Crystal Growth of Rare-Earth Compounds with Tungsten Crucible Welding by Electron Beam†

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Abstract

Remarkable improvement have been made on the crystal growth of Rare earth compounds by the construction of the electron beam welding system of tungsten crucible with large glove box and vacuum HF furnace. This system have really worked on getting of better quality of single crystal and made easy to explore unknown material of rare earth compounds. Interesting and attractive physical properties on the crystal produced by these system were obtained and could extend new scope of the heavy fermion physics.

KEY WORDS : (Electron Beam Welding) (W Crucible) (Single Crystal) (Rare Earth Compound) (HF Furnace) (Heavy Fermion Physics)(Glove Box)

1. Introduction

It had been believed 4f electron to be localized in the solid state of the Rare earth compounds[1]. However it was recently revealed that the localized state is not always true but sometime f electron can move in the crystal. Typical examples are valence fluctuation and heavy Fermion state[2)-3)]. These states indicate the interesting unusual phenomena in their transport, magnetic, optical and thermal properties and suggest the fundamental importance of the many body effects of the f-electron to understand them[4]. For this consequence in the solid state physics, it has been attracted much attention of many researcher in the world and extensively carried out the studies in both experiments and theories. To progress these studies successfully, one of the most important works is to get a large and high quality single crystal of rare earth compounds. Neutron scattering experiments for the investigation of magnetic excitation need rather large single crystal of the cm-size of cube and on the other hand, de Haas van Alphen (dHvA) effect measurement for the observation of the Fermi surfaces requires absolutely pure single crystal of mm-size for the satisfactory detection of the signal. However it is not so easy to get such a single crystal especially in rare earth compounds with pnictogen atoms (N, P, As, Sb, Bi) or chalchogen atoms (S, Se, Te). The melting point of the 1:1 compound usually exceeds 2000C and the vapor pressure at this temperature is also very high. So if we apply the method of crystal growth adapted in the open system such as Czochralski pulling method heated by arc or electric high frequency power to these materials, samples are easily vaporized and escaped substantially even so introducing high pressure of Ar gas. Ar gas only reduces the evaporation of the sample kinematically. It is important to suppress the partial pressure of the sample. This is the reason that crystal growth in such a compound should be done in the closed system with crucible. Available crucible materials are limited only on W,Mo and Ta metal because of their stability in such ultra high temperature, processing material(not so easy) and capability of welding in vacuum. The best one in three metals is tungsten with due regard to the reactivity between W and these compounds.

Up to 1983 in Japan, there is only one group(Department of Physics, Tohoku University) to be able to get single crystals of these compound which have a high frequency furnace up to 3000C. Most weak point of this group is crucible welding process in their crystal growth procedure. They used a usual metal melting equipment by electron beam (Accelerating voltage 5kV, Beam current 500mA) and are limited to employment Mo crucible or very expensive special thin W crucible because this elec-

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tron beam cannot weld usual from of W crucible due to its wrong focuses. Single crystals to be get from Mo crucible were not so good due to its reactivity. Fortunately by the financial support of Ministry of Education in 1984, we could construct a most suitable electron beam welding system for this purpose and make a great progress in our activities. Now we are a rare group which has a superior total system to growth crystals of rare earth compounds. Here we shall report the performance of our constructed electron beam welding system and how to improve the quality of the crystal and our activities with measured results of several physical properties.

2. Electron Beam Welding System

It is shown in schematically our constructed electron beam welding system in **Fig. 1**. Upper parts of this figure are electron beam gun consisted with direct-heat type tungsten ribbon cathode of 3×3 mm and anode with 5mmϕ small hole. Middle parts are made of two magnetic lens act as focusing and deflecting electron beam respectively. Lowest part is a crucible supporting table with water cooled copper hearth which is able to rotate and shift in basal plane by external handling. Between the gun and its lower part there is a vacuum valve to make vacuum independently in each parts to maintain a clean state of the gun. This equipment is directly connected with large glove

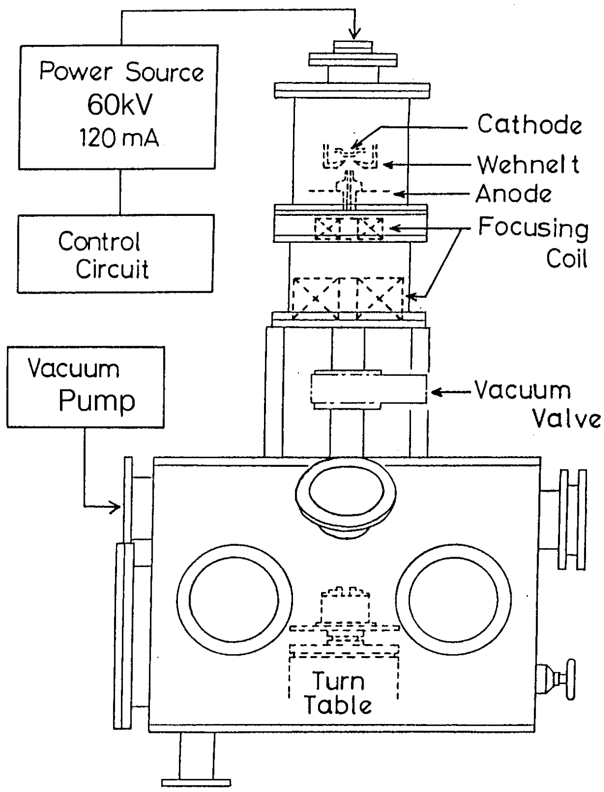

Fig. 1 Electron beam welding system for W crucihle.

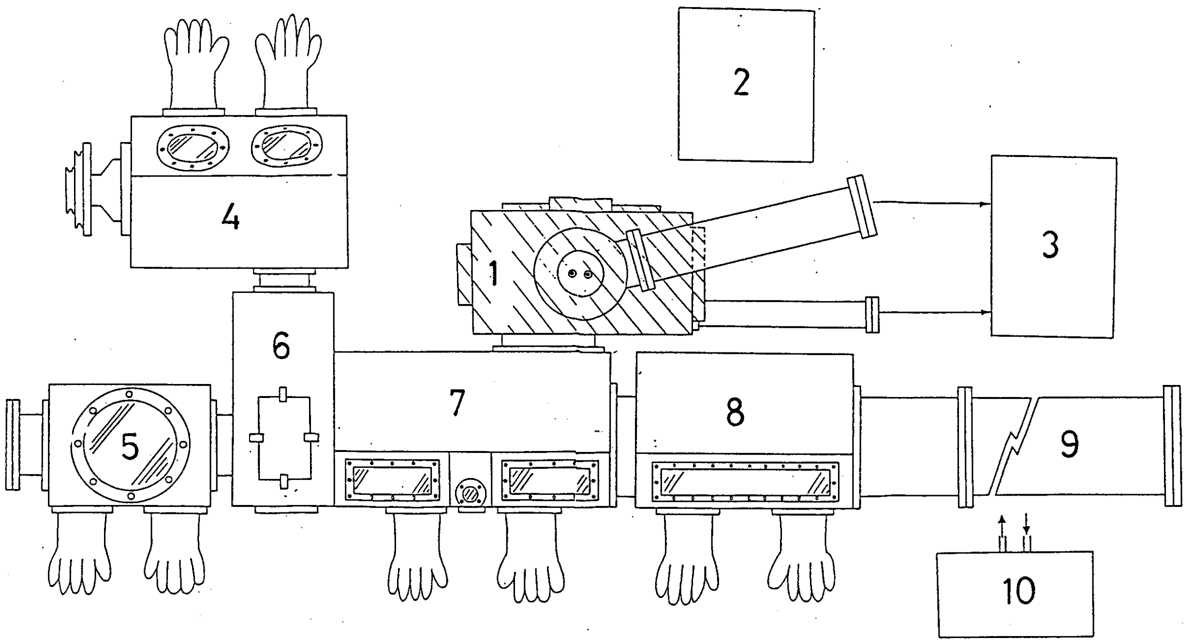

Fig. 2 Electron beam welding system and large glove box for many purpose : 1 : Electron beam welding system, 2 : Power source of electron beam welding system, 3 : Vacuum pumps for welding system, 4 : Glove box for cutting the raw rare earth metal by lathe and weighing of the constituted element of the compounds before synthesize. 5 : Glove box for lapping, shapping and cutting the single crystal, 6 : Entrance and exit room to glove box. 7 : Glove box for preparation and arrangement the W crucible and prereacted sample before welding. 8 : Glove box for sample setting to measuring holder in this room. 9 : Entrance and exit room the measuring holder.

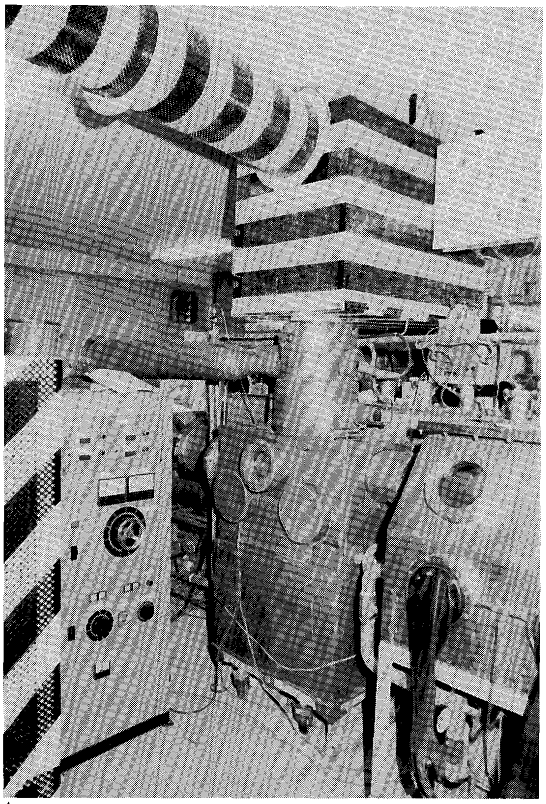

Fig. 3 Exterior view of the welding system

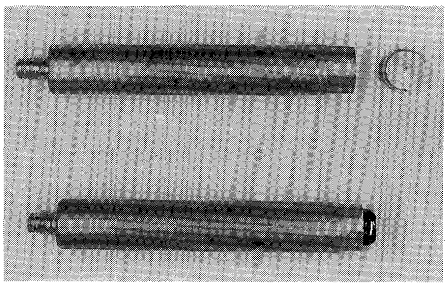

Fig. 4 Typical example of weld W crucible.

box for many purposes and can make to handle a curcible and sample without exposing in air from glove box to this welding system through the vacuum tight door. The connected systems are schematically shown in **Fig. 2**. Power source is capable to supply the maximum DC accelerating voltage and beam current being 60kV and 120mA respectively within 0.1% fluctuation. It is concentrated on the control panel to do many operation such as location the electron beam on the welding part of the crucible by magnetic lens and adjusting the beam power just watching the bombardment of crucible through the lead window. The exterior view of this system is shown in **Fig. 3**. Thus we got satisfactory result of welding W crucible in very short time of typically 30 sec without escaping by evaporation of the sample. This is considered to make important role to improve the quality of the crystal as mentioned after. We could also weld the W crucible made by ourself with rather low cost instead of very expensive commercial thin wall one. This is very important point for us to research much more compound in the limited budget. Typical example of our weld W crucible is shown in **Fig. 4**. Accelerating voltage is 50kV and beam current is 60mA in this case. Another advantage of this system is to be able to enclose the sample in very thin and small Ta or W container by welding in very short time without evaporating the sample. This is very important in the case of measuring differential specific heat in thermoanalysis for establishment of the phase diagram in research of new rare earth compounds. In this case, welding should be carried out in extreme focusing condition by applied large wehnelt voltage in highest accelerating voltage in this system. Beam diameter is about 0.5mm and welding conditions are 60kV, 10mA, 80mm/min for W crucible with thickness 0.1mm.

3. Crystal Growth of Rare Earth Compounds and their Physical Properties.

Before welding W crucible, several pretreatment procedure should be done. Careful ultrasonic and chemical cleaning of shaped crucible is carried out after making the handicraft of the W rod in cutting, drilling and lathe working. Final cleaning is take place in vacuum heated up to 1800C which is the dissociation temperature of WO_2. After welding W crucible contained sample, the crucible is settled in vacuum furnace heated by HF power up to melting temperature and then Bridgeman method is applied. Up to 1983 we used the HF furnace with high pressure Ar gas atmosphere which was constructed to crystal growth of rare earth hexaboride by floating zone method. Ar gas prevent a evaporation of the sample during zone process. However if we applied Bridgemann method in this furnace, strong convection of Ar gas brought temperature fluctuation around crucible. So we construct of another vacuum type HF furnace as shown in **Fig. 5**. Thus the stability of the temperature improve remarkably. One of the most severe check of the quality of obtained single crystal is whether the detection of the signal in dHvA effect is possible or not. We shall show the typical example of CeSb. We had succeeded the observation of the dHvA effect on single crystal of CeSb grown in Mo crucible and HF furnace with Ar gas atmosphere in 1980[5] for the first time as shown in **Fig. 6**. There are only three branches to be able to observe correspond to hole and electron Fermi surfaces respectively. After this, the effort to detect other Fermi surfaces made a progress

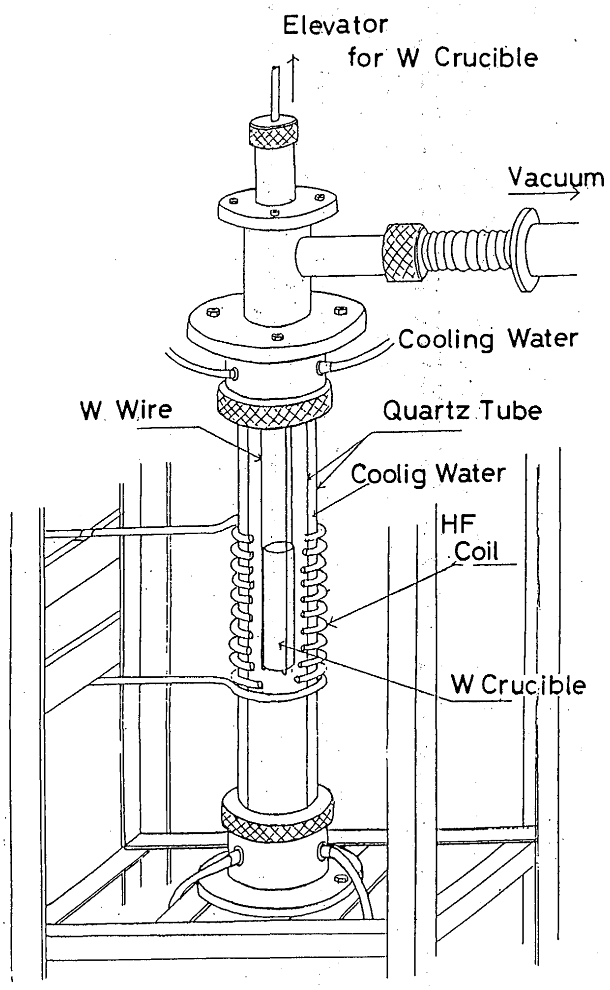

Fig. 5 Vacuum type of HF furnace in schematically

by both our and Argonne group independently with more extended magnetic field up to 13T and lower temperature down to 0.5K. The results of both group were obtained just same as shown in **Fig. 7**[6)7)]. At this time, very severe discussion are occurred between theoretical Sendai group and Argonne group. Sendai group argued that there should be another undetected branch from their band calculation taking into account of many body interaction of f electron[8)]. Argonne group opposed this argument based on their usual band calculations[9)]. The continuous endeavor for search of the existence of undetected branch in dHvA effect have been done by our group in mainly following two improvement. One is the getting more superior quality of the single crystal. Most important improvements in all procedure of crystal growth are the construction of the genuine electron beam welding system with large glove box for many purpose and elevation of the stability of the temperature in the furnace as mentioned above. Another is the extension of measuring temperature region of dHvA effect down to 20mK. Then recently we succeed to observe the new branch of the Fermi surface in CeSb and justify the rightness of the argument of theoretical Sendai group based on several improvement just mentioned above[10)].

Another important benefit of the success of the construction of the electron beam welding system with many purpose large glove box is to make possible to use W crucible more easy with low cost. If we challenge to explore for unknown rare earth compounds which has no phase diagram, it have to take a lot of W crucibles to estimate proper temperature for crystal growth. It is especially true for incongruent materials. A typical example of our research will be reported here on the case of Yb_4As_3. This compounds are known only existence of the phase with anti-Th_3P_4 structure. No signle crystal and no physical measurement had been obtained. We initially found out this material to be incongruent. We could successfully get single crystal after several try and errors by our new development of growth method. The point of this method is that starting material slides intentionally its stoichiometry to Yb rich side and to keep the temperature just below dissociation point of Yb_4As_3 for about one week. The rather large single crystal of Yb_4As_3 was obtained by segregation from its solution with the components of off stoichiometry which may act as a some kind of flux. Obtained crystal are shown in **Fig. 8**. Unusual and much interesting properties are discovered in this compound. Temperature dependence of the resistivity are shown in **Fig. 9**. as typical illustration of its physical properties. The resistivity jumps abruptly at about 300K corresponding to the crystal structure deformation due to the charge ordering state of f-electron in lower temperature side. At higher temperature it is a valence fluctuation state analogous to Sm_4As_3 or Eu_3S_4[11,12)]. The temperature dependence of the resistivity in this temperature region is strictly linear up to 600K which is very similar to that of High T_c superconductor of 123 yttrium compound[13)]. In this case, the extrapolation of the resistivity at O°K across the zero resistivity. Furthermore, the similarity to High T_c compound is its absolute value of the resistivity which suggest the few carrier concentrations and it confirms by Hall effect and optical reflectivity as 0.1% at 4.2K and few % above 300K of free carriers per formula unit respectively[14,15)]. Optical reflectivity of Yb_4As_3 are shown in **Fig. 10**. Clearly low plasma edge indicates low carrier concentration ; $\omega_p=\sqrt{N/m^*}$. The similarity are not only carrier concentration but also the sign of carriers which implies hole conduction in valence band. The mechanism of High T_c superconductor is most hot problem now. It should be a some similarity of the conduction mechanism and suggest the strong correlated electron system in both materials. Strong correlation of this material are indicated more remarkably in the low temperature behaviors. The coeffi-

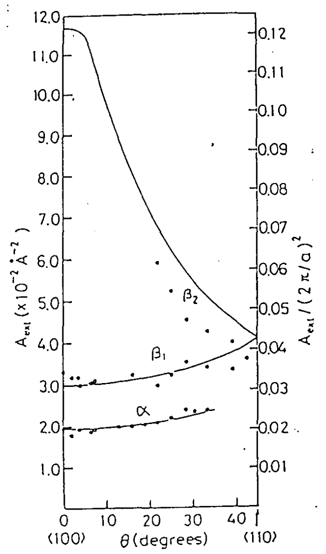

Fig. 6 The extremal cross sectional area of the Fermi surfaces as a function of the field direction on the (001) plane for CeSb.

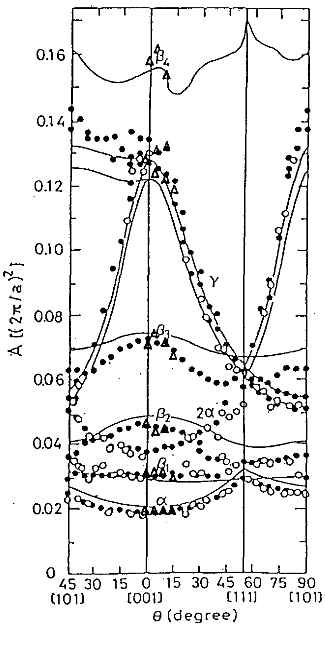

Fig. 7 The calculated cross area of Fermi surfaces in ferromagnetic CeSb[6] is shown by solid curves and experimental values are shown by solid circle[7], open circles[6] and triangles[9]

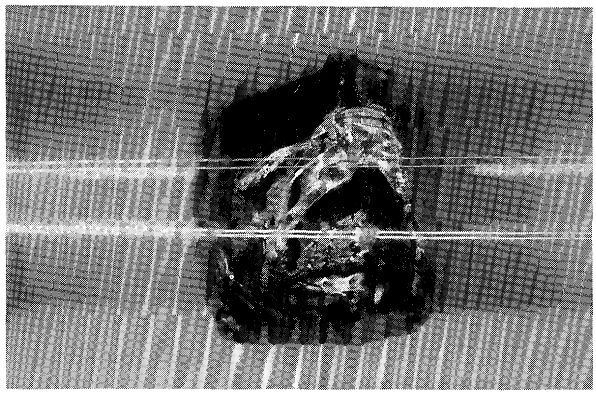

Fig. 8 Single crystal of Yb_4As_3 obtained by new method.

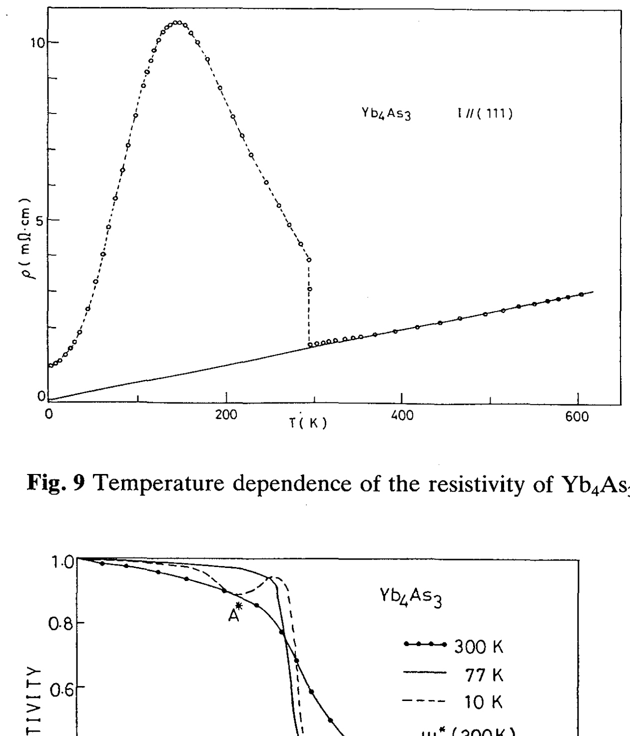

Fig. 9 Temperature dependence of the resistivity of Yb_4As_3

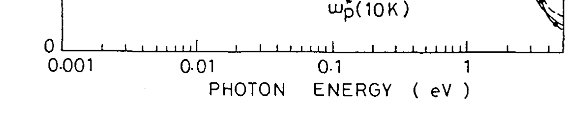

Fig. 10 Energy dependence of the optical reflectivity of Yb_4As_3

cient of linear term of the specific heat vers. temperature which is proportional to the density of state of electron are evaluated as 200mJ/mol.deg^2. and ratio between magnetic susceptibility at O°K and this electronic term of specific heat (so-called Wilson ratio) satisfy the Fermi liquid relations. Furthermore, the temperature dependence of the reisitivity obeys T^2 law pretty well from 4.2K to 100K. So it can conclude that Yb_4As_3 is obviously heavy Fermion system. However, such a heavy Fermion system with extremely low carrier concentration have not been discovered. There are only limited in usual metallic systems to be investigated currently. Simple extension of the single impurity problem in Kondo state can not absolutely accept the existence of the heavy Fermion state in low carrier concentration system because such a simple imagination demands complete cancellation of the localized spin of f-electron and spin of the conduction electron making a singlet ground state at absolute zero temperature. The low carrier concentration system have not enough carriers making singlet state with localized spin sited in each atomic site. The discover of the heavy Fermion state in low carrier concentration of Yb_4As_3 really extend the scope of the heavy Fermion physics and it was one of the most attractive topics in International Conference of Magnetism at Paris in 1988[16].

4. Summary

After complete the remarkable improvement of all procedure of the crystal growth equipment especially electron welding system with large glove box for many purpose, several good single crystals were obtained in addition to the crystals mentioned above, such as RX, R_4X_3(R = Ce,Sm,Yb.X = As,Sb,Bi)and we could get interesting information in these physical properties respectively[17,18,19]. However, since phosphide and nitride of 1:1 rare earth compounds has extremely high melting temperature, our vacuum furnace cannot operate in such a high temperature due to mainly lack of countermove for escape of radiation from heated crucible. Improvement of this point is making now in progress. Another desired improvement on the moving system of the W crucible in electron beam welding apparatus are to exchange hand moving for motor driving and now in progress too. Focusing of the electron beam are good enough for welding W crucible now but not enough to weld very thin and small sample container for in very short time. It shall be improved in near future. Any way, our constructed total system of the crytal growth of the rare earth compound could really do work and got much fruitful results.

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