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DE HAAS - VAN ALPHEN STUDY OF THE HEXABORIDES OF La, Ce, Pr, AND Nd; FIRST RESULTS.

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The de Haas-van Alphen effect has been observed in the hexaborides of La, Ce, Pr and Nd with the direction of the field parallel to [100]. The frequencies for the heavier rare-earth compounds are close to those for LaB<sub>6</sub>; large values for the mass compared to the ones in LaB<sub>6</sub> and strong anisotropy of scattering has been observed.

### Introduction

The rare earth (RE)-hexaborides form an interesting system of compounds. They all crystallize in the cubic CaB<sub>6</sub> structure. The lattice parameter at roomtemperature varies smoothly over the RE-series, with a maximum deviation from the mean by 1.5% for Eu. They undergo no crystallographic phase transition at low temperatures. Thus each compound will have its specific properties which depend only on the interaction of the valence band electrons with the 4f-shells, as long as the valency remains three.

Important compounds at the moment are SmB<sub>6</sub> and CeB<sub>6</sub>. The former for its intermediate valency properties, where the 4f-electrons have a strong influence on the Fermi-surface<sup>1/</sup>. This compound is intensively studied a.o. by P. Wachter and coworkers. CeB<sub>6</sub> behaves like a concentrated Kondo-system, as is clear from a resistivity study<sup>2/</sup>. Its magnetic structure has been studied by neutron diffraction recently<sup>3/</sup>, revealing an antiferromagnetic ordering below T = 2K.

Of the other hexaborides we mention PrB<sub>6</sub> and NdB<sub>6</sub>. Both order antiferromagnetically at low temperature, T<sub>N</sub> = 8.6 and 7.5 K respectively; their magnetic structure has been determined by neutron diffraction<sup>4,5/</sup>. Their resistivity, measured at zero magnetic field as a function of temperature showed a large and for each compound specific contribution of both aspherical Coulomb scattering and scattering from the different ionic levels of the RE-atom<sup>6,7/</sup>.

A de Haas-van Alphen study for these compounds gives information on the Fermi-surfaces, which presumably resemble closely when the RE-valency is three. By measuring the effective masses and Dingle-temperatures detailed information can be obtained on the various interactions of the electrons in the valence band with the degrees of freedom in the 4f-level system and with the lattice vibrations. Data are known for LaB<sub>6</sub> only. Its Fermi-surface (FS) has been determined from the dHvA-effect and compares

well with bandstructure-calculations<sup>8,9/</sup>. Both theory and experiment agree on large X-centered ellipsoids, that form the main body of the FS and are connected by smaller necks. Some discrepancy remains, however; one of the orbits observed is difficult to explain from the calculations, since it would involve an improbable magnetic breakdown. The two calculations do agree on a large difference between the observed and the calculated bandmasses. When this is interpreted in terms of electron-phonon interaction, an unexpectedly large value for  $\lambda$  of about 0.5 is found.

Here we report the first results of a dHvA-study on RE-hexaborides with RE = La, Ce, Pr and Nd for the field directed along the [100]-crystal axis.

### Experiment

Single crystals, with dimensions of about 0.5x0.5x3 mm<sup>3</sup>, have been grown from the elements, dissolved in molten Al as a flux<sup>10/</sup>. The temperature at which the crystals form is much lower than their own melting temperature, about 1400°C vs 2300°C. The crystals are close to stoichiometry, as is evidenced by the very observation of the dHvA-effect. Yet the residual resistivity is rather high, of the order of several  $\mu\Omega\text{cm}$ . This is especially true for CeB<sub>6</sub>, where its resistivity is dominated by the Kondo-effect and decreases only slowly below T < 2K<sup>2/</sup>.

The oscillations in the magnetization have been measured on a system where a slow pulsed magnet (maximum field 40 Tesla, pulse-duration 20 to 50 msec) is employed<sup>11/</sup>. The system is very useful in the case of materials where strong scattering of the conduction electrons is present, as is best demonstrated by the observation of the oscillations from the neck-orbit in Au<sub>0.85</sub>Ag<sub>0.15</sub><sup>12/</sup>. For this orbit a value for the scattering parameter  $m^*T_D$  - which determines the amplitude of the dHvA-oscillations - is observed

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equal to 9. The high magnetic fields were of critical importance for  $\text{CeB}_6$ , where a large value for  $m^*T_D$  is observed. In this preliminary study we measured the dHvA-spectra along the [100] crystal-axis, using field values between 10 and 35 Tesla. In order to determine the effective mass of the electrons on the orbits observed, data have been taken at several temperatures between 4.2 and 1.3 K.  $\text{LaB}_6$  has been included in this study as a reference-material.

### Frequencies

Examples of the dHvA-spectra of the four materials are given in fig. 1. They are obtained by a fast fourier transform of the signal from the oscillatory magnetization on a scale pro-

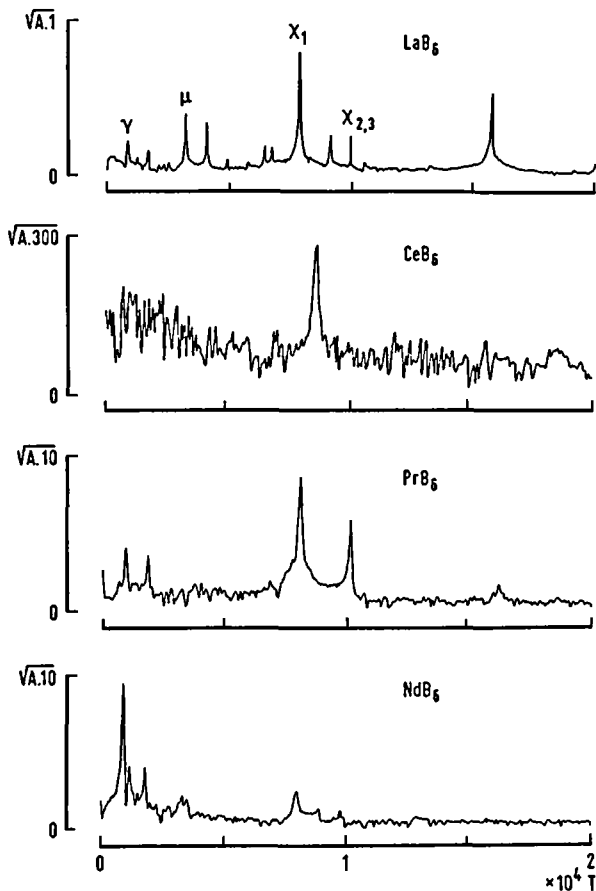


Fig. 1. Observed dHvA-spectra. The horizontal scale is in units of  $10^4$  Tesla. The vertical scale gives the average amplitude of the signal over the interval of 29-14.5 T for  $\text{LaB}_6$  and of 29-20 T for the heavier RE- $\text{B}_6$ . The amplitudes are multiplied by the relative gain of the signal amplifiers as indicated, and displayed after the square root has been taken in order to enhance low amplitude features.

portional to  $1/B$ , where  $B$  is the magnetic field during the pulse and is measured with an accuracy of better than  $10^{-5}$ . Those frequencies that are fundamental, i.e. that cannot be assigned as harmonic, sum or difference of the others in the spectrum are listed in table 1.

For  $\text{LaB}_6$  a strong signal is observed as was also found by Arko et al <sup>8/</sup>, rich in combination frequencies and harmonics, stemming from magnetic interaction. Indicated in fig. 1 are the fundamental frequencies, where we use the identification and the notation of Arko et al. The total signal is dominated by the frequencies labeled  $X_1$  and  $X_{2,3}$ , which both originate from belly orbits on the X-centered ellipsoids.

For the three other compounds a frequency is observed close to  $X_1$ . They deviate from  $X_1$  by +2.5% for  $\text{PrB}_6$  and by +1% for  $\text{NdB}_6$ . However, for  $\text{CeB}_6$  a difference of +10% is observed. When the  $\text{CeB}_6$  crystal is rotated in a (110)-plane this frequency can be detected up to at least 35 degrees from the [100]-axis; over this angular range the frequency and amplitude are constant to within an accuracy of 2% and 10% respectively.

Only for  $\text{PrB}_6$  a frequency comparable to  $X_{2,3}$  is observed with ample signal to noise ratio. In the case of  $\text{LaB}_6$  Arko et al had to invoke magnetic breakdown across the necks interconnecting the ellipsoids to explain the observation of  $X_{2,3}$  for the field along the [100]-axis. The detection of a similar orbit in  $\text{PrB}_6$ , that is known from resistivity and thermal expansion <sup>4/</sup> to exhibit a small anomaly at  $T=4.2\text{K}$ , suggests that here alternative explanations have to be considered too.

The necks themselves are associated with orbits labelled  $\gamma$  and  $\mu$ . For  $\text{PrB}_6$  and  $\text{NdB}_6$  similar frequencies are observed (see table 1). One frequency is found for both materials that has no equivalent in  $\text{LaB}_6$ .

Without pretending that one already knows the FS for the heavier RE- $\text{B}_6$  completely, we will follow the notation of Arko et al for their frequencies, with regard to the strong resemblance between the spectra.

### Masses and amplitudes

From the temperature and the field dependence of the amplitudes for the various frequencies one determines the effective cyclotron mass  $m^*$  and the scattering-parameter  $m^*T_D$ . The values for the effective masses are given in table 2.

In the case of  $\text{CeB}_6$  the signal could only be detected with sufficient signal to noise ratio at temperatures lower than 1.8 K. This is reflected by the value for the effective mass, being the highest observed among the compounds studied. For the crystal used in this experiment we also observed a high value of the scattering parameter,  $m^*T_D = 8 \pm 2$ .

For  $\text{PrB}_6$  and  $\text{NdB}_6$  the cyclotron mass of some orbits is determined from a comparison of the amplitudes in the spectra measured at temperatures between 1.3 and 4.2 K. Again, compared to  $\text{LaB}_6$  relatively high values are found for most orbits, their masses being about a factor 2 larger.

In the spectrum for  $\text{PrB}_6$  in fig. 1 one observes for  $X_1$  a larger amplitude than for  $\gamma$ ; for  $\text{NdB}_6$  the reverse is true. The crystals employed in our experiment have small values for the scattering parameter for both orbits,  $m^*T_D < 2$ . For the orbits  $X_1$  we observed  $m^*T_D$  equal to  $4 \pm 1$  and  $7 \pm 1$  for  $\text{PrB}_6$  and  $\text{NdB}_6$  respectively. Thus, one infers that in addition to possible

Table 1

Observed dHvA-frequencies for B//[100] in units of  $10^5$  T. The assignment given is based on the similarity between the spectra for LaB<sub>6</sub> and the heavier RE-B<sub>6</sub>. Nomenclature follows Arko et al<sup>8/</sup>. The lattice constant a in Å is given for comparison.

	LaB <sub>6</sub>	CeB <sub>6</sub>	PrB <sub>6</sub>	NdB <sub>6</sub>
	-	-	.58	-
γ	.83	-	.94	.92
	-	-	-	1.21
μ	3.24	-	3.23	3.39
X <sub>1</sub>	7.89	8.66	8.09	7.98
X <sub>2,3</sub>	10.03	-	10.14	-
a	4.156	4.139	4.121	4.128

Table 2  
Effective masses for B//[100].

	LaB <sub>6</sub>	CeB <sub>6</sub>	PrB <sub>6</sub>	NdB <sub>6</sub>
	ref.8			
γ	-	-	1.1±0.2	1.0±0.2
μ	-	-	1.6±0.2	-
X <sub>1</sub>	0.6±0.1	0.61	6±1	0.6±0.2
X <sub>2,3</sub>	0.7±0.1	0.64	2.1±0.2	-

geometrical factors of the FS the main cause in this differing behaviour stems from scattering, which is anisotropic over the FS and which is largely different for both materials.

Discussion

The data presented form the first direct measurements on the FS of some heavier RE-B<sub>6</sub>. A frequency X<sub>1</sub> of about  $8 \times 10^5$ T has been observed in all compounds. In LaB<sub>6</sub> this frequency belongs to a belly orbit on the major part of the Fermi-surface, corresponding to about one electron per formula-unit. At low temperatures all heavier compounds studied order antiferromagnetically in zero field, with up to 32 formula units per magnetic unit cell<sup>6,7/</sup>. We did not in-

vestigate whether this type of ordering prevails in the fields employed in our experiments. Most frequencies observed are close to the ones for LaB<sub>6</sub>, and fit into its nonmagnetic unit cell in reciprocal space. From this we conclude that the 4f-electrons have only minor influence on the geometry of the Fermi-surface.

However, the dispersion of the bands near the Fermi-energy is strongly altered, as is indicated by the high value of the masses. In the case of LaB<sub>6</sub> the enhancement of the electron-mass when compared to the bandcalculations, has been interpreted as electron-phonon interaction<sup>8/</sup>. In the heavier compounds the extra enhancement results from interactions between the sd-conduction- and the 4f-electrons, as there are magnons, spin-fluctuations and Kondo-effect. The trend in the mass of the orbit X<sub>1</sub> from Ce to Nd indicates the decrease in the interactions with increasing binding-energy of the 4f-electrons. In CeB<sub>6</sub>, in view of the Kondo-behavior, one has to allow for the possibility that the large value of the mass is partially caused by an extra temperature dependence of e.g. T<sub>D</sub>. This, and the other points of interest mentioned earlier, will be subject of further research.

Since the crystals are grown in an Al-flux one has to be cautious in assigning the observed dHvA-signals, in particular for CeB<sub>6</sub> where the only signal observed is very weak. The hexaborides and Al both have a cubic crystal-structure, with lattice-constants at room temperature that differ by 2%. Inclusions of Al in the hexaborides may tend to align their crystal-axes with those of the boride-matrix. A few Al-rich inclusions with cross-sections of several microns have been observed by electron-beam X-ray fluorescence in a CeB<sub>6</sub> crystal taken from the same batch. The frequency X<sub>1</sub> in CeB<sub>6</sub> does coincide with the one of the orbit ξ in Al<sup>14/</sup> to within the experimental accuracy. Based on the following arguments we believe the signal intrinsically due to CeB<sub>6</sub>. Firstly, the observed temperature dependence corresponds to a value for m\* of 6±1; the value for the Al ξ-orbit is 1.68, which is well outside the error. Secondly, as said before, the amplitude and the frequency hardly change when the crystal is rotated off the [100]-axis. In Al the ξ-orbit is situated on a thin ring around the X-point in the third zone; the corresponding signal can only be detected within 2.5 degree from [100]<sup>14/</sup>. Lastly, Al contains many other signals, which have lower frequencies and high amplitudes; those have not been observed.

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## References

1. see eg. I. Moerke, V. Dvorak and P. Wachter, Sol. St. Comm. 40, 331 (1981); I. Frankowski and P. Wachter, Sol. St Comm. 41, 577 (1982)
2. see eg. A Takase, K. Kojima, T. Komatsubara and T. Kasuya, Sol. St. Comm. 36, 461 (1980); Y. Aoki and T. Kasuya, Sol. St. Comm., 36, 317 (1980).
3. S. Horn, F. Steglich, M. Loewenhaupt, H. Scheurer, W. Felsch and K. Winzer, Z. Phys. B, 42, 125 (1981)
4. C.M. McCarthy, C.W. Tompson, R.J. Graves, H.W White, Z. Fisk, H.R. Ott, Sol. St. Comm., 36, 861 (1980)
5. C.M. McCarthy and C.W. Tompson, J. Phys. Chem. Sol., 41, 1319 (1980)
6. Z. Fisk and D.C. Johnston, Sol. St. Comm., 22, 359 (1977)
7. Z. Fisk, Sol. St. Comm., 18, 221 (1976)
8. A.J. Arko, G. Crabtree, D. Karim, F.M. Mueller, L.R. Windmiller, J.B. Ketterson and Z. Fisk, Phys. Rev. B 13, 5240 (1976).
9. A. Hasegawa and A. Yanase, J. Phys. F: Metal Phys., 7, 1245 (1977)
10. see eg. Z. Fisk, A.S. Cooper, P.H. Schmidt and R.N. Castellano, Mat. Res. Bull., 7, 285 (1972)
11. A.P.J. van Deursen and A.R. de Vroomen, Internal Report, Fysisch laboratorium, Katholieke Universiteit, Toernooiveld 6525ED, The Netherlands.
12. A.P.J. van Deursen, M.A.C. Devillers and A.R. de Vroomen, Physica 108B, 815 (1981)
13. A.V. Gold, Solid State Physics, The Simon Fraser University Lectures I: Electrons in Metals. Ed. J.F. Cochran and R.R. Hearing (Gordon and Breach, New York 1968).
14. J.R. Anderson and S.S. Lane, Phys. Rev. B, 2, 298 (1970)