Atomic Ordering in Superconducting Nb_3Al

K. Hechler and P. Volk

Institut für Angewandte Physik, Universität Gießen

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Samples of Nb_3Al produced by a melting process in an arc furnace show a pronounced increase in T_c by annealing them at 750 °C for 48 hours. This behaviour is accompanied by a small decrease in the lattice constant and an increase in the long-range order parameter. These two effects are thought to be responsible for the increase in T_c.

1. Introduction

Ever since the observation made by Kunz and Saur [1, 2] that the transition temperature T_c of Nb_3Al can be raised by about 1 K by suitable annealing of the as-cast samples, a number of further investigations [3–9] about this problem have been published. Some of these papers [7–9] mention a change in the atomic ordering as a possible cause for the improved T_c. This has been measured for other A15-compounds but not for Nb_3Al.

The present investigation has aimed at preparing very pure, stoichiometric, single phase samples of Nb_3Al and at finding a relation between T_c and the long-range order parameter S in these samples.

2. Experimental Procedures

The method of preparation of Nb_3Al by melting suitable quantities of Nb- and Al-powder in an arc furnace is well known [10]. With the purest niobium produced by CIBA AG and aluminium of 99.99% purity (obtained from Aluminiumhütte Rheinfelden GmbH) powder prisms ($6 \times 6 \times 42$) mm^3 were pressed. These prisms were outgassed at 600 °C for 10 hours in a vacuum better than 10^{-6} Torr. Immediately after cooling to room temperature the samples were placed in an arc furnace and this was evacuated and flushed several times with argon of a purity of 99.998%. Melting was done at a pressure of 350 Torr of argon while the current flowing between a tungsten electrode and a water-cooled copper crucible containing the sample was 220 A. Melting was done twice, turning over the samples in between. By standardizing the melting process with a stop watch it is possible to produce samples with nearly stoichiometric composition. The losses of aluminium by evaporation during the melting process can be accounted for in advance.

For the following investigations well defined plane boundaries of the samples were needed. These were obtained by grinding the samples in three mutually perpendicular planes, which were finished off by polishing. These planes were used to measure hardness, to obtain the positions and the intensities of X-ray reflections in an X-ray-goniometer and to investigate the material microscopically. T_c was measured in liquid hydrogen, which served as a thermometer and as a coolant as well. Most samples were measured by the standard 4 probe resistance method; but some of the best material was also measured by an inductance method, in order to check the homogeneity in the whole volume of the sample. Annealing of the samples was done at 750 °C for 48 hours in a vacuum better than 10^{-6} Torr. This condition was found to produce the largest shift in T_c.

3. Results

a) Transition Temperatures

The measured T_c-values of the Nb_3Al samples are given in Table 1. T_c is indicated as that value of T for which $R(T)/R(T_{ons}) = 0.5$. ΔT_c indicates the width of the transition to superconductivity. The change in T_c by annealing is shown in column 6. The increase of ΔT_c recorded by the inductive measurement of T_c always occurs in the last part of the transition curve as a low, long "foot". According to all investigations, samples A, B and C are single phase, while D, E and F still contain a certain amount of Nb_2Al or α-Nb, or both.

Table 1: Superconductive Properties of Nb_3Al.

	Resistive Measurements					Inductive Measurements	
1	2	3	4	5	6	7	8
Sample	T_c in K as cast	ΔT_c in K as cast	T_c in K annealed	ΔT_c in K annealed	Change of T_c in K by annealing	T_c in K annealed	ΔT_c in K annealed
A	17.40	0.11	18.55	0.10	1.15	18.11	1.50
B	17.48	0.11	18.50	0.07	1.12	18.49	1.65
C	17.42	0.12	18.52	0.07	1.10	18.39	1.25
D	17.42	0.02	18.56	0.02	1.14	18.49	1.40
E	17.50	0.10	18.64	0.08	1.14	18.48	2.00
F	17.52	0.08	18.63	0.07	1.11	18.50	0.90

Table 2. Lattice Parameter of Samples of Nb_3Sn Investigated.

Sample	A I	A II	A III	B I	B II	B III	C I	C II	C III
Lattice Parameter in Å as cast	5.1936	—	—	5.1914	5.1852	5.1870	5.1859	5.1863	5.1903
Lattice Parameter in Å as cast	5.1884	5.1852	5.1862	5.1862	5.1835	5.1864	5.1876	5.1834	5.1870
Change of Lattice Parameter in Å	-0.0052	—	—	-0.0052	-0.0017	-0.006	+0.0017	-0.0029	-0.0033

b) Hardness and Microscopic Investigation

Vickers-hardness of the samples was measured with the diamond pyramid loaded by 500 p. This produced impressions whose diagonals are about 30 μm in length. The measuring of hardness in three mutually perpendicular planes showed that the samples are anisotropic. This was later verified by X-ray investigations as well. As an average of hardness obtained from 6 measurements on each of the three planes a value of $HV_{500p} = 886\,kp/mm^2$ was found. Individual values as much as $40\,kp/mm^2$ lower and up to $30\,kp/mm^2$ higher do occur. By investigating the polished surfaces of the samples microscopically it is possible to check for different phases. The method of differential interference contrast due to a proposal by Nomarski [11] and not an etching technique was used. Different phases produce different interference colours. In the best samples only very few and small spherelike inclusions of a different non-identified phase could be observed.

c) X-Ray Investigations

The plane, polished surfaces of the samples were probed by X-rays in a goniometer in order to obtain the intensity and the angular position of the X-ray reflections. This method was chosen because the usual powder method always leads to undesirable and uncontrolable changes of the intensity of the X-ray reflections due to preferred orientation of the crystallites in the pressed powder. The X-ray measurements showed that the samples produced different intensity patterns in the three mutually perpendicular planes and that here too some preferred orientation exists. But using the polished surfaces of the samples makes sure that the preferred orientation is the same before and after annealing. Therefore, the observed changes in the intensity of the X-ray reflections due to annealing are caused by atomic ordering processes only. These were to be studied. From the recorded reflections the lattice constant and the area under each reflection were determined. With a method described by van Reuth and Waterstrat [12] the atomic ordering parameter S was calculated. The results of the X-ray investigations are given in Tables 2 and 3. In these tables the Roman numerals refer to the different planes; III means the cross section; II refers to a vertical plane at right angles to the cross section and I is a horizontal plane perpendicular to the other two. From these tables it can be seen that by annealing the samples of Nb_3Al the order parameter always surpasses the value in the material as-cast, and the lattice constant, with one exception, decreases.

Table 3. Order Parameter of Samples of Nb_3Al Investigated.

Sample	A I	A II	A III	B I	B II	B III	C I	C II	C III
Order Parameter as cast	0.77	—	—	0.87	0.87	—	—	0.82	—
Order Parameter annealed	0.83	0.87	0.93	0.88	0.91	0.88	0.96	0.88	—
Change of the Order Parameter	+0.06	—	—	+0.01	+0.04	—	—	+0.06	—

4. Conclusion

In a paper by Leger [13] a figure is given in which T_c is plotted vs. the lattice constant for various A15-compounds. The niobium based compounds Nb_3Ga, Nb_3Al and Nb_3In all have the same ratio $e/a = 4.5$ electrons per atom. By grouping the various A15-compounds with this parameter e/a, Leger found the three mentioned compounds to produce a straight line in the figure. Its slope is approximately -88 K/Å. The increase in T_c of Nb_3Al by annealing can be explained by the decrease in the lattice constant. But with the given slope of the straight line only a maximum change of T_c of 47% from the observed values can be accounted for. So the result leads one to the conclusion that the change in the lattice constant combined with the observed increase in atomic ordering is responsible for the increase in T_c by annealing. It would be interesting to measure I_c and H_{c_2} and to find out, how these values are affected by the changes in lattice constant and order parameter.

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