Superconducting Transition in Electron-Doped 12CaO-7Al2O3

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It was reported that a mixed light metal oxide compound, 12CaO-7Al2O3 (C12A7), which is known as a constituent of aluminous cement, became a superconductor at an ambient pressure by the exclusive replacement of extra-framework oxygen ions in subnanometer-sized crystallographic cages with electrons. Temperature dependences of resistivity, magnetic susceptibility, and magnetic field dependent resistivity of single-crystals and thin films revealed superconducting transition at temperature (Tc) of ~0.4 K and a critical magnetic field of ~30 mT. Tc varies 0.2–0.4 K with the electron concentration. The interaction of the anionic electrons in the free space (cages) with the cationic framework may be responsible for the emergence of the superconducting state. [doi:10.2320/matertrans.MBW200717]

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1. Introduction

Light metal oxides such as CaO, Al2O3 and SiO2 (i.e. oxides of typical ubiquitous elements), are the main constituents of earth’s crust. They are abundant in natural resources, benign for environment, but are typical electronic insulators. It is widely believed to be difficult to achieve electro-active functions in these materials. Especially, no metallic and superconducting states have been realized in the category of light metal oxides to date. Recently, the metallic and superconducting states has been realized in a typical refractory oxide 12CaO-7Al2O3 (C12A7) utilizing built-in nanoporous structure,1,2 in which subnanometer-sized cages are distributed regularly in the lattice framework and anionic electrons are possibly introduced into the cages.

C12A73–5) has a cubic lattice (a = 1.199 nm) with a unit cell composed of a positively-charged lattice framework, [Ca28Al28O64]4+. The framework has twelve subnanometer-sized cages and two extra-framework O2– ions (“free oxygen ions”) in a unit cell (Fig. 1(a)). The cages are three-dimensionally connected each other through a monomolecular-thick cage wall. Two out of the twelve cages are occupied by the free oxygen ions, while the other ten cages are empty. The free oxygen ions may be replaced with electrons by reducing processes such as thermal treatments under metal (Ca, Ti) vapor and reducing gas atmosphere,1,2,6–7) melt-solidification and glass-ceramics processes8,9) and hot Ar ion-implantation.10,11) The complete replacement leads to the formation of [Ca28Al28O64]4+ (4e−), which is regarded as a new type of inorganic electride.9,10

We have reported that the metal-insulator transition (MIT) in C12A7 has been realized by the high-density electron doping to \( \gtrsim 1 \times 10^{21} \text{cm}^{-3} \), which induced the homogenization of the cage geometry among the empty and electron occupied cages.7,9) Recently, Miyakawa et al. reported that the superconducting transition (SCT) have been observed in metallic C12A7 electrides.1

In this report, we review the MIT and SCT of C12A7 electrides. Specially, we focus on the SCT of C12A7 electrides in terms of temperature dependent electrical resistivity and magnetic susceptibility for different types (CZ and FZ) of single-crystals and thin films of the C12A7 electride (C12A7:x−) down to 85 mK. Furthermore, we discuss the effect of magnetic impurity on the superconducting properties and the plausible mechanism of the superconducting transition in metallic C12A7 electride.

2. Experimental Procedures

C12A7 single-crystals grown by floating zone (FZ)12–14) and Czochralski (CZ) methods15,16) were used as precursor of the electride. The single-crystals grown by the FZ method (FZ single-crystal) were transparent, but had a slight orange tint, which was attributed to Ir4+ ions incorporated in the crystal from the Ir crucible during the growth process. The Ir concentration measured by an inductively-coupled plasma emission (ICP) was \( 5 \times 10^{17} \text{cm}^{-3} \). The intentionally Ir-doped polycrystalline [Ca28Al28O64]4+(2O2−) samples used to examine the Ir effect on electrical transport properties were prepared by melting the C12A7 powders with Ir at 1450°C for 20 h and subsequent annealing at 1300°C for 1 h in an ambient atmosphere using alumina crucibles. These single-crystals and polycrystals were sealed in a silica glass tube (inner volume~10 cm3) with Ti metal powder (~5 g) under a vacuum of ~10−3 Pa. Then the sealed tube was thermally annealed at temperatures between 900–1100°C for 24–72 h (Ti-treatment). The doping level of electrons was controlled by the adjustment of the temperature and duration of the Ti-treatment. The Ti-treatment replaces the free oxygen ions with electrons through the reaction of Ti (surface) + xO2− (cage) \( \rightarrow \) TiO2 (surface) + 2xe− (cage). Due to the reaction, the electron-doped C12A7, [Ca28Al28O64]4+[(2−x)O2− . 2xe−] was formed. The electron concentration was estimated by analyzing the optical reflectance spectra of the single-crystals measured in the infrared to ultraviolet region (450 to 40,000 cm−1) at room temperature using Drude-Lorentz
model. The details of sample preparation for optical measurement and of numerical calculation were described in ref. 17).

The electrical conductivity was measured by the four-probe method using Pt electrodes, which were deposited on the surfaces of the Ti-treated samples after the TiO	extsubscript{x} layer were mechanically removed. The measurement of an ac magnetic susceptibility (χ) of C12A7 single-crystal electride was performed from the change in the mutual inductance between two small coils at 120 Hz in a dilution refrigerator. The absolute value (included χ 5% error) of χ was calibrated from the perfect diamagnetisms of Al and Ti metals.

3. Results and Discussions

3.1 Metal-Insulator transition of C12A7 electride

Figure 2(a) shows temperature dependences (T) of the electrical conductivities (σ) for the Ti-treated CZ single-crystals with different electron concentrations (N	extsubscript{e}). The T dependence of the σ of CZ single-crystals in Ref. 2) is reproduced. The T dependence of σ has a positive value (dσ/dT > 0) when the N	extsubscript{e} is low, indicating that a thermally-activated conduction mechanism such as the variable range hopping (VRH) controls the electron migration. On the other hand, the temperature dependence vanishes at N	extsubscript{e} ≈ 9 x 10	extsuperscript{20} cm	extsuperscript{-3}, demonstrating that the conduction changes to a degenerated type, and finally to metallic at higher N	extsubscript{e}. (b) Electrical conductivities at 300 K sharply increase as the carrier concentration increases at N	extsubscript{e} > N	extsubscript{c}. Electron mobilities at 300 K are low σ 1 cm	extsuperscript{2} V	extsuperscript{-1} s	extsuperscript{-1} at N	extsubscript{e} < N	extsubscript{c}, but sharply increases at N	extsubscript{e} > N	extsubscript{c}.
converted to a metal through MIT at $N_c \sim 1 \times 10^{21}$ cm$^{-3}$. It should be noted that the transition accompanies a sharp increase in the drift mobility ($\mu_d$) from $\sim 0.1$ to $4$ cm$^2$ V$^{-1}$ s$^{-1}$ as shown in inset of Fig. 2(b). This behavior suggests that the doping and conduction mechanisms in C12A7 are much different from those in conventional semiconductors$^{18,19}$, presumably due to the unique crystal and electronic structures of C12A7.

The mechanism of MIT was interpreted from the viewpoint of the relationship of the structural geometry of the cage with $N_c$. Theoretical calculations combined with experimental results have revealed that the cages in C12A7 form an additional conduction band, named “cage conduction band (CCB)”.$^{20-24}$ CCB is located $1$–$2$ eV below the bottom of “framework conduction band”, which is primarily composed of Ca 5s orbitals. CCB is partially occupied by the anionic electrons having an s-like nature. At low $N_c$, the electrons induce a large lattice deformation mostly due to the Coulomb attractive forces between the entrapped electron and the two Ca$^{2+}$ ions on the cage wall. The Coulomb force lowers the energy level of the entrapped electron from the CCB bottom, which causes the electron localization. Consequently, the conduction occurs via hopping of the electron from the deformed cage to an empty cage (The electron strongly reacted with the lattice is considered as “polaron”). This is the reason why the drift mobility is much smaller than $1$ cm$^2$ V$^{-1}$ s$^{-1}$. On the other hand, with the increase in $N_c > N_c$, the deformations of the cages are reduced or the lattice relaxation is weakened all over the lattice. Thus, the electrons are delocalized over the cages, resulting in the metallic state.

### 3.2 Superconducting transition of C12A7 electrode

#### 3.2.1 Superconductivity of C12A7 electrode

In order to investigate whether the superconducting transition occurs in the metallic C12A7 electrode or not, two electrode samples exhibiting the highest conductivity in each crystal growth method (FZ and CZ) were used for measurements of electrical properties at low temperatures. The electrical conductivities at $300$ K of the FZ and CZ single-crystal electrodes were $\sim 810$ S cm$^{-1}$ and $\sim 1500$ S cm$^{-1}$, respectively.

Figure 3 shows the temperature ($T$) dependence of the electrical resistivity ($\rho$) of two samples. The $T$ dependence of the $\rho$ of FZ and CZ single-crystal is reproduced from Refs. 1) and 2), respectively.

A sharp drop of the resistivity is observed in the FZ single-crystal electrode with an onset temperature of $\sim 0.2$ K. However, electrical resistivity of the metallic C12A7 electrode prepared from the CZ single-crystal never becomes zero down to $85$ mK, as shown in inset of Fig. 3. Figure 4 shows that the onset temperature in the FZ sample decreases with the application of magnetic field, which strongly suggests that the FZ single-crystal C12A7 electrode is a superconductor below a transition temperature of $\sim 0.2$ K. It is noted that the data is reproduced from the previous report.$^1$ The superconducting transition was further observed with the onset temperature of $\sim 0.16$ and $\sim 0.4$ K in epitaxial thin film electrodes with $N_c$ of $1.6 \times 10^{21}$ cm$^{-3}$ and $2.0 \times 10^{21}$ cm$^{-3}$, respectively.$^1$ The variation of $T_c$ in both single-crystal and thin film electrodes suggests that the increase in $N_c$ leads to an increase in $T_c$ in the C12A7 electrodes. Using a relation of $H_c(T) = H_c(0)[1 - (T/T_c)^2]$, the critical magnetic field $H_c(0)$ of the single crystal and epitaxial thin film is calculated to be $\sim 19$ mT and $\sim 33$ mT, respectively. The low transition temperature and the small critical magnetic field imply that the C12A7 electrode is a type-I superconductor.

![Fig. 3 Superconducting transition in FZ grown single-crystal electrodes.](image-url)

![Fig. 4 $\rho$-$T$ curves of FZ grown single-crystal C12A7 electrode (Sample A) at low temperatures for magnetic fields from 0 to 100 mT. A sharp drop of the resistivity is observed with an onset temperature of $\sim 0.2$ K, and the resistivity becomes an immeasurably small value below 0.18 K. The superconductivity is disappeared by the magnetic field above a critical magnetic field of 30 mT. The poor S/N resolution of the bulk samples is due to experimental limitation, i.e., small current is needed to suppress Joule-heating leading to shift of $T_c$. These data are reproduced from Ref. 1.)](image-url)
Figure 5 shows the ac magnetic susceptibility of the FZ single-crystal electrode as a function of temperature. This figure is reproduced from the previous report\(^1\) and magnified around 0.2 K to clearly show the behavior around \(T_C\). The sharp drop of \(\chi\) at \(\approx 0.20\) K and perfect diamagnetism \((\chi \approx -1)\) below \(0.20\) K demonstrates the bulk superconductivity of the C12A7 electrode and 100% volume fraction of superconducting phase. Observed broader transition region is due probably to the large sample size. The onset temperature in the \(\chi-T\) curve is slightly higher than that in the \(\rho-T\) curve, which is attributable to unavoidable Joule heat generated in the electrical resistivity measurement that induced possible temperature gradient between the sample and the temperature-monitoring point. The data of Fig. 4 was obtained using a current of \(\approx 30\) mA/cm\(^2\) to suppress the Joule heat of samples as small as possible in our measurements.

### 3.2.2 Kondo effects of C12A7 electrode

We have found that the CZ single-crystal electrode exhibited no superconducting transition in spite of the lower resistivity than that of FZ single-crystal electrode. The primary difference between two samples is the existence of the Ir ions. Thus, we expect that the magnetic Ir\(^{4+}\) ions in the CZ single-crystals suppress the superconducting transition in the metallic C12A7 electrode. To confirm this assumption, we compared the CZ single-crystal electrode (Ir concentration of \(\approx 5 \times 10^{17}\) cm\(^{-3}\)) with large-grained (typical grain sizes \(\approx 3\) mm) polycrystalline electrodes, in which Ir ions were intentionally doped up to a level of \(1 \times 10^{19}\) cm\(^{-3}\). Figure 6 shows temperature \((T\) dependences of electrical resistivities \((\rho)\) of the Ir-doped polycrystalline electrodes. The \(\rho\) of the polycrystalline samples in Ref. 2) is reproduced. It is noteworthy that the \(\rho\) values of samples with an Ir concentration \(\geq 1 \times 10^{18}\) cm\(^{-3}\) increase as the decrease of temperature at low temperatures, e.g. \(< 50\) K, showing a minimum at \(T_m\). Further, the \(T_m\) reasonably follows the relation in the Kondo effect,\(^{25}\) \(T_m \propto [\text{Ir}]^{1/5}\), suggesting that the interaction between the conduction electrons and spin moments localized at the Ir ions plays a dominant role in exhibiting the minimum in the \(\rho-T\) curve. That is, the involvement of the magnetic impurity Ir\(^{4+}\) ion in the metallic C12A7 electrode leads to the Kondo effect. Thus, the superconducting transition in the CZ single-crystal electrode might be suppressed due to the Ir incorporation in spite of the low concentration.

### 3.3 Mechanism of superconducting transition

In the Bardeen-Cooper-Schrieffer theory, \(T_C\) is expressed by McMillan’s formula,\(^{26}\) \(T_C = \frac{\theta_D}{\lambda} \cdot \exp\left[-1.04 \cdot (1 + \lambda)/\lambda \cdot (\lambda - \mu^+/(1 + 0.62 \cdot \lambda))\right]\), where \(\theta_D\) is the Debye temperature, \(\lambda\) is the phonon-electron coupling constant and \(\mu^+\) is the Coulomb pseudo-potential. \(\lambda\) is provided by \(\lambda = N(0) \cdot V\), where \(N(0)\) is the electron concentration at the Fermi energy, and \(V\) is phonon-mediated coupling constant for a single electron. Using the experimentally obtained value of \(\theta_D = 604\) K\(^{27}\) from heat capacity and the assumption of \(\mu^+\) as 0.2 in the low electron density system,\(^{28,29}\) we obtain \(\lambda \approx 0.45\), which is much larger than those of alkali metals as mentioned below. The observed increase in \(T_C\) with \(N_c\) is consistent with McMillan’s formula, provided that \(N_c\) is correlated with \(N(0)\).

Although the feature that the conduction electron in the electrode is \(s\)-electron is similar to that of the alkali metal, superconducting transition is observed in C12A7 electrode but not in alkali metals at ambient pressure except \(T_C = 0.4\) mK of Li.\(^{30}\) The difference might be attributable to the strength of the electron phonon interaction. The anionic electron may interact strongly with the rigid lattice framework that is formed due to the strong covalent and ionic bonds among Ca\(^{2+}\), Al\(^{3+}\) and oxygen ions. These facts possibly lead to the high values of \(\lambda\) (\(\approx 0.45\)) and \(\theta_D\) (604 K), which are much higher than those of alkali metals such as Li (\(\lambda = 0.38\), \(\theta_D = 420\) K), Na (\(\lambda = 0.20\), \(\theta_D = 150\) K), and K (\(\lambda = 0.14\), \(\theta_D = 100\) K).\(^{31-33}\) That is, the strong electron-phonon interactions likely resulted from the covalent and ionic bond nature of the oxide framework, is responsible for the emergence of the superconductivity in the C12A7 electrode.
4. Summary

Zero resistivity, magnetic field dependent resistance, and perfect diamagnetism clearly indicate that the light metal oxide based C12A7 electride is a type-I superconductor with a transition temperature of 0.2–0.4 K, which depends on the electron concentration. The conduction electron, which is responsible for the superconductivity, has $s$-orbital like character, concentrating on the empty cage space in the lattice. The strong interaction of the electron with the cationic framework in the C12A7 electride, which overcomes the small electron concentration, plays a critical role in the appearance of the superconductivity. Further, the electrides with a rigid framework structure and with electrons in free space is a new category of superconductors, providing new platform to further understand the emergence of the superconducting phase and to explore high $T_c$ superconductors.

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REFERENCES