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Some Doping Effects on the Semiconducting Properties of Gd_2CuO_4

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Some doping effects on the semiconducting properties of the Gd_2CuO_4 compound were investigated. The ZrO_2 or ThO_2 (0.5 mol%) lowered the resistivity of the Gd_2CuO_4 at room temperature by a factor of 10^4. The thermoelectric powers of the same samples were negative. These were explained as being due to the Cu^+ ions formed by the dopants. The CaO dopant lowered the resistivity by a factor of ten and converted the sign of the thermoelectric power from negative to positive. The resistivity of the BaO-doped samples increased with an increase in the dopant concentration up to 0.5 mol%, and decreased with an increase in the dopant concentration in the concentration region lower than that. This suggested that the dopant of BaO was less effective on the resistivity-lowering than was the CaO. The samples doped with the ZrO_2 and CaO simultaneously gave a trend similar to those doped with the BaO in the concentration dependence of the resistivity. Silver oxide and indium oxide were also employed as dopants, but no doping effects were observed on either resistivity or the lattice parameters.

The Ln_2CuO_4 compounds (Ln=Gd, Sm, Nd, and Pr) are semiconductive, and their resistivities increase with an increase in the atomic number of Ln.[1] It has been suggested that the most important electron-carriers come from cuprous cations, Cu^+, probably formed by a thermal decomposition of cupric cations, Cu^{2+}.[1] The trend for the resistivities to increase with an increase in the atomic number of Ln was explained as being due to: (1) a variation in the number of the donor centers or (2) a variation in the activation energy.[1] However, it is not known which factor is more important.

As is well known, some dopants introduce donor

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[1] T. Kenjo and S. Yajima, This Bulletin, **46**, 1329 (1973).

centers.[2,3,5,6] If the dopants do not change the activation energy very greatly, any electrical effects due to the dopants can be ascribed to the first case. The X-ray diffraction data indicated that the lattice parameters for the Gd_2CuO_4 did not shift with doping, suggesting no variation in the activation energy. Therefore, the comparison of the doped to undoped Ln_2CuO_4 in the semiconducting properties may give an answer to the above problem.

Dopants usually lower the resistivity. Therefore, the most marked doping effect can be expected for the compound whose resistivity is the greatest. Since the Gd_2CuO_4 showed the greatest resistivity in the Ln_2CuO_4 series, it was chosen as the compound to be doped.

Donor centers are formed when the valence of the dopant is greater than that of the site.[2,3,5,6] Zirconium oxide, ZrO_2, and thorium oxide, ThO_2, were chosen as dopants which could be expected to occupy the Gd^{3+} sites, because they are chemically similar to the rare earth oxides.

Acceptor centers will be formed by dopants whose valences are smaller than those of the site. The most probable acceptor centers in this case are the Cu^{3+} or the Gd^{4+} cations. Since both of them are unstable and are not well known, it would be of interest to see if doped divalent cations lower the resistivity of the Gd_2CuO_4. Alkaline earth oxides are most suitable for the above purpose, because they are chemically similar to Gd_2O_3 and because they are expected to occupy the Gd^{3+} sites. Barium oxide, BaO, and calcium oxide, CaO, were employed as the dopants here.

Silver oxide, Ag_2O, and indium oxide, In_2O_3, were expected to occupy the Cu^{2+} sites and to form acceptor and donor centers respectively. They were also used as dopants.

Experimental

Reagents and Materials. An aqueous solution of $Gd(NO_3)_3$ was prepared by dissolving Gd_2O_3 (Nippon Yttrium Co., Ltd., 99.9%) in nitric acid (Wako Pure Chemical Co., Ltd., GR grade). The maximum contents of the impurities contained in the Gd_2O_3 used were Fe_2O_3, 10 ppm; CuO, 10 ppm; CaO, 30 ppm; ZrO_2, 10 ppm and ThO_2, 10 ppm.[7] An aqueous solution of $Cu(NO_3)_2$ was prepared by dissolving GR-grade $Cu(NO_3)_2 \cdot 3H_2O$. The maximum contents of the impurities contained in the $Cu(NO_3)_2$ used were; Fe, 30 ppm; Zn, 50 ppm; Ni, 40 ppm; Ba, 20 ppm; Ca, 4.5 ppm; Zr, 10 ppm, and Th, not detected.[8] The aqueous solutions of the nitrates of Zr, Ag, and Th were prepared by dissolving GR-grade $ZrO(NO_3)_2$, $AgNO_3$, and $Th(NO_3)_4$ respectively. The aqueous solutions of $Ca(NO_3)_2$, $Ba(NO_3)_2$, and $In(NO_3)_3$ were obtained by dissolving GR-grade $CaCO_3$, $BaCO_3$, and EP-grade In_2O_3 respectively in nitric acid. The concentration of the $AgNO_3$ solution was determined gravimetrically. The concentrations of the other solutions were determined chelatometrically against a standard EDTA solution.

Procedure. The samples were prepared by the same method as in a previous work.[1] Aliquot portions of $Gd(NO_3)_3$, $Cu(NO_3)_2$, and the nitrate of the dopants were mixed, and a sodium hydroxide solution (1M) was stirred in. After the mixture had stood overnight, filtering-washing was repeated until no sodium ion was detected in the filtrate by the flame test. The mixed hydroxides thus obtained were dried at 120 °C and preheated at 750 °C for 4 hr in air. The lumped oxide mixtures were milled, pressed into 15-mmϕ pellets, and heated at 1000 °C for 15 hr in air. The pellets thus obtained were removed from the furnace and cooled to room temperature. These samples thus obtained were cut into rods 12—13 mm long and 3—4 mm thick for the electrical measurements. The resistivity was measured by the 4-probe method using Du Pont No. 4622 Conductive Silver Coating Materials. The thermoelectric power was measured by means of the method of the previous work.[1] The bulk densities of the samples thus obtained were essentially the same as those of the undoped Gd_2CuO_4.

Results

The concentrations of the dopants are expressed as a mol% of the dopants against the total moles of the Gd_2CuO_4 and the dopants used. The signs for the values of the thermoelectric power are the same as in the previous work, being positive for a p-type and negative for an n-type.

Figures 1, 2, 3, and 4 show the data for the ZrO_2- or ThO_2-doped Gd_2CuO_4. As will be described in a later section, the mole ratio of raw oxide mixtures was: Gd_2O_3: CuO: $ZrO_2 = 1-x : 1 : x$. The sample containing 5 mol% ZrO_2 gave only the X-ray diffraction pattern of the Gd_2CuO_4 phase, while the ZrO_2 phase was found for the sample containing 10 mol% ZrO_2. This indicated that the solubility of ZrO_2 in Gd_2CuO_4 was between 5 and 10 mol%.

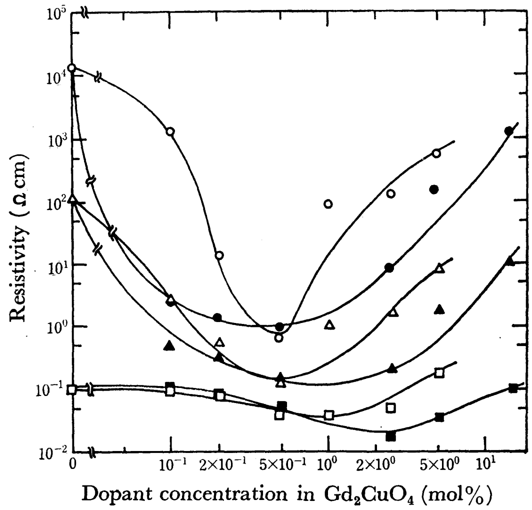

Fig. 1. Variation of resistivity with dopant concentration in Gd_2CuO_4.
○: room temperature for ZrO_2-doping, △: 200 °C for ZrO_2-doping, □: 800 °C for ZrO_2-doping, ●: room temperature for ThO_2-doping, ▲: 200 °C for ThO_2-doping, ■; 800 °C for ThO_2-doping.

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2) G. H. Jonker, *Philips Research Reports*, **24**, 1 (1969).

3) T. Kawaguchi, "Handotai no Kagaku," Maruzen Co., (1971), p. 56.

4) R. W. G. Wyckoff, "Crystal Structures," Vol. 3, Interscience Publishers, New York, N.Y. (1965) p. 68.

5) Stephan P. Mittof, "Progress in Ceramic Science," Vol. 4, edited by J. E. Burke, Pergamon Press, p. 217.

6) O. Kubaschewski and B. E. Hopkins, "Oxidation of Metals and Alloys," Butterworths, London (1967), p. 15.

7) Private communication, Nippon Yttrium Co., Ltd.

8) Private communication, Kanto Chemical Co., Ltd.

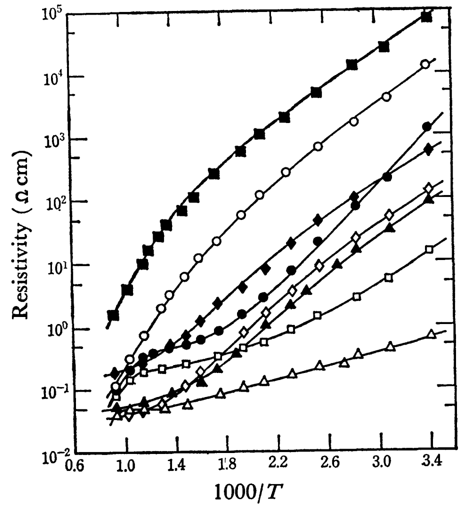

Fig. 2. Temperature dependence of resistivity for ZrO_2-doped Gd_2CuO_4.
○: undoped Gd_2CuO_4, ●: 0.1 mol%, □: 0.2 mol%, △: 0.5 mol%, ▲: 1 mol%, ◇: 2.5 mol%, ◆: 5.0 mol%, ■: less dense specimen of undoped Gd_2CuO_4

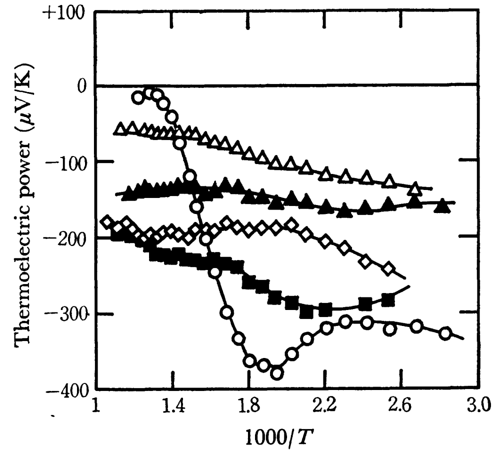

Fig. 3. Temperature dependence of thermoelectric power for ThO_2- or ZrO_2-doped Gd_2CuO_4.
○: undoped Gd_2CuO_4, ◇: 0.5 mol% ThO_2, △: 15 mol% ThO_2, ■: 0.5 mol% ZrO_2, ▲: 5 mol% ZrO_2.

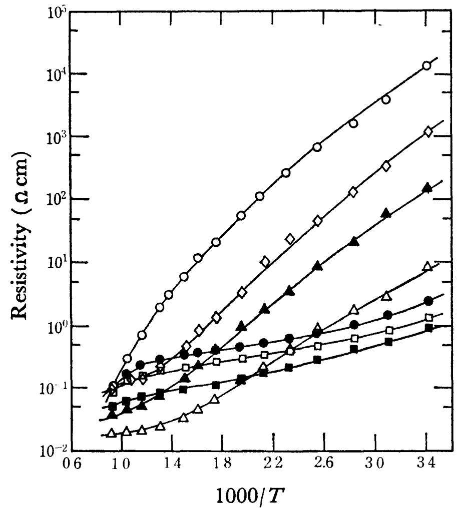

Fig. 4. Temperature dependence of resistivity for ThO_2-doped Gd_2CuO_4.
○: undoped Gd_2CuO_4, ●: 0.1 mol%, □: 0.2 mol%, ■: 0.5 mol%, △: 2.5 mol%, ▲: 5 mol%, ◇: 15 mol%.

The resistivity, ρ, particularly at room temperature, decreases with an increase in the concentration of ZrO_2 up to 0.5 mol%. Beyond this concentration, however, the resistivity increases with an increase in the concentration of ZrO_2 (Fig. 1). Figure 2 shows the temperature dependence of the resistivity for the various contents of ZrO_2. The resistivity-lowering due to the dopant is the most marked at room temperature. The log ρ *vs.* $1/T$ plots for the samples of $x<0.5$ mol% show shoulders in the high-temperature region. As is indicated by the black squares in Fig. 2, the resistivity of the less dense specimen is ten times that of the denser one (open circles); the bulk density of the former is 0.64 of the theoretical value, while that of the latter is 0.90 of the same value. The curves for the two specimens are parallel. Figure 3 indicates that the ZrO_2-doped Gd_2CuO_4 are *n*-type semiconductors.

The solubility of ThO_2 in the Gd_2CuO_4 was between 15 and 20 mol%. The ThO_2-doped samples are similar to the ZrO_2-doped ones in the dependence of the resistivity on the dopant concentration and in the thermoelectric power data; the resistivity is at a minimum at 0.5 mol% ThO_2, and the thermoelectric power is negative.

Figures 5, 6, and 7 give the data for the CaO- or BaO-doped Gd_2CuO_4. The solubility of CaO in the Gd_2CuO_4 was between 1 and 5 mol%. Figure 5 shows that the resistivity decreases with an increase in the dopant concentration, but not so markedly as in the case of the ZrO_2- or ThO_2-doping. The log ρ *vs.* $1/T$ plots (Fig. 6) indicate that the ρ values for the CaO-doped samples, as well as their slopes, approach those for the undoped Gd_2CuO_4 in the high-temperature region. Figure 7 shows that the thermoelectric

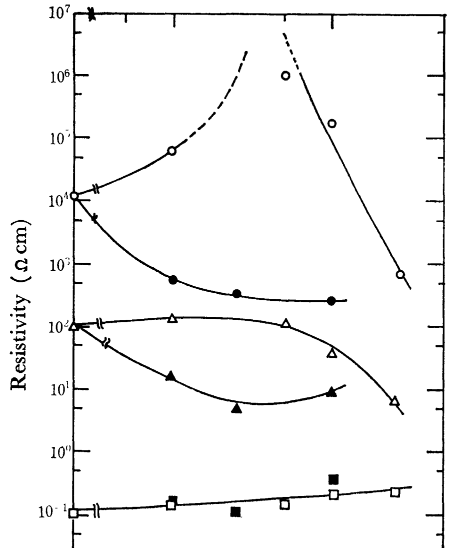

Fig. 5. Variation of resistivity with dopant concentration in Gd_2CuO_4.
○: room temperature for BaO, △: 200 °C for BaO-doping, □: 800 °C for BaO-doping, ●: room temperature for CaO-doping, ▲: 200 °C for CaO-doping, ■: 800 °C for CaO-doping.

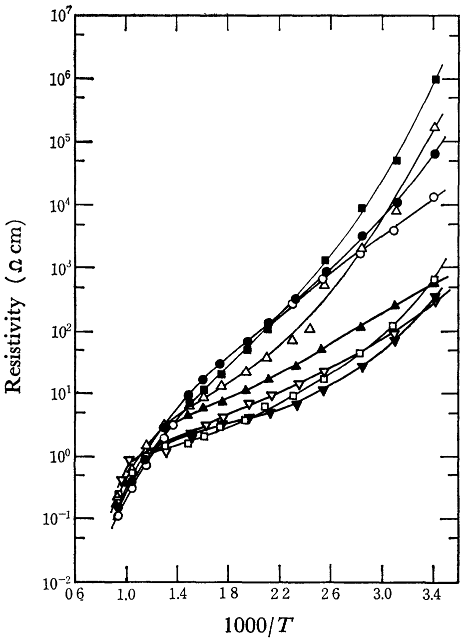

Fig. 6. Temperature dependence of resistivity for BaO- or CaO-doped Gd_2CuO_4.
○: undoped Gd_2CuO_4, ●: 0.1 mol% BaO, ■: 0.5 mol% BaO, △: 1 mol% BaO, □: 2.5 mol% BaO, ▲: 0.1 mol% CaO, ▲: 0.25 mol% CaO, △: 1 mol% CaO.

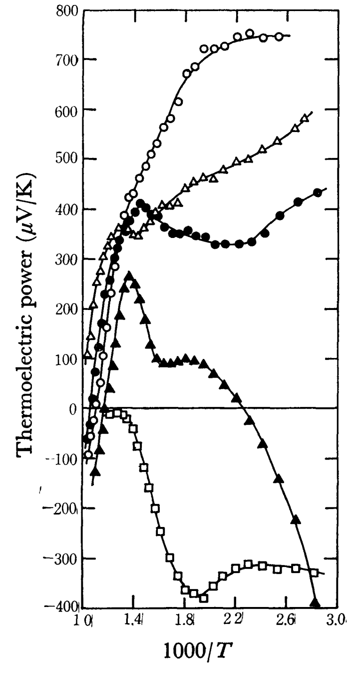

Fig. 7. Temperature dependence of thermoelectric power for CaO- or BaO-doped Gd_2CuO_4.
□: undoped Gd_2CuO_4, ○: 0.25 mol% CaO, △: 1 mol% CaO, ▲: 0.5 mol% BaO, ●: 2.5 mol% BaO.

power was changed from negative to positive values by doping the CaO.

The solubility of BaO in the Gd_2CuO_4 was between 2.5 and 5 mol%. The plots of the resistivity *vs.* the dopant concentration (Fig. 5) show the maximum resistivity value at 0.5 mol% BaO. Figure 6, showing the temperature dependence of the resistivity, is similar to the plots for the CaO-doped samples. The samples containing large amounts of BaO give positive thermoelectric powers, except in the high-temperature region (Fig. 7). The sample containing 0.5 mol% BaO, the resistivity of which is the maximum (Fig. 5), changes its sign of the thermoelectric power at 180 and 580 °C.

Figures 8, 9, and 10 show the data for the Gd_2CuO_4 doped both with ZrO_2 and with CaO simultaneously with a constant total mole value of the ZrO_2 and CaO.

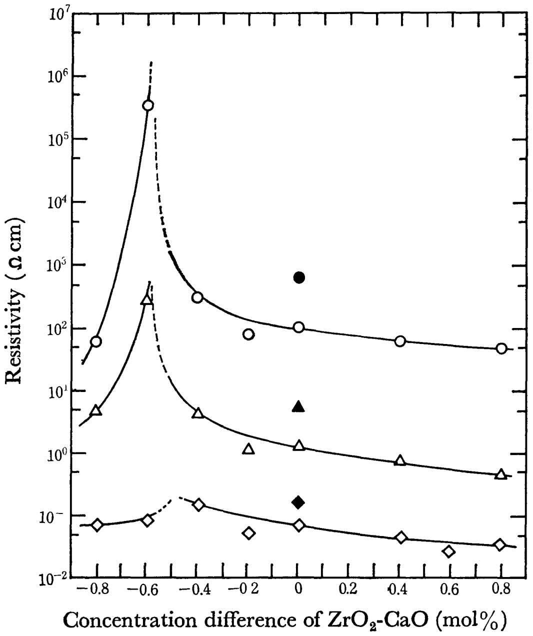

Fig. 8. Variation of resistivity with concentration difference, ZrO_2-CaO, in Gd_2CuO_4.
○: room temperature for ZrO_2+CaO=1 mol%, △: 200 °C for ZrO_2+CaO=1 mol%, ◇: 800 °C for ZrO_2+CaO=1 mol%, ●: room temperature for ZrO_2+CaO=10 mol%, ▲: 200 °C for ZrO_2+CaO=10 mol%, ◆: 800 °C for ZrO_2+CaO=10 mol%.

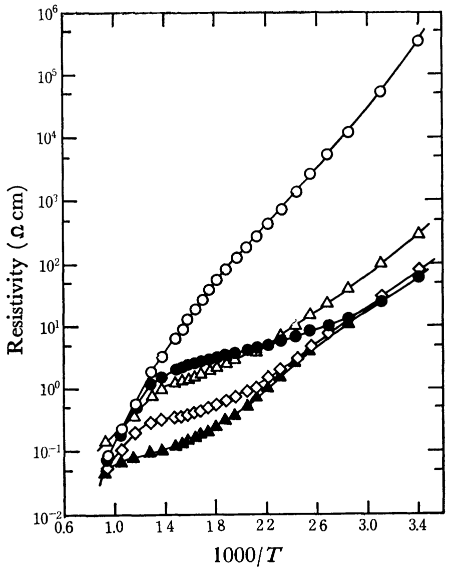

Fig. 9. Temperature dependence of resistivity for ZrO_2- and CaO-doped Gd_2CuO_4.
●: ZrO_2=0.1 mol%, CaO=0.9 mol%, ○: ZrO_2=0.2 mol %, CaO=0.8 mol%, △: ZrO_2=0.3 mol%, CaO=0.7 mol%, ◇: ZrO_2=0.4 mol%, CaO=0.6 mol%, ▲: ZrO_2=0.7 mol %, CaO=0.3% mol%.

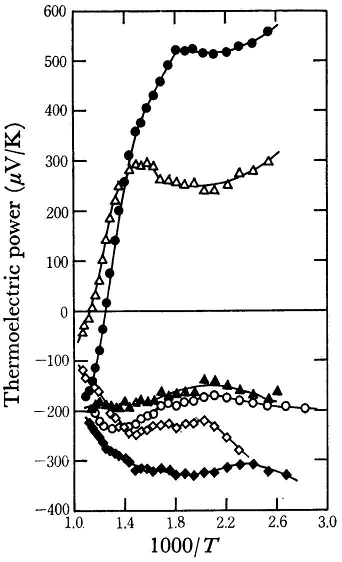

Fig. 10. Temperature dependence of thermoelectric power for ZrO_2- and CaO-doped Gd_2CuO_4.
△: $ZrO_2 = 0.1$ mol%, CaO$=0.9$ mol%, ●: $ZrO_2=0.2$ mol%, CaO$=0.8$ mol%, ◇: $ZrO_2=0.3$ mol%, CaO$=0.7$ mol%, ◆: $ZrO_2=0.4$ mol%, CaO$=0.6$ mol%, ○: $ZrO_2=0.5$ mol%, CaO$=0.5$ mol%, ▲: $ZrO_2=0.6$ mol%, CaO$=0.4$ mol%.

Figure 8 shows the dependence of the resistivity on the composition of ZrO_2–CaO in mol%. The ρ value is at its maximum at the concentrations of 0.2 and 0.8 mol% of ZrO_2 and CaO respectively. The CaO- and ZrO_2-rich samples show essentially the same trend as the CaO-doped and ZrO_2-doped samples respectively in the temperature dependence of their resistivities.

Discussion

The lattice sites occupied by a dopant can be estimated by the use of an X-ray diffractometer when the dopant concentration is higher than its sensitivity limit. When the ZrO_2, for example, is doped, the mole ratio of the raw oxide mixtures, $CuO:Gd_2O_3:ZrO_2$, is $1:1-x:x$ or $1-x:1:x$, where x is the dopant concentration. The former ratio is used when the ZrO_2 is expected to occupy the Gd^{3+} sites; the dopant in the latter case is expected to occupy the Cu^{2+} sites. If the ZrO_2 occupies the Gd^{3+} sites, the ZrO_2 phase will be found in the samples prepared in the latter fashion. If the ZrO_2 occupies the Cu^{2+} sites, the same phase will be found in the former samples. The X-ray diffraction data indicated that ZrO_2 phase was present in the samples when $CuO:Gd_2O_3:ZrO_2=1-x:1:x$, and that no ZrO_2 phase was present when $CuO:Gd_2O_3:ZrO_2=1:1-x:x$; $x<0.1$ for both cases. Consequently, the doped ZrO_2 or the ThO_2 was found to occupy the Gd^{3+} sites in the concentration region of $0.1>x>0.05$.

The X-ray diffraction data described above still leave two problems: (1) it is not known which sites are occupied by the dopants in the $x<0.05$ concentration region, and (2) a small amount of the ZrO_2 or ThO_2 may be present in the Cu^{2+} sites, although an X-ray diffractometer does not detect them. It is difficult to give a clear answer to the above problems, but the following assumptions may be made: (1) the ZrO_2 or ThO_2 occupies the Gd^{3+} sites also in the $x<0.05$ concentration region, and (2) the fraction of the Cu^{2+} sites which might be occupied by the dopants is so small that the electrical effects due to them are negligibly small. The above two assumptions seem reasonable, because the sites occupied by the dopants are unlikely to depend upon the dopant concentration, and because the ZrO_2 or ThO_2 is chemically more similar to Gd_2O_3 than to CuO.

The doped Gd_2CuO_4 decreases in its resistivity with an increase in the concentration of ZrO_2 up to 0.5 mol%. This suggests the presence of donor centers. The doped Zr^{4+} cations occupy the Gd^{3+} sites and may be initially reduced to Zr^{3+} cations to minimize the strain energy due to the oxygen vacancies, but the Zr^{3+} cations formed, if they were fixed at the sites, do not act as donor centers because they are on the Gd^{3+} sites, where an appreciable electron-overlapping cannot be expected.[1] The Cu^{+} ions, on the other hand, seem to be more probable donor centers, because they are on the Cu^{2+} sites, where an electron-overlapping *can* be expected.[1] The Cu^{+} ions are formed by the reduction of the Cu^{2+} ions while the Zr^{3+} ions are oxidized to Zr^{4+} ions—that is, $Cu^{2+}+Zr^{3+}=Cu^{+}+Zr^{4+}$. This reaction is an electron-transfer from the Zr^{3+} to Cu^{2+} ions, and results in excess positive and negative charges at the Zr^{4+} and Cu^{+} ion respectively. It is electrostatically unstable. However, the electrostatic energy needed for the electron-transfer is compensated for by the energy difference between the Cu^{+} formation and the excitation of the Zr^{3+} to the Zr^{4+} ion, because the Cu^{+} ion seems to be more stable than the Zr^{3+} ion.

The increase in the resistivity with the increase in the concentration of ZrO_2 beyond 0.5 mol% is unexpected. An increase in the resistivity is usually ascribable to a decrease in the number of carriers or to a decrease in the mobility.[3,5,6] In this case, however, a decrease in the number of carriers is not likely, because such a doping effect as would decrease the number of carriers cannot be expected. A decrease in the mobility is not likely either, although the mobility might be lowered because of the electron scattering by the lattice vacancies. Therefore, some changes in the grain boundary are more likely to be causes of the above fact. As can be seen in Fig. 2, the less dense specimen is greater than the denser one in its resistivity, while the slopes in the log ρ *vs.* $1/T$ plots are the same. This is simply because the less dense sample is smaller than the denser one in the contacting area of the grains. The ZrO_2 dopant, on the other hand, enhances not only the resistivity but also the slopes of the plots. Therefore, a decrease in the contacting area of the grains, which is one of the changes in the grain boundary, is not a cause of the increase in the resistivity with the increase in the concentration of ZrO_2. Another possible change in the grain boundary would be a deposit of some insulators on the grain boundary. A small amount of ZrO_2, for example, one too small to be detected by an X-ray diffractometer, might increase both the resistivity and the activation energy of the samples.

The previous work[1)] revealed that the resistivity of Ln_2CuO_4 decreases with a decrease in the atomic number of Ln. This fact was explained as being due to: (1) a variation in the activation energy, or (2) a variation in the number of the donor centers formed by the thermal decomposition of the Cu^{2+} to the Cu^+ ions. However, it is not known which factor is the more important. The activation energy corresponds to the energy gaps between the split 3d-electron energy levels of the Cu^{2+} ions, which are affected by the ligand-field strength at the Cu^{2+} sites.[1)] The ligand-field strength is determined by the distance between the Cu^{2+} ions and the closest neighbors. Since no change is indicated in the lattice parameters of the doped Gd_2CuO_4, the distance described above may also be unchanged by doping. On the basis of the above discussion and the X-ray diffraction data, it seems reasonable to assume that the ligand-field strength at the Cu^{2+} sites is unchanged by doping; therefore, the doping method varies the number of donor centers without a great variation in the activation energy. The activation energy is related to the thermoelectric power by this equation: $\alpha \propto -E/T$, for the Maxwell distribution, where α is the thermoelectric power; E, the activation energy, and T, the temperature.[1,3)] Therefore, the dopants are expected to lower the resistivity without a great variation in the thermoelectric power. In fact, Fig. 2 shows that the Gd_2CuO_4 doped with 0.5 mol% ZrO_2 is lower than the Pr_2CuO_4[1)] in its resistivity, while the former is greater than the latter in its thermoelectric power. The $\alpha \propto -E/T$ relationship is applied to the data for the Ln_2CuO_4 compounds. If the trend for the resistivity of the Ln_2CuO_4 to decrease with a decrease in the atomic number of Ln was simply due to an increase in the number of donor centers, and not to a variation in the activation energy, the thermoelectric powers of the Ln_2CuO_4 compounds would not depend upon the atomic number of Ln. However, their thermoelectric powers increase with an increase in the atomic number of Ln,[1)] suggesting that the above trend is ascribable to an increase in the activation energy. The X-ray diffraction data seem to support this suggestion; the lattice parameter of the tetragonal Ln_2CuO_4, c/a, increases with a decrease in the atomic number of Ln.[1,4)]

Figure 5 shows that the resistivity decreases with an increase in the concentration of CaO, suggesting a formation of acceptor centers. It has been suggested on the basis of the X-ray diffraction results that the doped Ca^{2+} or Ba^{2+} ions occupy the Gd^{3+} sites. If they occupy the Gd^{3+} sites without oxygen vacancies, the doped alkaline earth cations would be forced to be in a trivalent state. Trivalent alkaline earth cations, however, are very unstable. The Cu^{2+} ions, on the other hand, seem to be more readily oxidized to Cu^{3+} ions, although the Cu^{3+} ions may still be unstable. As in the case of the Cu^+ formation, the formation of the Cu^{3+} ions is an electron transfer from the Cu^{2+} ions to the Ca^{3+} ions which might be initially formed. This electron-transfer is again electrostatically unstable. The electrostatic energy needed for the electron-transfer may be compensated for by the energy difference between the formation of the divalent alkaline earth cations and the excitation of the Cu^{2+} to Cu^{3+} ions. The Cu^{3+} ions would not be very stable, so many acceptor centers cannot be expected to be formed. This may be one of the reasons why the CaO-doping is not so effective on the resistivity-lowering as the ZrO_2- or ThO_2-doping. The presence of the acceptor centers is directly suggested by the positive thermoelectric power (Fig. 7).

The number of acceptor centers formed at a given dopant concentration is such a number as will minimize the total energy of the strain due to the oxygen vacancies and that of the excitation of the Cu^{2+} to Cu^{3+} ions. The strain energy may be made smaller by doping larger cations. Therefore, the number of acceptor centers formed at a given dopant concentration can be made smaller by doping larger cations. The experimental results for the BaO-doped Gd_2CuO_4 show the expected behavior (Figs. 5—7). The resistivity increases with an increase in the dopant concentration in the concentration region of $x<0.5$ mol%. The sample doped with 0.5 mol% BaO shows a medium trend between the undoped and 2.5 mol% BaO-doped samples in the temperature dependence of the thermoelectric power. These data suggest that the donor centers initially formed by the thermal decomposition are recombined with the acceptor centers formed by doping the BaO, and that the former still number more than the latter. In concentration region of $x<0.5$ mol%, the CaO-doped samples are p-type semiconductors and decrease in resistivity with an increase in the concentration of the CaO. These results indicate that the BaO dopant at a given concentration produces a smaller number of acceptor centers than the CaO dopant. In the concentration region of $x>0.5$ mol%, the BaO-doped samples behave much like the CaO-doped ones; the resistivity decreases with an increase in the concentration of BaO, and the thermoelectric power is positive, over the temperature range investigated. These facts suggest that the acceptor centers number more than the donor centers in this concentration region.

The recombination of the donors with the acceptors can be made by doping the ZrO_2 and CaO simultaneously. Since the donor centers consist of Cu^+ ions formed by the ZrO_2-doping and those formed by the thermal decomposition of the Cu^{2+} ions, the dopant concentration where the resistivity is at its maximum will shift to a CaO-rich composition because of the donor centers formed by the thermal decomposition. Figure 8 shows the expected results; the maximum resistivity can be seen at $CaO=0.8$ mol% and $ZrO_2=0.2$ mol%. The thermoelectric power data correspond to the resistivity data; the sign is changed at the same concentration.

On the basis of the series of data shown in Figs. 5 to 10, it can be concluded that the most important donor centers in the Ln_2CuO_4 compounds are the Cu^+ ions formed by the thermal decomposition of the Cu^{2+}

ions.

An attempt to dope Ag_2O and In_2O_3 was unsuccessful. This failure may be partly due to too great a difference in the ionic radii between the Cu^{2+} ion and either the Ag^+ or the In^{3+} ion (Cu^{2+}=0.72 Å, Ag^+= 0.97 Å, and In^{3+}=0.81 Å) and partly to too small a latitude of the Cu^{2+} site for the ionic size. This may be related to the covalent nature of the Cu–O bonds.