JOURNAL OF SOLID STATE CHEMISTRY 112, 222–227 (1994)

Studies on the Conduction Process of Cadmium-Substituted Copper Chromite Spinels

D. Basak and J. Ghose[1]

Department of Chemistry, Indian Institute of Technology, Kharagpur 721 302, India

Received June 16, 1993; in revised form November 1, 1993; accepted November 4, 1993

Electrical resistivity (ρ) and thermoelectric power (α) measurements were carried out in air on $Cu_{1-x}Cd_xCr_2O_4$ ($0 \leq x \leq 1.0$) spinel oxides in the temperature ranges 300–873 K and 300–723 K, respectively. Thermal activation energy (E_a), carrier concentration (n), activation energy for carrier concentration generation (E_n), and mobility (μ) values have been calculated from the resistivity and thermoelectric power data. The results show that conduction in cadmium-substituted $CuCr_2O_4$ samples is by hopping of charge carriers on the octahedral sites. The charge carrier hopping is, however, impeded at lower temperatures due to the larger Cr_{oct}–Cr_{oct} distance when the large Cd^{2+} ion (97 pm) is substituted for the Cu^{2+} ion (72 pm) in the tetrahedral site of the $CuCr_2O_4$ lattice. The temperature dependence of α shows a change in the sign of the slope at the temperature at which hopping conduction becomes evident. © 1994 Academic Press, Inc.

INTRODUCTION

$CuCr_2O_4$ is a tetragonally distorted normal spinel undergoing a tetragonal-to-cubic phase transition at 800 K (1–3). Electrical resistivity measurements on $CuCr_2O_4$ have shown that the tetragonal-to-cubic phase transition is manifested as a hysteresis loop in the log ρ vs $1/T$ heating and cooling plots and p-type conduction in $CuCr_2O_4$ is by hopping of charge carriers between the octahedral site Cr^{3+} and Cr^{4+} ions (4). Electrical resistivity measurements on $Cu_{1-x}Mg_xCr_2O_4$ and $CuCr_{2-x}Al_xO_4$ samples indicated that the conduction mechanism does not change when Cu^{2+} is substituted by Mg^{2+} or Cr^{3+} is substituted by Al^{3+} (5). Thermoelectric power measurements on Cu Cr_2O_4 show p-type conduction and the Seebeck coefficient (α) increases with increasing temperature. This is quite unusual for a semiconductor but has also been found in other semiconductors reported earlier (5, 6); in p-type magnesium-substituted chromite spinels, i.e., $Cu_{1-x}Mg_x$ Cr_2O_4, Padmanaban found an increasing trend of α with increasing temperature (7). However, in aluminum-substituted $CuCr_2O_4$ spinels, i.e., $CuCr_{2-x}Al_xO_4$, it is observed that the conduction type changes from p-type to n-type and initially α decreases with increasing temperature—the usual change expected for a semiconductor—but above a certain temperature α increases with increasing temperature (5).

The aim of the present work was to investigate the effect of substituting Cd^{2+} in $CuCr_2O_4$ ($Cu_{1-x}Cd_xCr_2O_4$) on the conduction type of the spinel chromite and to study the temperature dependence of the Seebeck coefficient.

EXPERIMENTAL

Solid solutions of $Cu_{1-x}Cd_xCr_2O_4$ for x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.45, 0.6, 0.8, and 1.0 were prepared following the usual ceramic technique described elsewhere (8).

X-ray diffraction analyses of all the samples were carried out using a Philips X-ray diffraction until (Model PW 1710) using Cu$K\alpha$ radiation with a Ni filter.

Resistivity measurements and thermoelectric power measurements of all the samples were carried out in air in the temperature ranges 300–873 K and 300–723 K following the procedure described elsewhere (4, 5). All the samples were annealed before each measurement to eliminate any grain boundary effect.

RESULTS

Table 1 gives the chemical compositions of various cadmium-substituted $CuCr_2O_4$ samples and their code names, degree of tetragonality (c_0/a_0), distance between octahedral site cations (B–B distance), and room temperature resistivity (ρ).

Resistivities of all the samples followed the exponential law

$$\rho = \rho_0 \exp(E_a/kT)$$

in the studied temperature range, where ρ is resistivity in ohm-cm, T the absolute temperature, k the Boltzmann constant, and E_a the thermal activation energy. Figures 1 and 2 show the log ρ vs $1/T$ heating and cooling plots for all the cadmium-substituted copper chromite samples, i.e., $Cu_{1-x}Cd_xCr_2O_4$ (x = 0.0 to 1.0). The results in Figs.

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[1] To whom correspondence should be addressed.

0022-4596/94 $6.00

TABLE 1
Sample Composition, Code Name, c_0/a_0, Apparent B–B Distance, and Room Temperature Resistivity (ρ) in $Cu_{1-x}Cd_xCr_2O_4$ System

Sample composition	Code name	c_0/a_0	B–B distance (Å) (±0.003)	ρ (ohm-cm)
$CuCr_2O_4$	CD0	0.915	2.912	1.00×10^5
$Cu_{0.9}Cd_{0.1}Cr_2O_4$	CD1	0.925	2.930	7.08×10^4
$Cu_{0.8}Cd_{0.2}Cr_2O_4$	CD2	0.930	2.932	5.62×10^4
$Cu_{0.7}Cd_{0.3}Cr_2O_4$	CD3	0.940	2.946	1.12×10^5
$Cu_{0.6}Cd_{0.4}Cr_2O_4$	CD4		2.976	1.12×10^5
$Cu_{0.4}Cd_{0.6}Cr_2O_4$	CD6		2.982	1.77×10^5
$Cu_{0.2}Cd_{0.8}Cr_2O_4$	CD8		3.006	2.818×10^5
$CdCr_2O_4$	CD10		3.015	7.94×10^6

1 and 2 show that for all the samples, the cooling plots retrace the heating plots except in the temperature range where a hysteresis loop appears in heating and cooling plots of the tetragonal samples. The experiments were repeated several times and the results were always found to be reproducible. The heating plots were not retraced by the cooling plots in the unannealed samples, a result attributed to grain boundary effect (4). Table 1 shows that the room temperature (~300 K) resistivity values (ρ) do not change with cadmium substitution, except for $CdCr_2O_4$. Thermal activation energy (E_a) values have been calculated for cadmium-substituted $CuCr_2O_4$ samples from the slopes of the log ρ vs $1/T$ plots and are given in Table 2.

The reduced thermoelectric power α' ($\alpha' = \alpha e/k$) vs $1/T$ plots for all the cadmium-substituted $CuCr_2O_4$ samples are shown in Fig. 3. The results show that the $Cu_{1-x}Cd_xCr_2O_4$ samples remain p-type in the temperature range

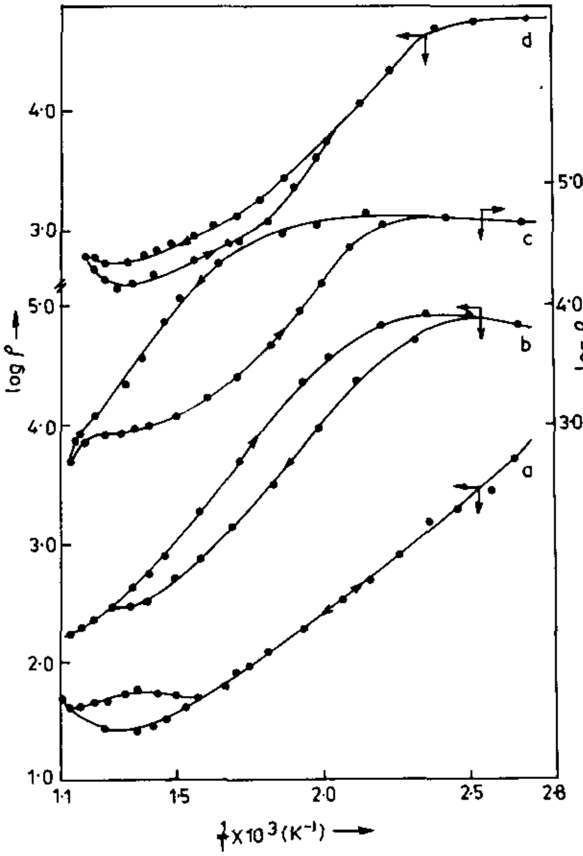

FIG. 1. Heating and cooling plots of log ρ vs $1/T$ for (a) CD0, (b) CD1, (c) CD2, and (d) CD3.

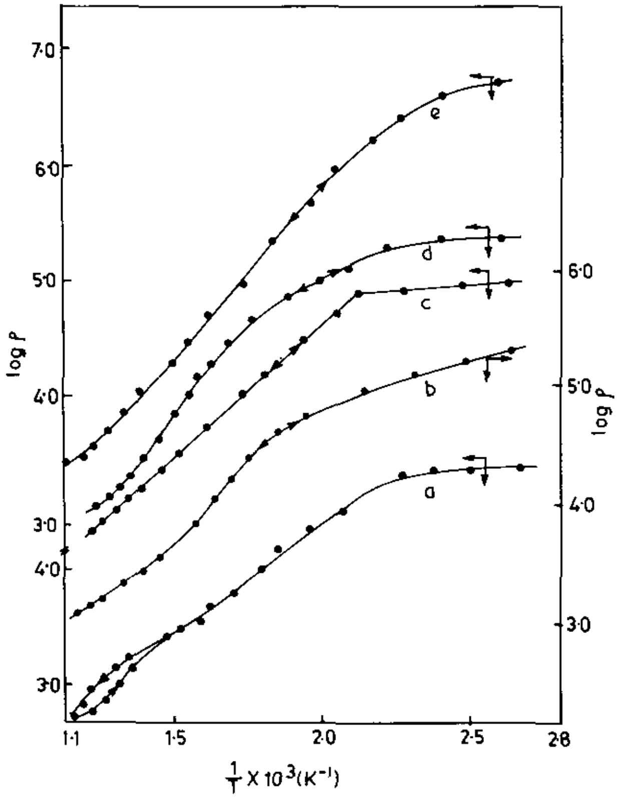

FIG. 2. Heating and cooling plots of log ρ vs $1/T$ for (a) CD4, (b) CD5, (c) CD6, (d) CD8, and (e) CD10.

TABLE 2

Density of States (N), Charge Carrier Concentration (n), Optical Phonon Frequency (ν_0), Thermal Activation Energy (E_a) and Activation Energy for Charge Carrier Generation (E_n) for Various $Cu_{1-x}Cd_xCr_2O_4$ Samples

				Temperature range			
				313–473 K		473–773 K	
Sample code	$N \times 10^{22}$ (cm^{-3})	n (cm^{-3})	ν_0 (sec^{-1})	E_a (eV)	E_n (eV)	E_a (ev)	E_n (eV)
CD0	5.727	5.10×10^{21}	3.30×10^{11}	0.40	0.11	0.35	0.73
CD1	5.621	2.03×10^{21}	1.83×10^{11}	0.14	0.15	0.58	0.19
CD2	5.609	2.68×10^{21}	7.38×10^{11}	0.0	0.20	0.65	0.20
CD4	5.367	3.02×10^{22}	2.50×10^{9}	0.04	0.33	0.36	0.17
CD6	5.337	1.50×10^{22}	1.37×10^{10}	0.04	0.58	0.45	0.49
CD8	5.208	1.09×10^{22}	4.61×10^{9}	0.09	0.46	0.56	0.62
CD10	5.162	4.10×10^{22}	8.43×10^{9}	0.16	0.41	0.56	0.30

studied. However, the plots show a change in the sign of the slope above a certain temperature. From the values of α, the values of carrier concentration n have been calculated using the formula

$$n = N \exp(-\alpha/k),$$

where N is the density of states involved in the conduction process, k is the Boltzmann constant, and α is the Seeback coefficient. N values have been calculated following the method of Metselaar *et al.* (10) and are shown in Table 2.

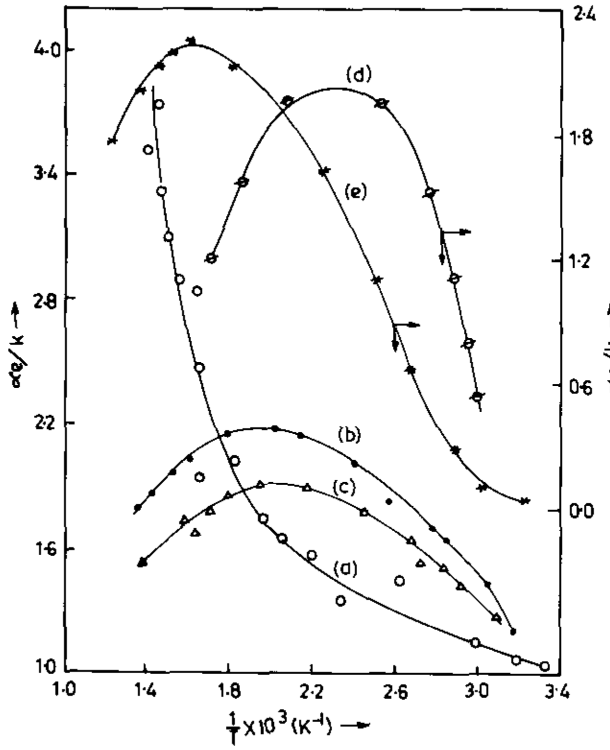

FIG. 3. Plots of $\acute{\alpha}$ vs $1/T$ for (a) CD0, (b) CD1, (c) CD3, (d) CD6, and (e) CD10.

The plots of ln n vs $1/T$ for $CuCr_2O_4$ and cadmium-substituted samples are shown in Fig. 4. The plots show that carrier concentration decreases linearly up to ~200 K, and above this temperature, it increases. For $CuCr_2O_4$, however, n always decreases with increasing temperature, the decrease being much steeper above ~200 K. From the slope of the plot, E_n was calcualted following Morin *et al.* (11) and the values are shown in Table 2.

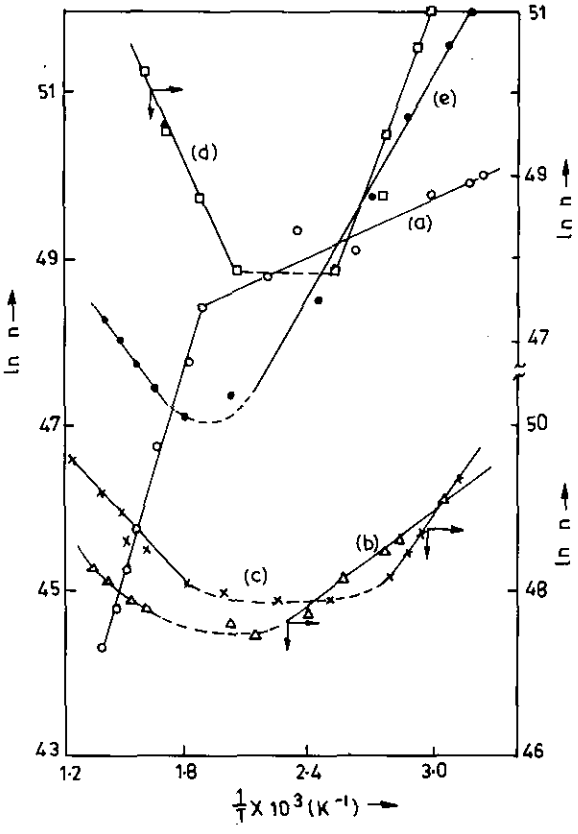

FIG. 4. Plots of ln n vs $1/T$ for (a) CD0, (b) CD1, (c) CD3, (d) CD6, and (e) CD10.

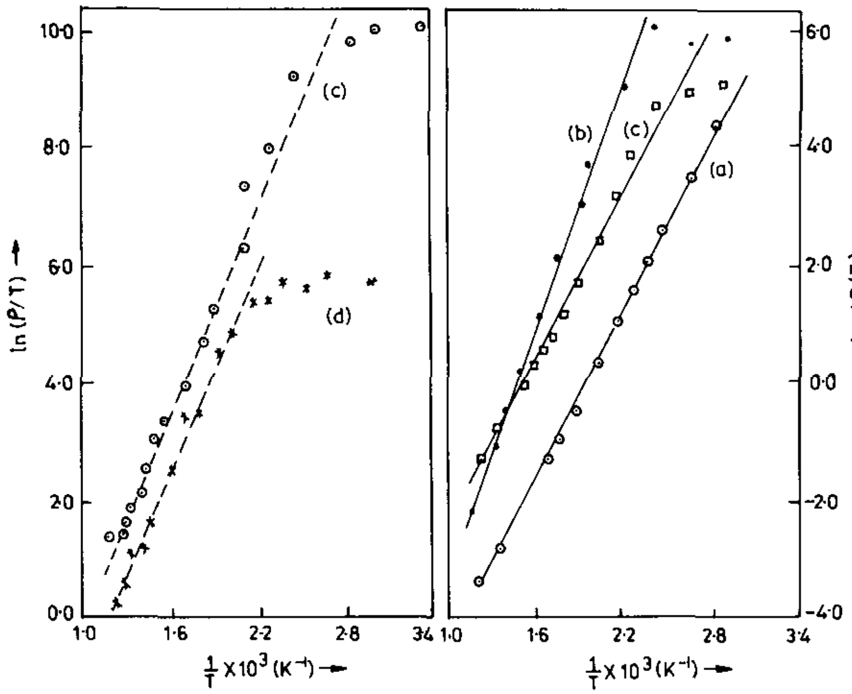

FIG. 5. Plots of ln (ρ/T) vs $1/T$ for (a) CD0, (b) CD2, (c) CD3, (d) CD6, and (e) CD10.

ln (ρ/T) vs $1/T$ plots for $Cu_{1-x}Cd_xCr_2O_4$ samples are shown in Fig. 5. For $x = 0.0$ (CDO), the plot is linear, but for $x > 0$, the plots become nonlinear, particularly at low temperatures. Taking the linear part of the ln (ρ/T) vs $1/T$ plots, the optical phonon frequency values (ν_o) and mobility values (μ) at different temperatures have been calculated following the procedure described in Ref. (10). Table 2 shows that the optical phonon frequencies (ν_o) do not change much up to $x = 0.2$ but for $x > 0.2$, they change. Figure 6 shows that the mobility values of Cu Cr_2O_4 show some change at lower temperatures but remain unchanged at higher temperatures. The mobilities of the cadmium substituted samples increase at higher temperatures but show very little change at lower temperatures.

DISCUSSION

Earlier studies by Basak *et al.* (8) have shown that a complete solid solution, i.e., $Cu_{1-x}Cd_xCr_2O_4$ ($x = 0$ to $x = 1.0$), is formed when copper is substituted by cadmium in $CuCr_2O_4$ spinel oxide and the samples with $x \leq 0.4$ are tetragonal. The results of resistivity measurements on $Cu_{1-x}Cd_xCr_2O_4$ show very little change in the room temperature resistivity with x except for $CdCr_2O_4$. The log ρ vs $1/T$ heating and cooling plots of the tetragonally distorted cadmium-substituted samples in Figs. 1 and 2 show the presence of hysteresis loops similar to the plot of $CuCr_2O_4$. In $CuCr_2O_4$, the presence of a hysteresis loop in the log ρ vs $1/T$ heating and cooling plots was attributed to a reversible, diffusionless, fast, martensitic type of phase transition (tetragonal to cubic) (4) and hence the presence of a hysteresis loop in the log ρ vs $1/T$

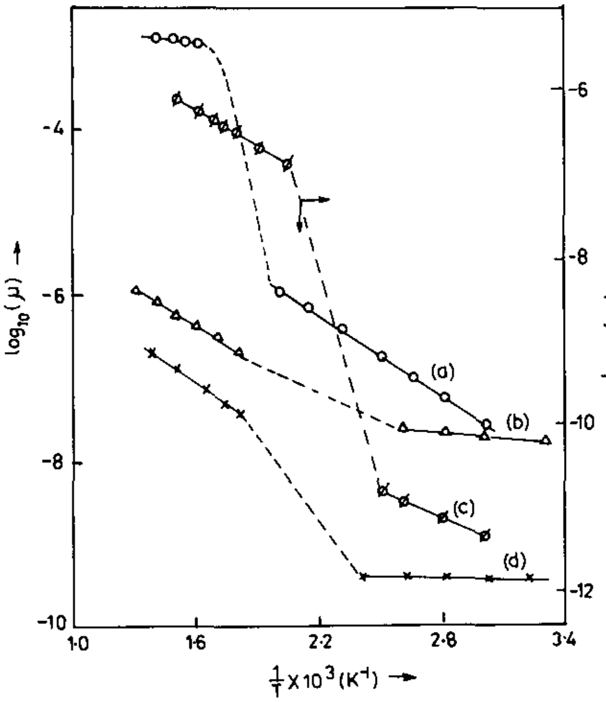

FIG. 6. Plots of $\log_{10} \mu$ vs $1/T$ for (a) CD0, (b) CD3, (c) CD6, and (d) CD10.

plots of cadmium-substituted samples suggests that these samples also undergo tetragonal to cubic phase transition. However, in the absence of high temperature X-ray data, the phase change temperatures could not be ascertained. Also the formation of cubic phase at high temperatures could not be recorded. Figure 1 shows the presence of a very small hysteresis loop in CD4, which suggests that this sample is tetragonal. Its X-ray pattern, however, shows only broad lines and could not be identified as a tetragonal sample. The plot of CD5 has no hysteresis loop, indicating that it is a cubic sample not undergoing any phase transition. These results indicate that the $Cu_{1-x}Cd_x Cr_2O_4$ samples with $x \geqslant 0.45$ are cubic spinels, which could not be ascertained from X-ray powder diffraction analysis alone.

Thermoelectric power (α) measurements show that all the cadmium-substituted $CuCr_2O_4$ samples are p-type in the temperature range studied. This is expected, as the valencies of copper and chromium are not changed by cadmium substitution. The results of reduced thermoelectric power (α') in Fig. 3 show that in the cadmium-substituted samples, as in $CuCr_2O_4$, α' increases with increasing temperature. However, this trend changes above a certain temperature and α' decreases with increasing temperature. This behavior is observed even for a very small substitution of cadmium ($x = 0.2$).

The values of the charge carrier density (n) calculated from α show that in $CuCr_2O_4$, n decreases with increasing temperature, but in the cadmium-substituted samples, initially n decreases and then increases (Fig. 4) as has been found in various other ferrites (9). The mobilities of these samples increase with rise in temperature, the initial increase being very small (Fig. 6). The mobility of $CuCr_2O_4$, however, increases initially but then becomes constant. These results suggest that the cadmium-substituted chromite spinels remain p-type for all the values of x, i.e., 0.0 to 1.0, and show normal semiconductor behavior only above a certain temperature. As the Cr^{3+}_{oct} content is not altered during Cu^{2+}_{tet} substitution by Cd^{2+}, the charge carrier concentration is expected to be the same in all the samples; this is shown in the values of n calculated at room temperature for the various $Cu_{1-x}Cd_xCr_2O_4$ samples (Table 2).

In order to ascertain the conduction mechanism in these samples, E_n values were compared with E_a values. Table 2 shows that in the tetragonal samples, particularly in the higher temperature range, $E_a > E_n$, which implies that hopping conduction occurs in all these samples. For $CuCr_2O_4$, in the lower temperature range, $E_a > E_n$ and the mobility also increases with an increase in temperature, showing that in this spinel oxide hopping conduction occurs, as was suggested by Murthy *et al.* (4). However, in the high temperature range, $CuCr_2O_4$ shows that $E_n > E_a$. Also, the mobility does not show any change in this temperature range. This implies that at higher temperatures, the conduction in $CuCr_2O_4$ is probably not by charge hopping. Also the carrier density changes by almost one order of magnitude in this temperature range. These results suggest that at higher temperatures, $CuCr_2O_4$ may be following band conduction, as was found by Reddy *et al.* for lithium ferrites (9). However, in the latter as well as in $CuCr_2O_4$, the mobilities are smaller than is usually found in band conduction. Moreover, Padmanaban *et al.* (5) have shown that for $CuCr_2O_4$, the $\ln(\rho/T)$ vs $1/T$ plot is linear and the calculated ν_0 values are in the optical phonon frequency range, implying hopping conduction in the temperature range studied. Thus it seems that even if $E_n > E_a$ and the mobility is independent of temperature, the semiconductor may not follow band conduction. However, the results of $CuCr_2O_4$ do indicate that some change in its conduction process is occurring above ~500 K. Figure 5 shows that for $Cu_{1-x}Cd_xCr_2O_4$ samples, $\ln(\rho/T)$ vs $1/T$ plots are linear above 370 K for $0 < x < 0.4$, i.e., in the tetragonal samples only. The plots of the cubic samples are nonlinear, the values are also smaller, and comparison of E_n and E_a values seems to suggest that these samples follow band conduction. However, too much emphasis cannot be put on the ν_0 values, as these have been calculated from the approximated, linear portions of the $\ln(\rho/T)$ vs $1/T$ plots. Large distances between the octahedral site cations (Table 1) cannot favor band formation by orbital overlap, and hence these semiconductors cannot be expected to follow band conduction. The small mobility values also do not support band conduction. Thus it appears that the substitution of a larger Cd^{2+} ion (97 pm) for Cu^{2+} (72 pm) in the tetrahedral site of the spinel lattice does not change the conduction type to band conduction, but seems to impede the hopping of charge carriers between the octahedral site cations, and so there is very little change in resistivity as the temperature is increased (Figs. 1 and 2). However, as the temperature continues to increase, the impediment is reduced, which is manifest in an increase in conductivity, mobility, and number of the charge carriers. Thus, at lower temperatures, $\ln(\rho/T)$ changes nonlinearly with temperature, but as temperature increases, hopping of the charge carriers between the octahedral site cations become possible, giving rise to linear $\ln(\rho/T)$ vs $1/T$ plots. From these results it may be concluded that substitution of Cd^{2+} in $CuCr_2O_4$ does not change the conduction type of the spinel oxide; i.e., it remains p-type and as in $CuCr_2O_4$, conduction in $Cu_{1-x}Cd_xCr_2O_4$ samples are by hopping of holes between the octahedral site cations.

ACKNOWLEDGMENTS

The authors thank DST for financial support and Professor A. K. Kar for his constant encouragement and help.

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