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Crystal Field Effects on the Elastic Constants of Single Crystals of $PrAl_2$ and $NdAl_2$

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Abstract. We report measurements of the sound velocity of single crystals of $PrAl_2$ and $NdAl_2$ between 4.2 K and 280 K. For the elastic constants we find at 280 K (in 10^{11} N/m^2): $C_{11} = 1.382 \pm 1.2\%$; $C_{12} = 0.42 \pm 3.6\%$; $C_{44} = 0.452 \pm 1.0\%$ for $PrAl_2$ and $C_{11} = 1.41 \pm 1.2\%$; $C_{12} = 0.470 \pm 3.6\%$; $C_{44} = 0.429 \pm 1.0\%$ for $NdAl_2$. Some modes of the sound velocity increase with increasing temperature over a large range above the Curie temperature. This increase is interpreted in terms of the interaction between the crystal field and the strains.

Introduction

The chemical and physical properties of the $REAl_2$ intermetallic compounds (RE = rare earth) are similar in many respects. All members of the series have the $MgCu_2$ Laves phase structure [1] and their melting points vary between 1370°C and 1500°C only [2, 3]. With the exception of $EuAl_2$ and $YbAl_2$ the $REAl_2$ compounds contain RE ions which are three valent. Detailed investigations of the crystal field in several of the $REAl_2$ compounds show that the 4th and 6th order terms change little from one RE to another [4]. Magnetization measurements demonstrate that most of the $REAl_2$ compounds order ferromagnetically (for a review on magnetic properties of polycrystals see Ref. [5], for single crystals see Ref. [4, 6–9]).

However measurements on the electronic specific heat [10] and the exchange interaction [6, 7] in some of the $REAl_2$ compounds reveal important deviations from the expected similarities. This is an indication for a change in the band structure and consequently in the chemical binding when replacing one rare earth by another. Under these circumstances it is interesting to investigate the elastic constants of the $REAl_2$ series in a systematic way because of their close connection to chemical binding. It is also of interest to look for the effect of the crystal field on the elastic constants.

Single crystal elastic constants of $LaAl_2$ and $GdAl_2$ [3, 11], $TbAl_2$ [12] and $DyAl_2$ (only two combinations) [13] are reported earlier. In the present work, we determine the elastic constants of single crystals of $PrAl_2$ and $NdAl_2$ in the temperature range from 4.2 K to 280 K. The temperature dependence of some elastic constants is analyzed in terms of the interaction between the crystal field and the strains. A comparison of the elastic constants of $PrAl_2$ and $NdAl_2$ with those of $LaAl_2$, $GdAl_2$, $TbAl_2$ and $DyAl_2$ does not show an obvious systematic behaviour.

Experimental Results

The $REAl_2$ compounds are prepared from 99.9% pure RE and 99.999% pure Al. Single crystalline cylinders with the axis parallel to [110] and [100] have been obtained by the Czochralski method [14]. By spark cutting and polishing we obtained samples of approximately 4 mm diameter and 3 to 9 mm length with faces parallel within 0.1 μ. The misorientation was smaller than 1°. The room temperature densities of $PrAl_2$ and $NdAl_2$ were 5.013 ± 0.005 and 5.097 ± 0.005 g/cm^3 which compare well with the theoretical densities of 5.0277 and 5.1682 g/cm^3 [15].

The elastic constants were determined by the ultrasonic technique using pulses of 10 MHz and 1 μ sec. length. From 4.2 K to 35 K the temperature was measured with a germistor, for higher temperatures a copper–constantan thermocouple was used. The temperature was stabilized by an Artronix (Model 5301) temperature controller within 0.01 K. The absolute accuracy in the temperature read was of the order of ± 0.5 K in the region from 25–45 K and ± 0.1 K otherwise.

For the $PrAl_2$ and $NdAl_2$ we measured the sound velocities of the longitudinal and the transverse modes with propagation along [100] and [110]. For all modes we observed considerable attenuation and in no case more than 14 echoes could be detected. One set of measurements of the sound velocities allowing for a determination of the complete set of C_{ik}'s is given in Figure 1 for $PrAl_2$ and in Figure 2 for $NdAl_2$. The absolute error in the experimental sound velocities is of the order of ± 15 m/sec and for the relative error we estimate ± 5 m/sec. In Table I and II we give the elastic constants C_{11}, C_{12} and C_{44} deduced from Figures 1 and 2.

Discussion

In Figures 1 and 2 we see that the sound velocities exhibit a sharp minimum at $T_c = (31.0 \pm 0.5)$ K for $PrAl_2$ and at $T_c = (77.2 \pm 0.1)$ K for $NdAl_2$. These anomalies are due to the ferromagnetic-paramagnetic phase transition. The T_c value of $PrAl_2$ compares well with the result of specific heat measurements ($T_c = 31.8$ K) [16] and is also in fair agreement with data obtained from neutron ($T_c = 34$ K) [17] and magnetization ($T_c \approx 34$ K [18]; $T_c = 32$ K [19]) measurements. For $NdAl_2$ one deduces from specific heat data $T_c = 77.2$ K [16] and from magnetization data $T_c = 80$ K [18]. In view of the uncertainty of a Curie point determination in a neutron or magnetization experiment on materials like the $REAl_2$ compounds, we find good agreement between our T_c values and those reported in the literature.

In all measurements of the sound velocities of $NdAl_2$ we observe a broad maximum at 35 K and around 4.2 K a rather steep decrease with decreasing temperature accompanied by strong attenuation. Below 4 K no accurate measurement of the sound velocity was possible. However, for the C_{44} mode with propagation along [100] we have evidence that saturation is obtained in the sound velocity around 1.2 K at a value which is roughly 10% below the 4.2 value.

A detailed discussion of the temperature dependence of the sound velocities in Figures 1 and 2 is difficult. In particular, this is the case in the ferromagnetic region because details of the domain structure are important. Above the Curie temperature, we separate the temperature dependence into two contributions. The first contribution comes from the crystal field and the second from all other effects, which do not contain the crystal field. As can be seen from $LaAl_2$ [11] the latter contribution is

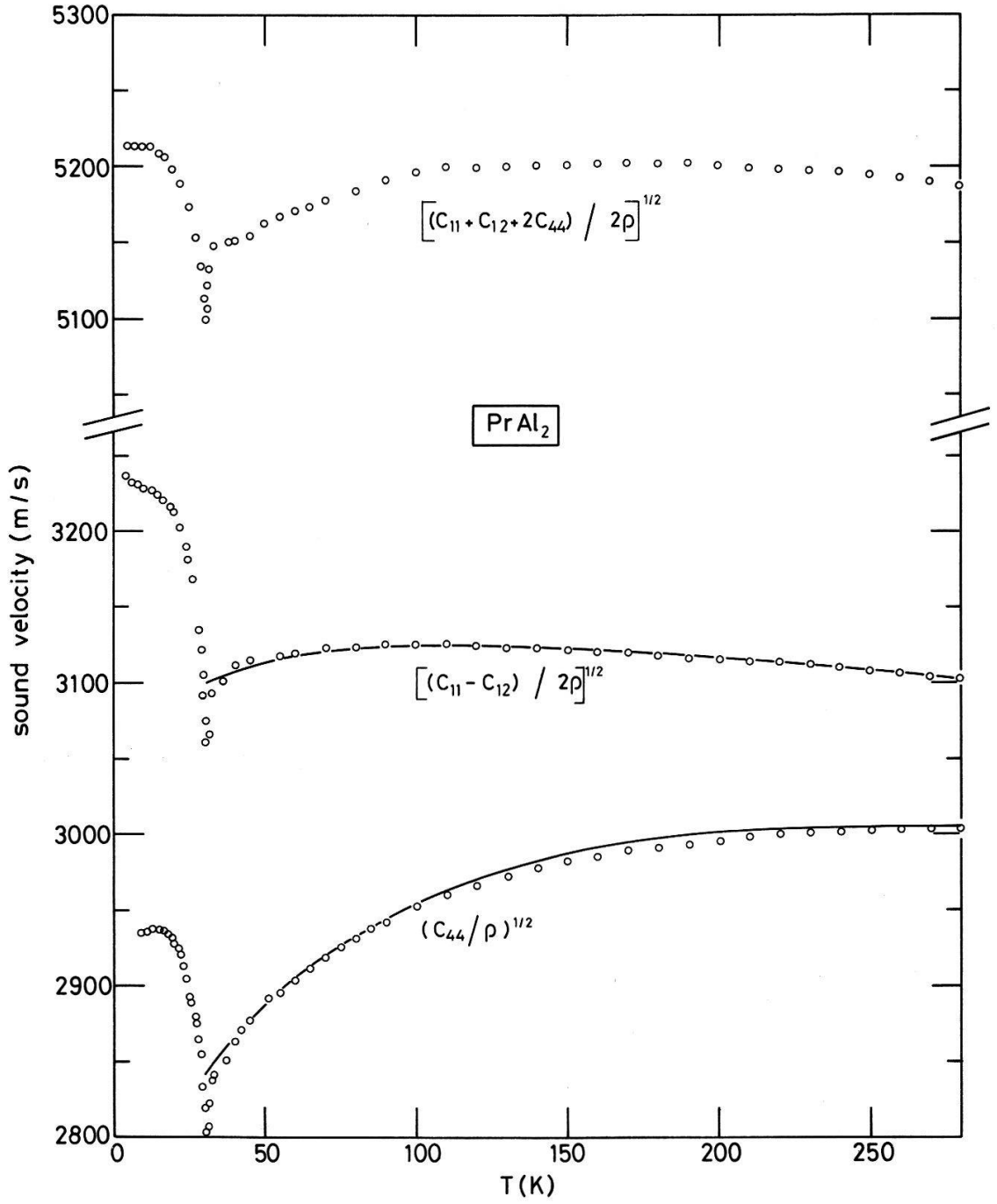

Figure 1
Experimental points and fitted curves of the sound velocities of $PrAl_2$ plotted as a function of temperature. The C_{44} mode is measured along [100] the other modes along [110].

approximately linear in temperature from 80 K to 280 K. We therefore write the temperature dependence of the elastic constants as [22]

$$C_\Gamma = C_\Gamma^0(1 - \alpha T)(1 - g_\Gamma^2 \chi_\Gamma(T)) \tag{1}$$

C_Γ is a combination of elastic constants specified by Γ. C_Γ^0 is a constant, α the temperature coefficient and g_Γ^2 the coupling parameter between the crystal field and the strains ε_Γ.

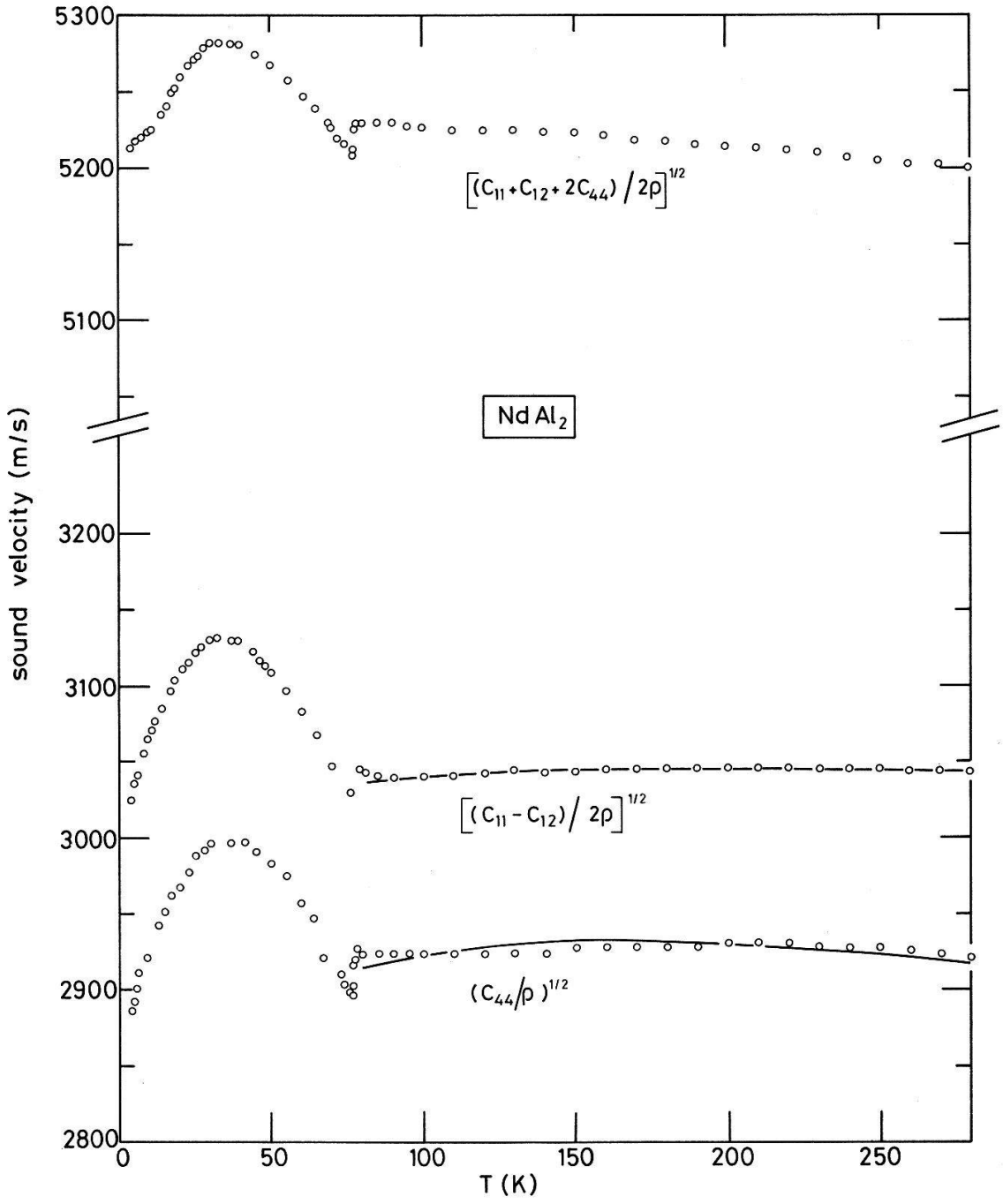

Figure 2
Experimental points and fitted curves of the sound velocities of $NdAl_2$ plotted as a function of temperature. The C_{44} mode is measured along [100] the other modes along [110].

To calculate $\chi_\Gamma(T)$ in equation (1) for $C_\Gamma = (C_{11} - C_{12})$ and $C_\Gamma = C_{44}$ we assume that the magnetoelastic Hamiltonian has the form [20, 21]

$$\hat{H}(C_{11} - C_{12}) = -g_2(((C_{11}^0 - C_{12}^0)/N)(1 - \alpha_2 T))^{1/2} O_2^0 \cdot (2\varepsilon_{zz} - \varepsilon_{xx} - \varepsilon_{yy})$$
$$\hat{H}(C_{44}) = -g_3((C_{44}^0/N)(1 - \alpha_3 T))^{1/2} O_2^{-2} \cdot (2\varepsilon_{xy}) \qquad (2)$$

Here N is the number of magnetic ions, ε_{ij} are the strains, O_l^m are the equivalent Stevens operators [22]. According to [23] χ_Γ can then be written as

Table 1
Elastic constants of $PrAl_2$

$PrAl_2$			
T (°K)	C_{11} $\times$ (10^{11} N/m^2)	C_{12} $\times$ (10^{11} N/m^2)	C_{44} $\times$ (10^{11} N/m^2)
4.2	1.455	0.406	0.431
10	1.453	0.408	0.431
20	1.443	0.409	0.429
31	1.400	0.462	0.394
40	1.404	0.434	0.410
50	1.406	0.433	0.418
60	1.407	0.432	0.423
70	1.407	0.430	0.427
80	1.407	0.430	0.430
90	1.406	0.428	0.434
100	1.406	0.428	0.437
110	1.406	0.428	0.439
120	1.406	0.429	0.441
130	1.406	0.429	0.443
140	1.405	0.428	0.444
150	1.403	0.427	0.445
160	1.401	0.426	0.446
170	1.400	0.425	0.447
180	1.400	0.426	0.448
190	1.399	0.426	0.449
200	1.398	0.425	0.450
210	1.397	0.425	0.450
220	1.395	0.424	0.451
230	1.393	0.423	0.451
240	1.389	0.420	0.451
250	1.387	0.419	0.452
260	1.386	0.419	0.452
270	1.384	0.419	0.452
280	1.382	0.418	0.452

$$\chi_\Gamma = (1/Z)\Big\{\sum_n \exp(-E_n/KT)|V_{\Gamma nn}|^2/KT - 2\sum_{n>m}[\exp(-E_m/KT) - \exp(-E_n/KT)](E_m - E_n)^{-1}|V_{\Gamma n,m}|^2\Big\} \quad (3)$$

where V_Γ is O_2^0 and O_2^{-2} respectively, Z is the partition function and E_m, E_n the eigenvalues of the ground state of the free RE^{3+} ion experiencing a cubic crystalline field [24]. To calculate the E_m, E_n and the matrix elements $V_{\Gamma nm}$ we use the crystal field parameters obtained from magnetization measurements on $PrAl_2$ and $NdAl_2$ [4]. We remark that χ_Γ is always positive.

To obtain the calculated sound velocities $v_{\text{ii}} = (C_\Gamma/\rho)^{1/2}$ for the $(C_{11} - C_{12})$- and the C_{44}-mode we choose C_Γ^0, α and g_Γ^2 to obtain good agreements of equation 1 with experiment. The results of the fits are given for α and g_Γ^2 in Table I, and for the sound velocities in Figures 1 and 2 (as a full line). We note that deviations from a '$LaAl_2$ like' temperature dependence are well described by the calculated curves above the Curie temperature.

Table 2
Elastic constants of $NdAl_2$

$NdAl_2$			
T (°K)	C_{11} $\times$ (10^{11} N/m^2)	C_{12} $\times$ (10^{11} N/m^2)	C_{44} $\times$ (10^{11} N/m^2)
4.2	1.469	0.544	0.366
10	1.421	0.471	0.433
20	1.440	0.464	0.445
30	1.451	0.461	0.453
40	1.450	0.460	0.454
50	1.441	0.464	0.450
60	1.429	0.469	0.442
70	1.420	0.481	0.430
77.2	1.409	0.481	0.424
80	1.418	0.482	0.432
90	1.417	0.483	0.432
100	1.415	0.481	0.432
110	1.415	0.481	0.432
120	1.415	0.480	0.432
130	1.415	0.480	0.432
140	1.415	0.479	0.432
150	1.413	0.477	0.433
160	1.413	0.476	0.433
170	1.411	0.474	0.433
180	1.411	0.472	0.433
190	1.410	0.473	0.433
200	1.408	0.471	0.434
210	1.408	0.470	0.434
220	1.407	0.469	0.434
230	1.407	0.470	0.433
240	1.405	0.468	0.433
250	1.405	0.467	0.432
260	1.407	0.470	0.429
270	1.406	0.470	0.430
280	1.406	0.470	0.428

In Figure 3, we compare the room temperature bulk modulus $(C_{11} + 2C_{12})/3$, the shear modulus $(C_{11} - C_{12})/2$ and the anisotropy $(C_{11} - C_{12})/2C_{44}$ of different $REAl_2$ compounds. We see that the represented elastic parameters have no simple systematic behaviour as might have been expected from the similarity of many of the physical properties.

Conclusion

In the present work, we see that the temperature dependences of the elastic constants of $PrAl_2$ and $NdAl_2$ show strong crystal field effects. In some cases these effects dominate the usual $LaAl_2$ like temperature dependence and lead to a fairly large increase of the elastic constants with increasing temperature. Qualitatively we were able to give a correct description of these crystal field effects. However, from Table III, we see that the values of α vary considerably when comparing $LaAl_2$, $PrAl_2$ and $NdAl_2$. We conclude therefore that either the values of α are simply very

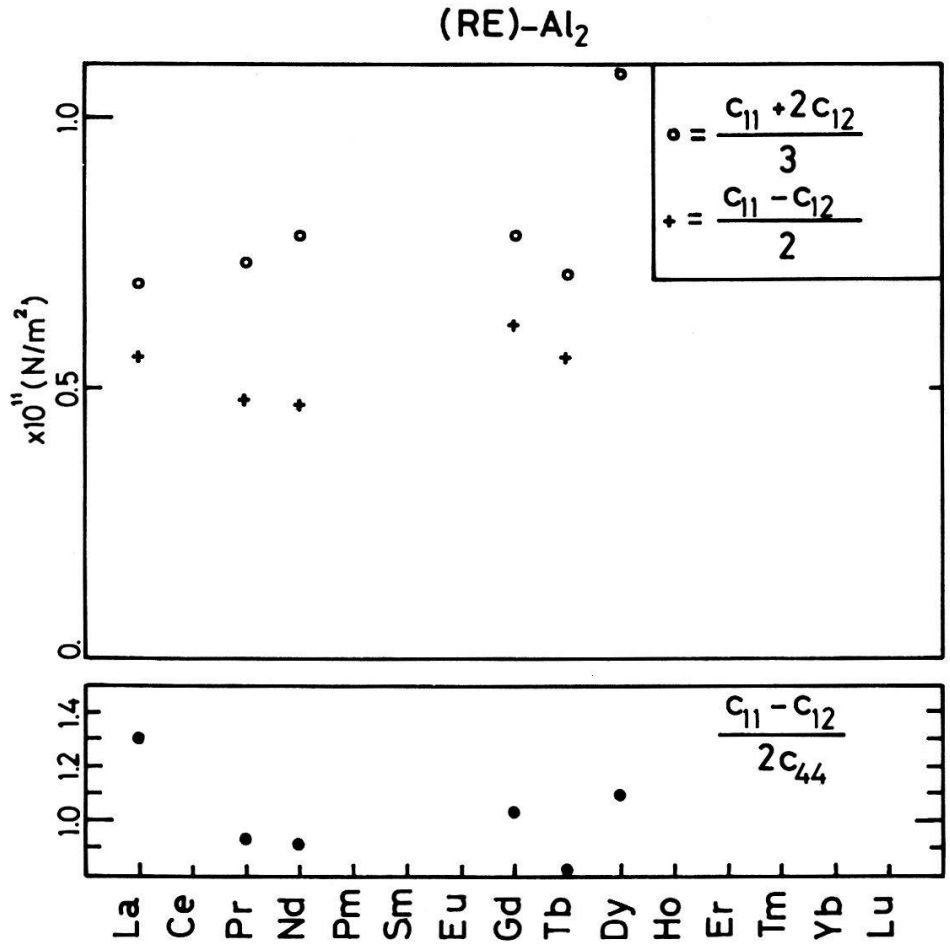

Figure 3
Bulk modulus $(C_{11} + 2C_{12})/3$, shear modulus $(C_{11} - C_{12})/2$ and anisotropy $(C_{11} - C_{12})/2C_{44}$ of some $REAl_2$ compounds at room temperature. The data for $LaAl_2$ and $GdAl_2$ are taken from Ref. [11], those of $TbAl_2$ and $DyAl_2$ from Ref. [12] and [13].

	$C_{11} - C_{12}$		C_{44}	
	$\alpha(10^{-5}\,°K)$	$g_\Gamma^2(10^{-3}\,°K)$	$\alpha(10^{-5}\,°K)$	$g_\Gamma^2(10^{-3}\,°K)$
$PrAl_2$	14.0	4.9	18.4	41.7
$NdAl_2$	3.0	2.5	20.3	12.4
$LaAl_2$	16.4	—	5.7	—

Table 3
Parameters α and g_Γ^2 describing the temperature dependence of elastic constants of $REAl_2$ compounds according to equation (1). The values of $LaAl_2$ are taken from Ref. [11].

different from one $REAl_2$ to another, or that α contains also magneto-elastic contribution so that equation (3) is only a qualitative expression for the effect of the crystal field on the elastic constants.

From the systematic comparison of the bulk modulus, the shear modulus and the anisotropy in Figure 3, we conclude that no simple systematic behaviour is followed. From the investigation of elastic constants we therefore believe that the lattice forces and the chemical binding vary considerably throughout the series even though these compounds are very similar in many other respects.

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