence for the crystal field splitting in these singlet ground state materials to that predicted by PCM. The experimental result [2] of an increase in the Knight shift was corroborated by direct measurements of the susceptibility by Guertin et al. [3] who, however, interpreted their results as stemming from the pressure dependence of exchange (assuming the PCM was valid).

Our techniques are discussed in Refs. [2] and [4]. We have summarized our experimental results for the Pr pnictides and chalcogenides in table I. The logarithmic pressure derivatives of the Knight shift are defined as

\[ \frac{d \ln (K(P) - K(P = 0))}{dP} = \frac{K}{K(P = 0)} \]

We assume that the measured Knight shift for \(^{141}\text{Pr}\) in the compounds is equal to the exchange enhanced orbital shift. This is easily shown to have an insignificant effect on our basic conclusions. Under this condition, the Knight shift is given by

\[ K = A_{orb} \chi \]  

(1)

Table I. — Summary of measured (Km) and calculated (Kc) Knight shifts for \(^{141}\text{Pr}\), exchange constant (\(\theta\)), material compressibility, \(K_T\), and Knight shift pressure derivative for a series of singlet ground state compounds. Also listed are derivatives for \(\theta\) derived from NMR and EPR shift measurements and from pressure measurements of \(K\) assuming PCM.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Km (%/kbar)</th>
<th>Kc (%/kbar)</th>
<th>(\theta) (°)</th>
<th>(K_T) (°/kbar)</th>
<th>d ln (K/dP) NMR (%)/kbar</th>
<th>(d(\theta/dP)) EPR K/kbar</th>
<th>(d(\theta/dP)) PCM K/kbar</th>
</tr>
</thead>
<tbody>
<tr>
<td>PrN</td>
<td>287</td>
<td>34</td>
<td>0.07</td>
<td>0.22</td>
<td>0.026</td>
<td>0.007</td>
<td>0.375</td>
</tr>
<tr>
<td>PrP</td>
<td>634</td>
<td>20 (0.14)</td>
<td>(°)</td>
<td>0.83</td>
<td>0.060</td>
<td>0.015</td>
<td>0.516</td>
</tr>
<tr>
<td>PrAs</td>
<td>650</td>
<td>14</td>
<td>0.13</td>
<td>0.62</td>
<td>0.057</td>
<td>0.014</td>
<td>0.403</td>
</tr>
<tr>
<td>PrSb</td>
<td>930</td>
<td>5</td>
<td>0.20</td>
<td>1.0</td>
<td>0.092</td>
<td>0.023</td>
<td>0.437</td>
</tr>
<tr>
<td>PrS</td>
<td>394</td>
<td>1 (0.14)</td>
<td>(°)</td>
<td>-0.19</td>
<td>0.053</td>
<td>0.012</td>
<td>0.015</td>
</tr>
<tr>
<td>PrSe</td>
<td>440</td>
<td>3</td>
<td>(0.14) (°)</td>
<td>-0.18</td>
<td>0.055</td>
<td>0.012</td>
<td>0.013</td>
</tr>
</tbody>
</table>

(*) Determined from crystal field parameters in Ref. [1].

(*) Estimates of \(K_T\).

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where \( A_{orb} \) is essentially independent of volume and the susceptibility is given by

\[
\chi = C_f f_j(A, T) \left[ T - f_j(A, T) \right].
\]

In the low temperature limit \( f_j \propto T/A \) and the susceptibility takes on the Van Vleck form \( \chi \propto 1/A \). Within the point charge model (PCM), \( A \propto R^{-3} \) and ignoring exchange (\( \theta = 0 \)), we expect a decrease in \( K \) as pressure is applied to a sample. This effect is observed for the chalcogenides, but a large increase in \( K \) was observed for the pnictides.

From Eq. (2) it is clear that the anomalous behaviour of the pnictides can be due either to changes in \( A \) or \( \theta \). A single determination of \( K \) or \( \chi \) cannot resolve this point. Studying the temperature dependence of Knight shifts in PrP, PrAs, and TmP we previously argued that effects of \( \theta \) are small. In contrast, by assuming that EPR determination of \( \theta \) from a series of pnictides and chalcogenides represent the volume dependence of \( \theta \), Davidov et al. [6] find that exchange effects may, in fact, account for our pressure experiments. However, we can make an analogous determination of \( \theta \) from the \( K \) measurements in table I and now examine these results.

Using neutron diffraction measurements of \( A \), we can calculate the unenhanced shift \( (K) \) using Eqs. (1) and (2) with \( \theta = 0 \). These values are also listed in table I along with \( \theta \) determined from

\[
\theta = T f_j(T, A) \left[ 1 - K_j K_m \right],
\]

where \( K_m \) are measured shifts. Figure 1 shows a plot of \( \theta \) against the sample lattice constant for NMR and EPR data. The exchange constants \( J \) in Ref. [6] are related to \( \theta \) by

\[
\theta = (C_f \epsilon g_j/|\epsilon|^{2}) J,
\]

where the symbols have their usual meaning.

In order to demonstrate the significance of exchange effects, we calculate the value of \( d\theta/dP \) needed to account for the observed \( d\ln K/dP \) when PCM is assumed valid, i.e., \( d\ln A/dP = -5/3 K_T \), where \( K_T \) is the material compressibility. In this case, Eq. (1) gives

\[
\frac{d\theta}{dP} = \frac{T}{f_j(T, A)} \left[ \frac{T - \theta f_j}{T} \right] \frac{d\ln K}{dP} + \frac{5}{3} K_T.
\]

We have tabulated results of Eq. (5) and values derived from \( d\theta/dP = -(K_T a/3) d\theta/da \), where \( d\theta/da \) are slopes of the lines shown in figure 1. For all pnictides the values of \( d\theta/dP \) needed to substantiate PCM are much larger than we can derive from \( \theta \) vs \( a \) plots. For the chalcogenides, the exchange effects are consistent with the observed changes, which implies PCM is valid for these materials.

We note that Davidov et al. [6] used a logarithmic derivative derived from figure 1 to determine exchange effects in PrAs. This procedure unrealistically (we believe) overestimates the effect since the EPR determined \( \theta \) is near zero in this compounds (figure 1). Our interpretation recently received strong corroboration with the direct measurement of the crystal field splitting with pressure by neutron diffraction by Vettier et al. [7]. Their measurement of \( d\ln A/dP \) is in excellent quantitative agreement with our determination. It is tempting to attribute this failure of PCM in the pnictides to conduction electron effects. Devine and coworkers [8] have discussed this approach. Our work on PrN where quantitatively similar results are observed to the other pnictides presents a serious difficulty to this approach because this compound is not metallic. The resolution of this problem is not evident at this point.

References