過渡元素材料的電子結構及磁特性之研究

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計畫主持人：呂欽山

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過渡元素材料的電子結構及磁特性之研究（2/3）

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本成果報告包括以下應繳交之附件：

□ 赴國外出差或研習心得報告一份
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□ 出席國際學術會議心得報告及發表之論文各一份
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執行單位：國立成功大學物理系

中華民國94年05月17日
27Al NMR measurements were performed on the D023-structure trialuminides Al3Zr and Al3Hf. The Knight shifts, quadrupole splittings, and spin-lattice relaxation times for each of the three crystallographic sites have been resolved. Universally small Fermi-contact Knight shifts and long relaxation times are found for both alloys. Results provide a measure of s-character Fermi-level density of states $N_s(E_F)$ and an indication of orbital weights. In addition, there is evidence that $N_s(E_F)$ correlates with the structural stability of the studied materials. Our NMR measurements confirm that Al3Zr is more stable than Al3Hf with respect to the DO23 structure.

**Keywords:** NMR, Knight shift, quadrupole interaction, spin-lattice relaxation, Fermi-level density of states

**簡介:**

Transition metal based tri-aluminides, Al3M, exhibit a unique combination of properties such as high melting points, low mass densities, and low oxidation resistances. A great deal of research has been devoted to investigating these materials for the understanding of their electronic properties and structural phase stability.

Among these Al3M alloys (where M is the early transition element, Ti, V, Zr, Nb, Hf,...), the possible crystal structures are L12, D022, as well as D023. For Al3Zr and Al3Hf, the low-temperature ground state D023 is energetically favored, while Al3Hf is more stable with D022 at high temperatures.

Theoretically, electronic structure calculations performed simply by optimizing the c/a ratio could not predict a correct ground state for both alloys. On the other hand, allowing the internal atoms shifting off their ideal positions is a key source responsible for the D023 structure stability. The calculated total density of states (DOS) exhibited a deep valley at the Fermi level, attributed to hybridization between Al-p and M-d playing an important role for the DOS reduction. Nevertheless, there has been little experimental work associated with
these scenarios, essential to interpret their structural stability.

In this paper, we will present NMR measurements including the Knight shifts, quadrupole transitions, and spin-lattice relaxation times in Al₃Zr and Al₃Hf as related to their local electronic characteristics. The information about the local environments is mainly obtained through the quadrupole interactions as well as through the hyperfine interactions in this investigation.

Fig. 1

In order to explore the local electronic properties for each Al site, we performed quadrupole transition measurements providing well-resolved satellite lines for individual sites. In this investigation, wide-line satellite spectra were mapped out by integrating spin echo signals of various excitations. Due to electric quadrupole coupling, the $^{27}$Al NMR spectra ($I = 5/2$) are composed of 5 transition lines per site, so that three non-equivalent Al sites in D0₂₃ result in 15 lines, as demonstrated in Fig. 2 and Fig. 3 (three central transition lines have been displayed separately in Fig. 1.). For
powdered samples, as in our experiment, these lines exhibit as typical powder patterns, with distinctive edge structures corresponding to the quadrupole parameters. The four edge singularities for each Al site correspond to \( m = \pm 1/2 \leftrightarrow \pm 3/2 \) and \( m = \pm 3/2 \leftrightarrow \pm 5/2 \) transitions. Since the first order quadrupole shift is the main effect shaping the satellite line, the quadrupole frequency, \( \nu_Q \), was determined directly from these lines. Due to the axial symmetry for Al-II and Al-III, the \( \nu_Q \) values can be obtained from the difference between \( m = -1/2 \leftrightarrow -3/2 \) and \( m = +1/2 \leftrightarrow +3/2 \) edges. Site identification for the Al\(_3\)Zr alloy has been given by Bastow et al. Accordingly, the smaller \( \nu_Q \) has been assigned to site II, and the larger one to site III. For Al-I, however, the point symmetry (\( mmm \)) is non-axial which yields a nonzero asymmetry parameter \( \eta \). Such the asymmetry effect splits the \( m = \pm 1/2 \leftrightarrow \pm 3/2 \) transitions to two edges.

Table I

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Site</th>
<th>( \eta )</th>
<th>( \nu_Q ) (MHz)</th>
<th>( T_1 ) (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al(_3)Zr</td>
<td>I</td>
<td>0.028</td>
<td>1.345</td>
<td>125</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>0</td>
<td>0.445</td>
<td>126</td>
</tr>
<tr>
<td></td>
<td>III</td>
<td>0</td>
<td>1.690</td>
<td>54</td>
</tr>
<tr>
<td>Al(_3)Hf</td>
<td>I</td>
<td>0.027</td>
<td>1.375</td>
<td>127</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>0</td>
<td>0.440</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>III</td>
<td>0</td>
<td>1.760</td>
<td>29</td>
</tr>
</tbody>
</table>

We can thus determine \( \nu_Q \) using the central position of these lines and the \( \eta \) factor from the observed splitting for this site. All extracted \( \nu_Q \) and \( \eta \) values for Al\(_3\)Zr and Al\(_3\)Hf were summarized in Table I. It is interesting that the differences in \( \nu_Q \) and \( \eta \) between the compounds are marginal, indicative of the similar local charge environments within both alloys.
As seen from Fig. 1, three Al NMR lines are strongly mixed, leading to the difficulty of the separation of individual sites from the central transition signals. We thus measured the spin-lattice relaxation time \( T_1 \) using the satellite lines, providing distinctive peaks for each Al site. We found each \( T_1 \) by centering the transmission frequency at the \( m = -1/2 \leftrightarrow -3/2 \) quadrupole-split powder pattern edges, where the resonance is dominated by one site. The spin-lattice relaxation time measurement was carried out using the inversion recovery method. We recorded the signal strength by integrating the recovered spin echo signal. In these experiments, the relaxation process involves the adjacent pairs of spin levels, and the corresponding spin-lattice relaxation is a multi-exponential expression.

Thus \( T_1 \) values can be obtained by fitting to this multi-exponential recovery curve. To provide accurate values, each \( T_1 \) has been measured several times and the averaged \( T_1 \) for each Al site is enumerated in Table I. While nonconduction mechanisms may contribute to the relaxation, they were excluded by the Korringa relation. Measurements performed at various temperatures yield Korringa behavior (constant \( T_1T \)), indicative of a conduction-electron mechanism for the observed relaxation.

The spin-lattice relaxation time measurement is known as a direct probe of the Fermi surface feature in non-magnetic materials. For the present Al\(_2\)Zr and Al\(_2\)Hf, the relaxation of Al nuclei is dominated by their coupling to the spin of the s-character electrons. In the absence of the collective electron effects, the relaxation rate is simply governed by the initially occupied and finally unoccupied electronic states, associated with the hyperfine field arising from contact electrons. Under such the approximation, the spin-lattice relaxation rate can be written as

\[
\frac{1}{T_i} = 2\hbar g_T \gamma N_s (E_F) H_{HF}^s T_1^s \left[ \sum_{\nu} N_s (E_{\nu}) \right]^2.
\]

For the aluminum atom, the states around the Fermi surface are predominately s- and p-like, the mixture of d states being rather small. Since p and d hyperfine fields are generally an order of magnitude smaller than s hyperfine fields, the main hyperfine field in such alloys arises from contact electrons. Taking \( H_{HF}^s \sim 1.9 \times 10^6 \) gauss in Al metal and experimental \( T_1 \)’s, the Fermi level DOS of s-electrons for each individual site can be obtained from Eq. 1, with the results listed in Table II. Higher s-DOS at the Fermi surface occurring at site III implies that more s-electrons exist at that site, identical with the observation for site I in the D\(_{022}\) structure. Together with the \( \nu_0 \) results, we conclude that Al-III in D\(_{023}\) plays a similar role for the local electronic properties and phase stability as Al-I in D\(_{022}\).
Table II

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Al-I</th>
<th>Al-II</th>
<th>Al-III</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₃Zr</td>
<td>0.0147</td>
<td>0.0146</td>
<td>0.0223</td>
<td>0.0172</td>
</tr>
<tr>
<td>Al₃Hf</td>
<td>0.0145</td>
<td>0.0232</td>
<td>0.0304</td>
<td>0.0227</td>
</tr>
</tbody>
</table>

From $T_1$ analysis, small Fermi level densities of states were found for both studied alloys, in good agreement with theoretical predications of the presence of pseudogap near the Fermi level due to hybridizations. Our high-temperature $T_1$ measurements further indicated that these hybridized pseudogaps are not as deep as those in semimetals. Moreover, we demonstrated that Al₃Zr contains less Al s-character Fermi-level DOS than that in Al₃Hf. The lower Fermi-level DOS is often related to the higher phase stability. This can be understood as follows: If the Fermi-level DOS is small, it means that more electrons participate in bonding and get localized. As a result, the stability of the material will be larger. With this accordance, the present NMR study confirms that Al₃Zr is more stable than Al₃Hf with respect to the D0$_{23}$ structure. Such an argument is consistent with the fact that Al₃Hf becomes more favorable with D0$_{22}$ at high temperatures ($T > 650$ C).

**Note:**
Publications under this project are as follows:


