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Crystal Field Effects on the Elastic Constants of Single Crystals of PrAl₂ and NdAl₂

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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/m²): $C_{11}=1.382\pm1.2\%$; $C_{12}=0.42\pm3.6\%$; $C_{44}=0.452\pm1.0\%$ for $PrAl_2$ and $C_{11}=1.41\pm1.2\%$; $C_{12}=0.470\pm3.6\%$; $C_{44}=0.429\pm1.0\%$ 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 REAl₂ intermetallic compounds (RE = rare earth) are similar in many respects. All members of the series have the MgCu₂ Laves phase structure [1] and their melting points vary between 1370°C and 1500°C only [2, 3]. With the exception of EuAl₂ and YbAl₂ the REAl₂ compounds contain RE ions which are three valent. Detailed investigations of the crystal field in several of the REAl₂ compounds show that the 4th and 6th order terms change little from one RE to another [4]. Magnetization measurements demonstrate that most of the REAl₂ 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 REAl₂ 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 REAl₂ 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 LaAl₂ and GdAl₂ [3, 11], TbAl₂ [12] and DyAl₂ (only two combinations) [13] are reported earlier. In the present work, we determine the elastic constants of single crystals of PrAl₂ and NdAl₂ 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 PrAl₂ and NdAl₂ with those of LaAl₂, GdAl₂, TbAl₂ and DyAl₂ does not show an obvious systematic behaviour.

Experimental Results

The REAl₂ 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 PrAl₂ and NdAl₂ were 5.013 \pm 0.005 and 5.097 \pm 0.005 g/cm³ which compare well with the theoretical densities of 5.0277 and 5.1682 g/cm³ [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 $T_c = (31.0 \pm 0.5) \,\mathrm{K}$ for $\mathrm{PrAl_2}$ and at $T_c = (77.2 \pm 0.1) \,\mathrm{K}$ for $\mathrm{NdAl_2}$. These anomalies are due to the ferromagnetic-paramagnetic phase transition. The T_c value of $\mathrm{PrAl_2}$ compares well with the result of specific heat measurements ($T_c = 31.8 \,\mathrm{K}$) [16] and is also in fair agreement with data obtained from neutron ($T_c = 34 \,\mathrm{K}$) [17] and magnetization ($T_c \approx 34 \,\mathrm{K}$ [18]; $T_c = 32 \,\mathrm{K}$ [19]) measurements. For $\mathrm{NdAl_2}$ one deduces from specific heat data $T_c = 77.2 \,\mathrm{K}$ [16] and from magnetization data $T_c = 80 \,\mathrm{K}$ [18]. In view of the uncertainty of a Curie point determination in a neutron or magnetization experiment on materials like the REAl₂ 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 LaAl₂ [11] the latter contribution is

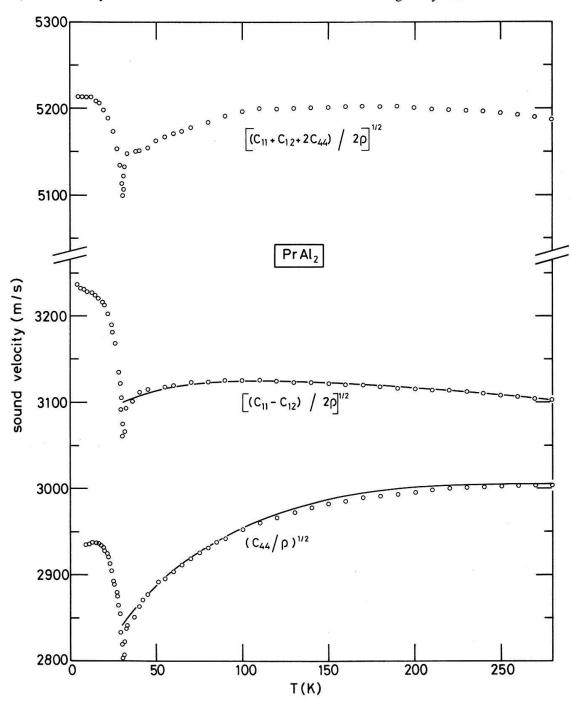


Figure 1 Experimental points and fitted curves of the sound velocities of $PrAl_2$ plotted as a function of temperature. The C_{44} mode is measured along [100] the other modes along [110].

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} .

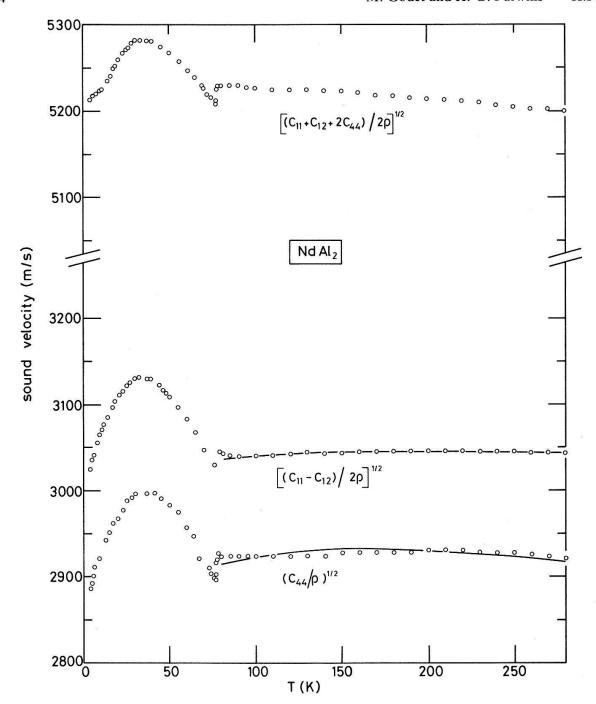


Figure 2 Experimental points and fitted curves of the sound velocities of NdAl₂ plotted as a function of temperature. The C_{44} mode is measured along [100] the other modes along [110].

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]

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

$$\hat{H}(C_{44}) = -g_3((C_{44}^0/N)(1 - \alpha_3 T))^{1/2} O_2^{-2} \cdot (2\varepsilon_{xy})$$
(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 PrAl₂

PrAl ₂					
T (°K)	$C_{11} \times (10^{11} \text{ N/m}^2)$	$C_{12} \times (10^{11} \text{ N/m}^2)$	$C_{44} \times (10^{11} \text{ N/m}^2)$		
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	0.451		
260	1.386	0.419	0.452		
270 270	1.384	0.419	0.452		
280	1.382		0.452		
200	1.302	0.418	0.432		

$$\chi_{\Gamma} = (1/Z) \left\{ \sum_{n} \exp(-E_{n}/KT) |V_{\Gamma nn}|^{2}/KT -2 \sum_{n>m} \left[\exp(-E_{m}/KT) - \exp(-E_{n}/KT) \right] (E_{m} - E_{n})^{-1} |V_{\Gamma n,m}|^{2} \right\}$$
(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 RE³⁺ 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 PrAl₂ and NdAl₂ [4]. We remark that χ_{Γ} is always positive.

To obtain the calculated sound velocities $v_{\rm FF} = (C_{\Gamma}/\rho)^{1/2}$ 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 'LaAl₂ like' temperature dependence are well described by the calculated curves above the Curie temperature.

Table 2 Elastic constants of NdAl₂

$NdAl_2$					
<i>T</i> (°K)	$C_{11} \times (10^{11} \text{ N/m}^2)$	$C_{12} \times (10^{11} \text{ N/m}^2)$	$C_{44} \times (10^{11} \text{ N/m}^2)$		
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 REAl₂ 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

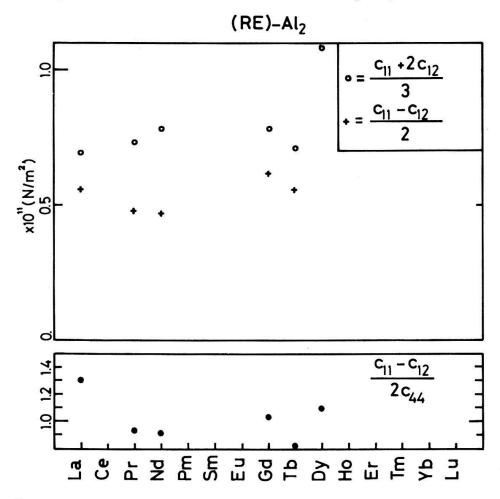


Figure 3 Bulk modulus $(C_{11} + 2C_{12})/3$, shear modulus $(C_{11} - C_{12})/2$ and anisotropy $(C_{11} - C_{12})/2C_{44}$ of some REAl₂ compounds at room temperature. The data for LaAl₂ and GdAl₂ are taken from Ref. [11], those of TbAl₂ and DyAl₂ from Ref. [12] and [13].

	$C_{11}-C_{12}$		C_{44}	
	$\alpha(10^{-5} {}^{\circ}\text{K})$	$g_{\Gamma}^{2}(10^{-3} {}^{\circ}\text{K})$	$\alpha(10^{-5} {}^{\circ}\text{K})$	$g_{\Gamma}^{2}(10^{-3} {}^{\circ}\text{K})$
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	4

Table 3 Parameters α and g_{Γ}^2 describing the temperature dependence of elastic constants of REAl₂ compounds according to equation (1). The values of LaAl₂ are taken from Ref. [11].

different from one REAl₂ 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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REFERENCES

- [1] J. H. WERNICK and S. GELLER, Trans. AIME 218, 866-8 (1960).
- [2] K. H. Buschow and J. H. N. Van Vucht, Z. Metallk. 57, 162-6 (1966).
- [3] R. J. SCHILTZ, Thesis, Iowa State Univ. Ames Iowa (1972).
- [4] H.-G. Purwins, E. Walker, B. Barbara, M. F. Rossignol, A. Furrer, J. Phys. C9, 1025–30 (1976).
- N. R. TAYLOR, Adv. Phys. 20, 551-660 (1971);
 W. E. WALLACE, Rare Earth Intermetallics, Academic Press, New York, London (1973).
- [6] W. BÜHRER, M. GODET, H.-G. PURWINS and E. WALKER, Solid State Commun. 13, 881-4 (1973).
- [7] J. G. HOUMANN, P. BAK, H.-G. PURWINS and E. WALKER, J. Phys. C7, 2691-6 (1974).
- [8] H.-G. Purwins, W. J. L. Buyers, T. Holden and E. C. Svensson, Proc. Int. Conf. MMM Philadelphia 1975, to be published.
- [9] H.-G. Purwins, E. Walker, B. Barbara, M. F. Rossignol and P. Bak, J. Phys. C7, 3573-82 (1974).
- [10] R. E. Hungsberg and K. A. Gschneider, J. Phys. Chem. Solids 33, 401–7 (1972).
- [11] R. J. Schiltz and J. F. Smith, J. Appl. Phys. 45, 4681–5 (1974).
- [12] M. GODET, Helvetica Physica Acta 46, 770-1 (1974).
- [13] G. Dublon, H. Klimker, U. Atzmony, M. P. Dariel, M. Rosen, A. Grayewski and D. Fekete, Phys. Lett. 53A, 23-4 (1975).
- [14] M. GODET, E. WALKER and H.-G. PURWINS, J. Less Common Metals 30, 301-2 (1973).
- [15] I. R. HARRIS, R. C. MANSEY and G. V. RAYNOR, J. Less Common Metals 9, 270-80 (1965).
- [16] C. DEENADAS, A. W. THOMPSON, R. S. CRAIG and W. E. WALLACE, J. Phys. Chem. Solids 32, 1853-66 (1971).
- [17] N. NERESON, C. OLSEN and G. ARNOLD, J. Appl. Phys. 39, 4605-9 (1968).
- [18] H. J. WILLIAMS, J. H. WERNICK, E. A. NESBITT and R. C. SHERWOOD, J. Phys. Soc. Japan 17, Suppl. B-I, 91–95 (1962).
- [19] B. BARBARA, M. F. ROSSIGNOL, H.-G. PURWINS and E. WALKER, Coll. Int. C.N.R.S. No. 242, 'Physique sous champs magnétiques intenses', 51–56.
- [20] E. R. CALLEN and H. B. CALLEN, Phys. Rev. 129, 578-93 (1963).
- [21] B. LÜTHI, M. E. MULLEN, K. ANDRES, E. BUCHER and J. P. MAITA, Phys. Rev. B8, 2639–48 (1973). B. LÜTHI, M. E. MULLEN and E. BUCHER, Phys. Rev. Lett. 31, 95–8 (1973).
- [22] K. W. H. STEVENS, Proc. Phys. Soc. A65, 209-15 (1952).
- [23] P. M. LEVY, J. Phys. C6, 3545-56 (1973).
- [24] K. R. LEA, M. J. M. LEASK and W. P. WOLF, J. Phys. Chem. Solids 23, 1381-405 (1962).