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## Investigation into the electrical resistivity of Ni–Al alloys

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**Abstract.** The electrical resistivity in the liquid and solid state for Ni-rich Ni–Al alloys was investigated. It was discovered that the character of the resistivity polytherms depends on the phase constitution of alloys. The polytherms have a hysteresis in the liquid state after heating to a definite temperature. This temperature can be called the critical temperature  $t_c$ . The reason for hysteresis is the destruction of clusters, the structure of which is inherited from the solid state. The resistivity isotherms have an extreme character. The magnitudes of  $\rho$  for the alloys which form intermetallics depend strongly on the Al content.

### 1. Introduction

The alloys of the Ni-rich Ni–Al system are attractive as structural materials for high-temperature use. These alloys are the basis of modern superalloys and advanced nickel aluminides. The practical value of Ni–Al alloys defines the main directions of the scientific investigations which include the following: study of the temperature and concentration limits of structure stability, investigation into the influence of different mixtures on the structure and properties of Ni<sub>3</sub>Al, and study of the nature of the order–disorder phase transition in Ni<sub>3</sub>Al.

Knowledge of the exact temperature and concentration boundaries of  $\gamma'$ - and  $\gamma$ -phases is very important because this defines the working limits of Ni–Al alloys in industry. According to the phase diagram given by Schramm [1], the peritectic and eutectic reactions in Ni<sub>3</sub>Al are as follows:



Confirmation that these reactions could take place was provided by Bremer *et al* [2], by Hilpert *et al* [3], and by Udovsky *et al* [4], although the temperatures of these reactions differed from those obtained by Schramm. According to the data of Hilpert *et al* and Udovsky *et al* the peritectic and eutectic reactions occur at 1645 K and 1642 K, respectively. Figure 1 shows the part of the phase diagram of the Ni–Al system obtained by Hilpert *et al* [3]. Some scientific investigations reveal that the Ni–Al system has such phases as Ni<sub>2</sub>Al

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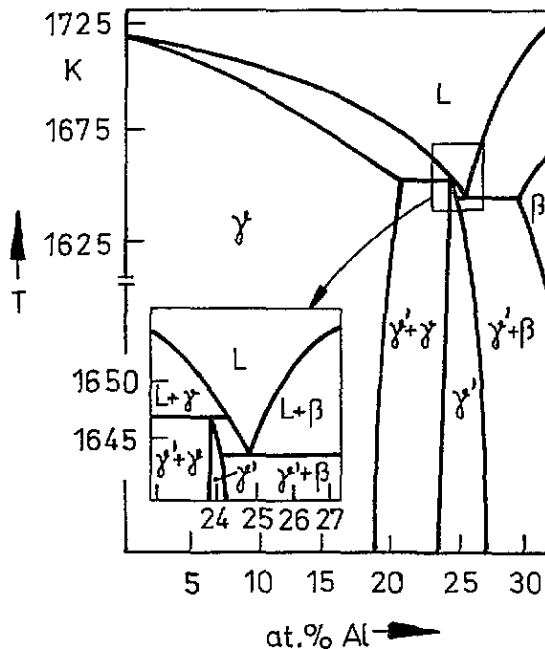


Figure 1. The phase diagram for the Ni-rich Ni-Al system.

and  $\text{Ni}_3\text{Al}_5$  [5, 6]. Archangelskaja *et al* [6] discovered that there were at least two different types of  $\text{Ni}_2\text{Al}$ . Unfortunately, these phases are not always displayed in the phase diagrams.

No common ideas about the magnitudes of temperature boundaries of  $\text{Ni}_3\text{Al}$  stability have been determined as yet. A number of scientists assume that  $\text{Ni}_3\text{Al}$  is ordered up to the melting point and is frozen directly into the ordered form [7, 8]. Other researchers note that the order-disorder process takes place before the melting point [9–11]. According to Ramesh *et al* [9], the maximum stability of  $\text{Ni}_3\text{Al}$  was observed only up to 873 K and then the order parameter decrease. It was also shown that the electrical resistivity falls beyond 1473 K for Al-rich (25.2 and 26.8 at.% Al)  $\text{Ni}_3\text{Al}$  alloys [10]. This has been attributed to sublattice disordering. In addition, the results of Stoeckinger and Neumann [11] on Ni–23 at.% Al, which indicated an upswing in the thermal expansion coefficient  $\alpha$  at temperatures above 1073 K, were also attributed to the onset of sublattice disordering.

In this paper the experimental results of temperature and concentration dependences of electrical resistivity for Ni–Al alloys are reported. The main purposes of this study are collection of new experimental data about the electrical resistivity values of Ni–Al alloys, investigation of peculiarities of the order-disorder phase transition in  $\text{Ni}_3\text{Al}$ , and research into the influence of both the  $\gamma'$ -phase composition and the melt heating temperature on the character of electrical resistivity polytherms and isotherms.

## 2. Experimental procedures

The Ni–Al alloys were prepared from the high-purity (99.999%) metallic element Al and high-purity (99.98%) Ni that had been vacuum degassed. The fusion of alloys was realized in a vacuum induction furnace at 1773 K with an argon atmosphere. Then vacuum arc melting was carried out. Alloys with the following Al contents were obtained: 5, 10, 15,

22.5, 24, 25, 26, 27 and 30 at.%. The atomic absorption analysis of the Al content confirmed the aforementioned Al contents with a real deviation of not more than +0.016 wt%. The structures of the intermetallic alloys were investigated using x-ray spectrum analysis and metallographic analysis. According to the results of these investigations it was confirmed that the samples were homogeneous on the whole. The oxygen and nitrogen contents in the samples were measured using Monomat-350 and Dinimat-450 gas analysers from Stroehlein. The average contents were 0.003 wt% O and 0.001 wt% N.

The electrical resistivity  $\rho$  of samples was measured using the contactless technique of a rotary magnetic field at 1300–2000 K [12]. The experiments were carried out in BeO crucibles in a helium atmosphere after initially pumping out the working volume of the experimental plant up to 0.01–0.001 Pa. The electrical resistivity values were obtained with a degree of accuracy of  $\pm 3\%$ .

### 3. Experimental results and discussion

#### 3.1. The temperature dependences of the electrical resistivities of Ni-Al alloys

The temperature dependences of the electrical resistivities for Ni-Al system alloys are shown in figures 2 and 3. Analysis of these results makes it possible to distinguish between three groups of alloys which have the characteristic peculiarities of temperature dependences of the electrical resistivity.

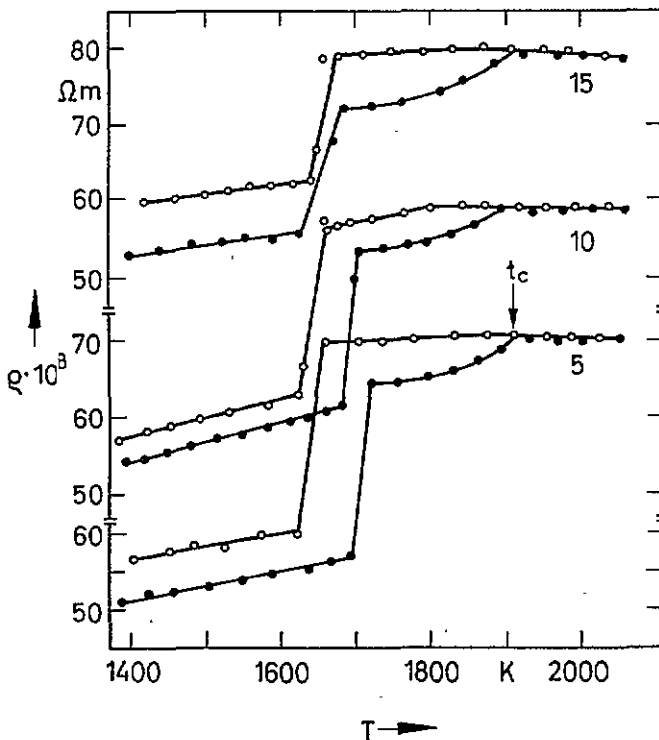


Figure 2. The resistivity temperature dependences for Ni-Al solid solution alloys: ●, heating; ○, cooling. The numbers under the curves are the aluminium contents.

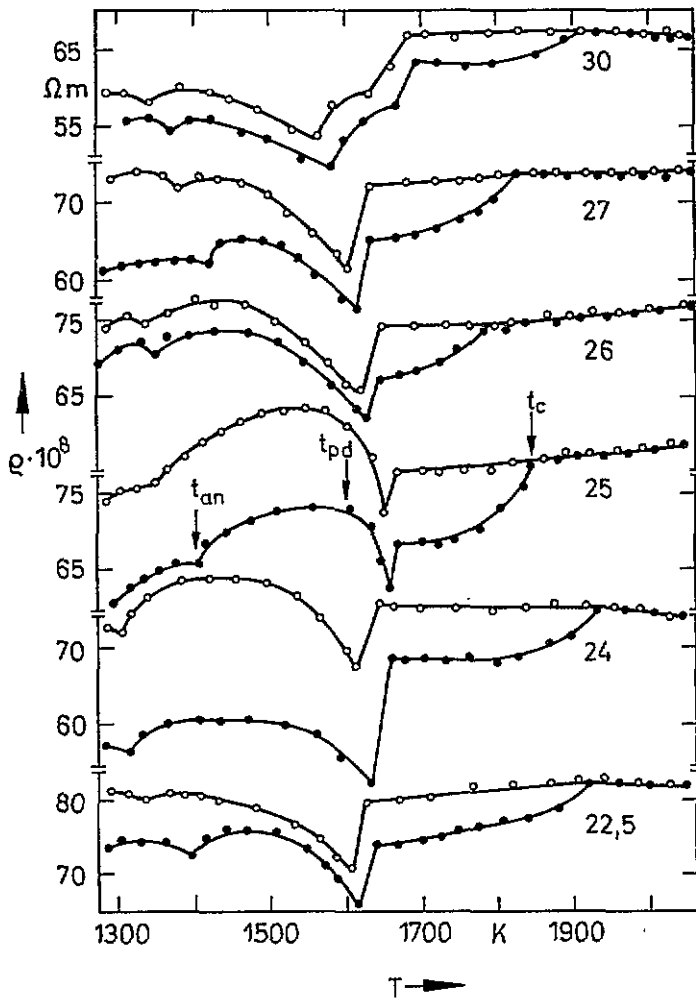


Figure 3. The resistivity temperature dependences for Ni-Al intermetallic alloys: ●, heating; ○, cooling. The numbers under the curves are the aluminium contents.

The alloys with 5, 10 and 15 at.% Al belong to the first group. Their common features are as follows: during heating in the solid state the absolute magnitudes of the electrical resistivity of the samples increase up to the solidus; then, after melting,  $\rho$  linearly increases up to 1823–1848 K; from these temperatures up to 1873 K an intensive increase in electrical resistivity is observed; further heating hardly changes the resistivity since the coefficient  $\delta\rho/\delta t$  is near zero; the cooling dependences of  $\rho$  are linear in the whole temperature interval of investigation; beginning with 1953 K, hysteresis is observed, i.e. a convergence of cooling and heating polytherms. The hysteresis is retained in the solid state too. The hysteresis temperature can be called the critical temperature  $t_c$ .

The second group includes alloys with 22.5, 24, 25, 26 and 27 at.% Al. These alloys are the  $Ni_3Al$  intermetallic compounds. The  $\rho = f(t)$  dependences have a more complicated character. In particular, on heating,  $\rho$  changes non-linearly up to a definite temperature  $t_{an}$ , where a break in the temperature dependences of  $\rho$  are observed. On heating above  $t_{an}$  the

absolute magnitudes of  $\rho$  increase again, but then a decrease in the electrical resistivity up to the melting point starts. The temperature at which this decrease begins is fixed with a deviation of  $\pm 10$  K and is denoted as  $t_{pd}$ .

The character of the temperature dependences in the liquid state for alloys of the second group is the same as for the first group of alloys. During cooling in the solid state the character of the temperature dependences of  $\rho$  for intermetallic alloys is the same as during heating. The  $\rho$  hysteresis is retained, but  $t_{an}$  decreases by 50–60 K. If the samples are heated above the melting point (but at a lower  $t_{pd}$ ), hysteresis during further cooling appears in the solid state, but the magnitude of convergence between cooling and heating dependences of  $\rho$  is smaller and  $t_{an}$  for cooling and for heating coincide (figure 4).

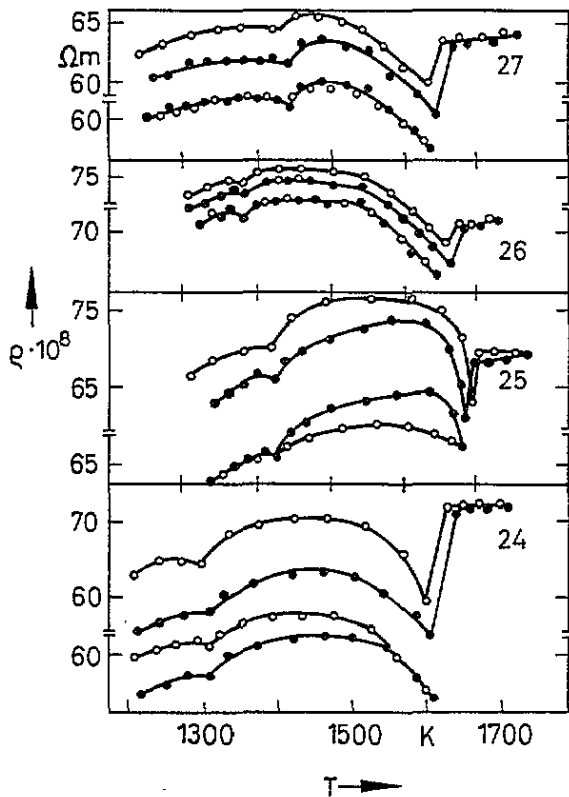


Figure 4. The resistivity temperature dependences for  $Ni_3Al$  alloys: ●, heating; ○, cooling. The numbers under the curves are the aluminium contents.

In this investigation the electrical resistivity below 1300 K was not studied, but additional investigations of resistivity by means of the contact technique on cooling from 1500 to 290 K were carried out. The electrical resistivities for Ni-25 at.% Al and Ni-24 at.% Al alloys without and with heating up to  $t_c$  were measured. It was discovered that the samples which were heated to  $t_c$  have higher  $\rho$  than the samples without heating. The difference between the  $\rho$  for these specimens decreases during the cooling process and below 850 K this difference is negligible. Thus, it seems that hysteresis does not occur below 850 K.

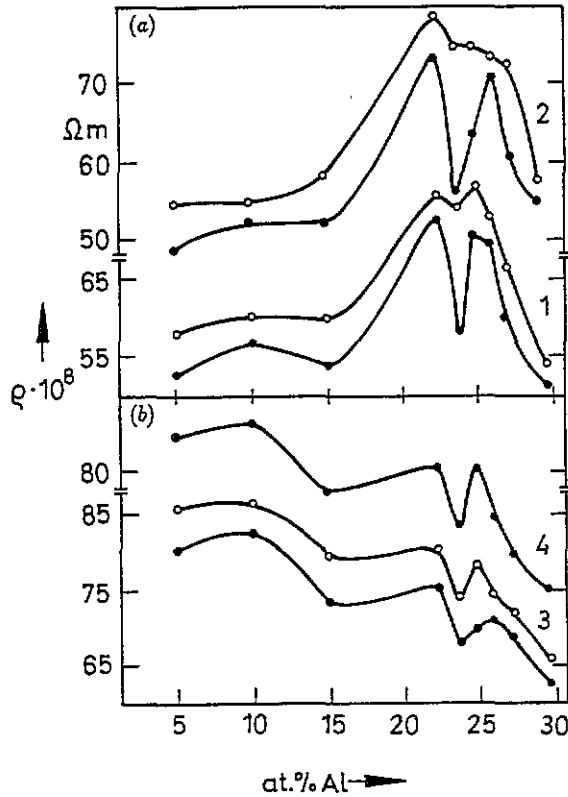


Figure 5. The resistivity isotherms for Ni-Al alloys (a) in the solid state at 1523 K (curves 1) and at 1323 K (curves 2) and (b) in the liquid state at 1773 K (curves 3) and at 2073 K (curve 4).

In previous scientific investigations of  $Ni_3Al$  alloys this complicated behaviour of the temperature dependences of resistivity in the solid state was observed, but the temperature dependences in the liquid state were linear [13, 14].

One can conclude that the type of temperature dependence of resistivity depends on the phase composition of alloys. For alloys with 5, 10 and 15 at.% Al which belong to heterogeneous substitutional solutions the electrical resistivity in the solid state is defined on the whole by the electron dispersion on the nodes of the crystal lattice. Therefore with temperature increase the electrical resistivity changes linearly.

For intermetallic compounds the nature of the process which takes place at  $t_{an}$  is not clear at present. The semiconductive type of electrical resistivity behaviour above  $t_{pd}$  is connected with the start of alloy disordering, which takes place up to the melting point. This disordering is accompanied by a decrease in covalent bond sharing in the  $Ni_3Al$  and an increase in the quantity of free conduction electrons, which leads finally to a decrease in resistivity.

The structure of all alloys in the solid state is different only after heating in the liquid state. However, for Ni-24 at.% Al and Ni-25 at.% Al alloys, even heating above  $t_{pd}$  in the solid state (but without melting) leads to hysteresis of the electrical resistivity. Evidently, for some intermetallic compounds, even such heating leads to the redistribution of atoms in the nodes of the crystal lattice. On further cooling, the ordered structure is slightly different

and the hysteresis of the resistivity testifies to this fact. For Ni-26 at.% Al to Ni-27 at.% Al alloys, heating in the solid state without their melting does not lead to hysteresis.

The Ni-30 at.% Al alloy constitutes the third group. Strictly speaking, such isolation is slightly artificial. The character of the temperature dependence for this alloy is the same as that of the second-group polytherms. The distinction is the increase in  $\rho$  in the 1593–1673 K temperature interval. This increase is comparable with the resistivity jump during melting. Note that the 1593–1673 K temperature interval agrees with the fields of  $\beta$ -phase existence (figure 1) and, hence, the increase in  $\rho$  is connected with the decrease in the quantity of free conduction electrons on intermetallic compound formation from  $\gamma' + \beta$  eutectic [15].

### 3.2. The electrical resistivity isotherms for Ni-Al alloys

The resistivity isotherms for alloys of the Ni-Al system which were drawn up from experimental data of the temperature dependences of resistivity are represented in figure 5.

Note that their character is complicated. In the solid state for alloys which form substitutional solutions,  $\rho$  increases with increasing Al content. This behaviour of the  $\rho$  isotherms is explained by the fact that these alloys belong to a solid solution; the more the alloy composition deviates from the pure element, the larger is its electrical resistivity owing to both distortion of the crystal lattice of the solvent and chemical interaction of components [15].

The isotherms of the intermetallic compounds have extreme character. In general, the alloys of this group possess much higher resistivities than solid solution alloys do. Among intermetallic alloys the Ni-24 at.% Al and Ni-27 at.% Al alloys have extremely low resistivities. The magnitude of resistivity for each intermetallic compound depends on the predominance of one of two competitive mechanisms of atom interaction. The first is intensification of chemical interaction of components during ordering and, consequently, a decrease in the quantity of free conduction electrons. This mechanism leads to an increase in electrical resistivity. The other is a higher degree of electrical field symmetry in the ion framework of the ordered crystal lattice. This mechanism results in a decrease in resistivity.

Figure 5(b) shows isotherms for Ni-Al alloys in the liquid state. A correlation between the types of isotherm in the liquid and solid state is observed.

In order to understand completely the nature of the processes which take place in the liquid state, the time dependences of resistivity at different temperatures were obtained. The sample used was Ni-25 at.% Al alloy. Summarizing the results of these experiments we can make the following observations [12].

(i) An exposure to a temperature lower than the temperature range of intensive increase in resistivity (i.e. up to 1780 K) does not change the resistivity.

(ii) An exposure to a temperature between 1780 K and  $t_c$  leads to an increase in  $\rho$ . The higher the temperature, the shorter is the time  $\tau$  for  $\rho$  to increase to maximal values. For instance, at 1780 K,  $\tau$  is 40 min and, at 1810 K,  $\tau$  is 15 min. The maximal  $\rho$ -values correspond to the magnitudes on the cooling curves.

(iii) Estimation of the activation energy  $E_a$  of the total process using

$$E = R(\ln v_1 - \ln v_2)(T_2^{-1} - T_1^{-1})$$

gives a value of 250+50 kJ mol<sup>-1</sup>. Note that the destruction energies for NiAl (200 kJ mol<sup>-1</sup>), NiO (344 kJ mol<sup>-1</sup>), and Ni<sub>3</sub>Al (154 kJ mol<sup>-1</sup>) are close to the value obtained. For comparison, the diffusion energies of different components in the Ni-based melts are 40–100 kJ mol<sup>-1</sup> [16, 17].



#### 4. The microheterogeneous character of the structure of the alloys in the liquid state

The data obtained were discussed according to the microheterogeneous structure model of metallic melts [18] with regard to some aspects given in [19].

A simplified description of the complicated spatial and chemical short-range order is given assuming the following ideas. The short-range-ordered volume elements are described as associates having a well defined stoichiometric composition, while the rest of the atoms are considered to be randomly distributed. The associates are in a steady dynamic equilibrium with the non-associate atoms. The volume fractions of the short-range-ordered regions (clusters) are determined at a given temperature and concentration from energy conditions. The mean lifetime of those clusters described as associates should be, however, longer than the time necessary for one diffusion step ( $10^{-13}$  s). In most cases, the composition of the associates also conforms to the stoichiometry of intermetallic phases and compounds in the solid state. It is necessary to assume that a number of impurities, especially oxygen, are included into the short-range-ordered regions and strengthen greatly the interatomic bonds.

The essential cause of the existence of volume elements with prevailing short-range order can be attributed to the non-metallic bonding character. According to the indirect estimation of Baum [18], the sizes of these clusters are 10–100 nm.

The fact that the major part of clusters have the stoichiometry of intermetallic phases can be proved by diffraction investigations [20, 21]. Romanova [21] revealed that intermetallic compounds near the liquidus have microgroups with the short-order structure of the initial crystal lattice. According to Matveeva and Kozlov [20],  $\text{Ni}_3\text{Al}$  after disordering and also melting has some fields with a high degree of order, which are similar to solid  $\text{Ni}_3\text{Al}$ . Thus, the structure of liquid intermetallic  $\text{Ni}_3\text{Al}$  near the liquidus has ordered clusters. It is also known that Ni–Al alloys which form substitutional solutions belong to heterogeneous substitutional solutions and have a local ordered distribution of atoms in the crystal lattice. For these alloys the cluster structure in the liquid state is inherited from short-range-ordered regions of the solid state.

The reason for the electrical resistivity hysteresis in the liquid state is the destruction of clusters, which occurs in a kinetic regime. This process leads to a great increase in electrical resistivity because of the essential increase in the number of dispersion centres for free conduction electrons. Above  $t_c$  the melt consists of a homogeneous system, which has a lower magnitude of free energy. This 'high-temperature' melt structure is stable up to the crystallization point as well as the liquidus temperature. Alloys which were frozen from the 'high-temperature' structure have a slightly different structure in the solid state, and the hysteresis in the solid state confirms this fact.

#### 5. Conclusions

(1) The temperature dependences and isotherms of the electrical resistivity  $\rho$  for binary Ni–Al alloys were obtained. The type of temperature dependence of  $\rho$  depends on the phase composition of the alloys. In the solid state for Ni–Al substitutional solutions the resistivity values increase with increasing temperature. In the solid state for  $\text{Ni}_3\text{Al}$  alloys the temperature dependence of  $\rho$  has a semiconductor character. The disordering of  $\text{Ni}_3\text{Al}$  starts long before melting and is manifested in the  $\rho$  decrease with a definite temperature  $t_{p1}$  up to the melting point. Resistivity hysteresis takes place in the liquid state after the heating of alloys up to the critical temperature. The  $\rho$  hysteresis is connected with the destruction of clusters, the structure of which is inherited from the solid state.

(2) The Ni–Al solid solutions have higher absolute magnitudes of  $\rho$  than do Ni<sub>3</sub>Al alloys in the solid state. On the contrary, in the liquid state,  $\rho$  for solid solutions are lower. The resistivity magnitudes of each intermetallic alloy depend strongly on the Al content.

(3) The quasi-chemical variants of the microheterogeneous structure model of metallic melts were put in concrete terms. According to this, the melt structure has clusters, which inherit the stoichiometry of the intermetallic in the solid state. The destruction of these clusters takes place at 1723–1843 K.

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