

Studies on the Decomposition of N₂O on the Solid Solution La₂Cu_{1-x}Ni_xO₄ (0 ≤ x ≤ 1)

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A series of solid-solution members having the formula La₂Cu_{1-x}Ni_xO₄ (0 ≤ x ≤ 1) have been synthesized and characterized using X-ray, electrical, and magnetic measurements. Decomposition of nitrous oxide has been carried out on these compounds at two different initial pressures, namely 50 and 200 Torr, in the temperature range 350–480°C. The observed irregular trends in the kinetics of decomposition on the solid-solution series have been interpreted on the basis of a solid-state polaron hopping mechanism. Physicochemical correlations observed between activity and frequency factor as also magnetic ordering have also been explained in light of the above mechanism. © 1985 Academic Press, Inc.

INTRODUCTION

In recent years, studies on various ternary and quaternary oxides with perovskite and perovskite-related structures have increased the applicability of these materials to serve as suitable substitutes for noble metals in a variety of areas including auto-exhaust conversion (1), electrocatalytic fuel cell electrodes (2), and oxidation reactions (3). Among various types of perovskites, those crystallizing with K₂NiF₄ structure have been found to exhibit interesting structural, solid-state, and catalytic properties (4). Many interesting oxides of the type Ln₂CuO₄ and Ln₂NiO₄ do crystallize in this structure. The coordination of the divalent transition metal ion is essentially six, while the trivalent rare earth ion prevails in a nine-coordinated oxide ion environment. Although compounds having substitutional pairs of cations at nine-coordinated sites are well known (5–10) very few reports in relation to octahedral substitution are available in the literature (11–13). In one of our

earlier communications (14), we reported the crystallographic study of the system La₂Cu_{1-x}Ni_xO₄ (0 ≤ x ≤ 1). Tetsuichi *et al.* (15) have recently examined the potentiality of various materials including La₂Cu_{0.1}Ni_{0.9}O₄ and La₂Cu_{0.5}Ni_{0.5}O₄ for the catalytic reduction of NO with ammonia. A significant improvement observed in the catalytic properties of these materials with the doping of small amounts of nickel in the lattice of La₂CuO₄ instigated a detailed investigation of relative catalytic efficiencies of the members of the solid-solution system La₂Cu_{1-x}Ni_xO₄ (0 ≤ x ≤ 1) toward the decomposition of N₂O. The present study is also aimed at gaining an insight into the functioning of these materials toward oxidation reactions.

MATERIALS AND METHODS

The solid-solution series La₂Cu_{1-x}Ni_xO₄ has been synthesized by firing a stoichiometric mixture of lanthanum oxalate, copper oxalate, and nickel dimethyl glyoxime (NiDMG) at 980°C for 26 h in air. The details of the structural characterization are reported elsewhere (14). The importance of NiDMG in the preparation of this series, lies in reducing the extent of nonstoi-

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TABLE I
Physicochemical Parameters for the Solid Solution $\text{La}_2\text{Cu}_{1-x}\text{Ni}_x\text{O}_4$ ($0 \leq x \leq 1$):

Compound	Symmetry ^a	Lattice parameters ^b			Surface area (m ² /g)	Seebeck coefficient ($\mu\text{V} \cdot \text{K}^{-1}$)	Magnetic susceptibility (CGS units) α^c	t^d
		<i>a</i>	<i>b</i>	<i>c</i>				
La_2CuO_4	O	5.362	5.409	13.169	0.5	228.0	0.165	0.863
$\text{La}_2\text{Cu}_{0.8}\text{Ni}_{0.2}\text{O}_4$	O	5.393	5.427	13.110	3.2	240.0	1.196	0.866
$\text{La}_2\text{Cu}_{0.6}\text{Ni}_{0.4}\text{O}_4$	O	5.406	5.419	12.995	2.1	270.0	2.158	0.868
$\text{La}_2\text{Cu}_{0.5}\text{Ni}_{0.5}\text{O}_4$	T	3.813	—	13.010	1.5	320.1	2.371	0.869
$\text{La}_2\text{Cu}_{0.4}\text{Ni}_{0.6}\text{O}_4$	T	3.836	—	13.017	0.3	350.2	2.101	0.870
$\text{LaCu}_{0.2}\text{Ni}_{0.8}\text{O}_4$	T	3.851	—	12.838	1.1	470.0	2.882	0.873
La_2NiO_4	T	3.865	—	12.660	0.4	600.2	4.538	0.875

^a O, orthorhombic; T, tetragonal.

^b In Ångstroms.

^c $\times 10^{-6}$.

^d Tolerance factor.

chiometry across the members. It has been realized that La_2NiO_4 prepared from lanthanum oxalate and NiDMG possessed higher activity owing to the low concentration of nickel(III) in this compound, compared to those prepared from either basic oxides or mixed oxalates (16). The tolerance factor values calculated from an expression suggested by Ackermann (17), are found to fall in the range prescribed for K_2NiF_4 -type oxides. The electrical conduction properties of the system were evaluated by means of a conventional two-probe cell. The variation of the electrical conduction with temperature in these oxides has been found to change gradually from La_2CuO_4 to La_2NiO_4 . For samples with $x > 0.5$ there is a transition in the semiconducting behavior around 260–300°C. The tetragonal crystal fields, which generally stabilize the $d_{x^2-y^2}$ orbitals relative to d_{z^2} orbitals in the K_2NiF_4 structure, can be assumed to stabilize a narrow $\sigma_{x^2-y^2}^*$ band as compared to that of $d_{z^2}^1$ level by about half the bandwidth (18). The electrostatic energy of the crystal is deemed to split the $\sigma_{x^2-y^2}, d_{z^2}^1$ band into two levels, which are responsible for the shift in the semiconducting property for samples with $x > 0.5$. The Seebeck coefficient values indicated that all these oxides are essentially *p*-type in nature.

The room-temperature magnetic susceptibility measurements were carried out in a

Guoy balance employing a field of 5000 G. The surface areas of these samples have been evaluated in a conventional BET apparatus using N_2 as adsorbate at liquid-nitrogen temperature. The physicochemical properties are presented in Table I.

The decomposition of nitrous oxide has been tested in a static reactor fitted with a gas recirculation assembly. The catalyst was subjected to the following pretreatment between the kinetic runs: (i) evacuation at 10^{-6} Torr and 500°C for 6 h; (ii) treatment with 100 Torr of oxygen gas at reaction temperature for 12 h; and (iii) mild evacuation at 10^{-3} Torr to remove gas-phase and weakly adsorbed oxygen. Two different initial pressures, namely 50 and 200 Torr, have been employed in the present investigation. The conversion at both the pressures has been limited to 6–15% per hour at any temperature to obtain a diffusion-free kinetic behavior. Further, the absence of heat and mass transfer processes featured in the rate-controlling steps has been confirmed by performing the kinetics at various recirculation rates of the reactant gas.

RESULTS AND DISCUSSION

The kinetics of the title decomposition reaction has been analyzed taking into consideration the following two equations (19)

$$-dP_{\text{N}_2\text{O}}/dt = k_1 P_{\text{N}_2\text{O}} \quad (1)$$

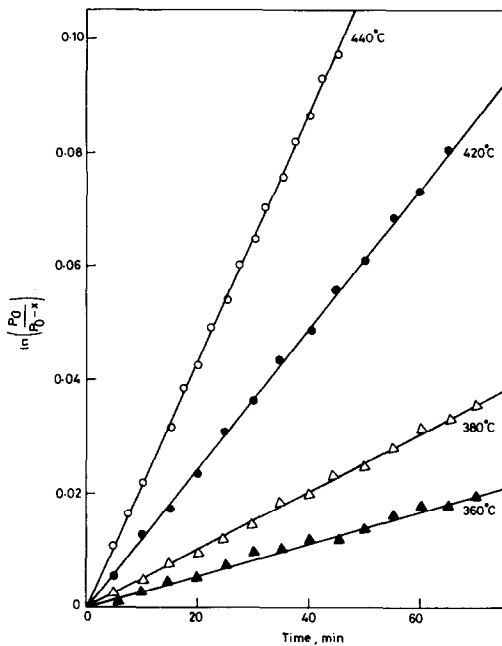


FIG. 1. Kinetic plots for N₂O decomposition at an initial pressure of 50 Torr on La₂Cu_{0.5}Ni_{0.5}O₄.

$$-dP_{\text{N}_2\text{O}}/t = k_2 P_{\text{N}_2\text{O}}/(P_{\text{O}_2})^{1/2}. \quad (2)$$

The integrated forms of Eqs. (1) and (2) are

$$\ln P_0/(P_0 - X) = k_1 t \quad (3)$$

$$(P_0^{1/2}/\sqrt{2}) \ln [(P_0^{1/2} + x^{1/2})/P_0^{1/2} - x^{1/2}] - \sqrt{2}x^{1/2} = k_2 t \quad (4)$$

where, P_0 = initial pressure of N₂O; x = pressure of N₂O decomposed at the time t ; $x/2$ = pressure of oxygen produced at time t .

They have been utilized to construct the kinetic plots at various initial pressures and temperatures and one such typical plot in the case of La₂Cu_{0.5}Ni_{0.5}O₄ at 50 Torr initial pressure of N₂O is shown in Fig. 1.

Equation (1) represents the importance of N₂O activation on the surfaces, while Eq. (2) corresponds to a strong inhibition by the product oxygen on the overall kinetics of N₂O decomposition. All the members of the solid-solution series showed an induction period (time required for the no-

ticeable amount of decomposition) ranging from 2 to 3 min. This time period decreased with an increase in either the total initial pressure of the reactant gas or the temperature. This induction period is due to the retention of oxygen produced in the initial stages of decomposition by the surface defects produced during the activation process.

At 50 and 200 Torr initial pressures of N₂O, the observed rate data on all the solid-solution members could be accommodated into an expression derived for first-order condition (Eq. (1)). However, the kinetics of decomposition of La₂Cu_{0.2}Ni_{0.8}O₄ alone exhibited a strong inhibition by the product oxygen. The solid-solution system has been fairly active toward the decomposition reaction in the temperature range 350–480°C.

Table 2 summarizes the values of rate constants at different temperatures and initial pressures and also the Arrhenius parameters. The activation energy and frequency factor values reported in this investigation have been evaluated from the Arrhenius plots (Figs. 2 and 3). Figures 4 and 5, respectively, depict interesting variation of rate constant at 440°C and activation energy with a change in the Cu/Ni ratio (or x), in La₂Cu_{1-x}Ni_xO₄.

The observation that the kinetic data could be accommodated in an equation corresponding to first-order dependence on the initial pressure of N₂O, reveals that the adsorption/activation of N₂O molecule on the surface constitutes the rate-controlling step on these series. The localized interaction between the cations of the lattice through the anion intermediacy can be expected to play a dominant role in the kinetics of the decomposition reaction (20). It is generally known that these interactions are further dependent on the local symmetry of the sites considered and the local dangling orbitals (21) that are involved in the electron relay mechanism.

Among the various combination of atoms on the surface which are responsible for the localized interactions, one can visualize

TABLE 2

Kinetic Data for the Decomposition of Nitrous Oxide on the Solid-State Solution System
 $\text{La}_2\text{Cu}_{1-x}\text{Ni}_x\text{O}_4$ ($0 \leq x \leq 1$)

Catalyst	Pressure (Torr)	Temp. (°C)	Rate constant ^a (10 ⁻¹)	Activation energy (kcal/mol)	Frequency factor ln A
La_2CuO_4	50	415	3.33	17.00	4.43
		435	4.40		
		460	6.02		
		482	9.64		
	200	432	2.67	10.83	-0.52
		450	2.90		
		470	4.26		
		480	5.33		
$\text{La}_2\text{Cu}_{0.8}\text{Ni}_{0.2}\text{O}_4$	50	405	6.00	7.18	-1.97
		440	8.75		
		495	12.50		
		390	8.35		
	200	440	11.50	1.05	-6.23
		460	14.20		
		480	17.50		
		375	9.14		
$\text{La}_2\text{Cu}_{0.6}\text{Ni}_{0.4}\text{O}_4$	50	446	20.50	10.62	1.25
		460	23.50		
		477	30.80		
		412	6.49		
	200	425	7.74	14.05	3.02
		480	16.60		
		380	10.40		
		422	12.70		
$\text{La}_2\text{Cu}_{0.5}\text{Ni}_{0.5}\text{O}_4$	50	455	19.40	6.90	-1.53
		485	24.00		
		360	22.83		
		380	4.62		
	200	420	12.40	23.92	10.79
		437	3.66		
		470	4.66		
		495	6.80		
$\text{La}_2\text{Cu}_{0.4}\text{Ni}_{0.6}\text{O}_4$	200	420	2.21	5.61	-4.05
		445	2.71		
		465	3.50		
		492	5.21		
	50	378	13.00	7.33	-0.38
		430	18.50		
		450	23.20		
		352	30.80		
$\text{La}_2\text{Cu}_{0.2}\text{Ni}_{0.8}\text{O}_4$		375	47.60		

TABLE 2—Continued

Catalyst	Pressure (Torr)	Temp. (°C)	Rate constant ^a (10 ⁻¹)	Activation energy (kcal/mol)	Frequency factor ln A			
La ₂ NiO ₄	200	400	51.30	2.98	-0.03			
		430	57.10					
		362	3.08					
		388	5.60					
	50	409	9.10	20.97	8.98			
		450	18.20					
		200	363			4.88	19.62	7.45
		393	11.00					
422	19.00							
448	26.70							

^a Units: (s⁻¹) for no inhibition and (mm^{1/2} sec⁻¹) for strong inhibition by oxygen.

clusters of the type A-O-B [A = La²⁺, Cu²⁺, Ni³⁺, and Ni²⁺; B = Cu²⁺, Ni²⁺, and Ni³⁺]. In view of various combinations suggested, it has not been possible to make any

theoretical calculations concerning the charge density (*q*) and energetics of each combination coupled with various orientations of the incoming reactant gas, N₂O. A

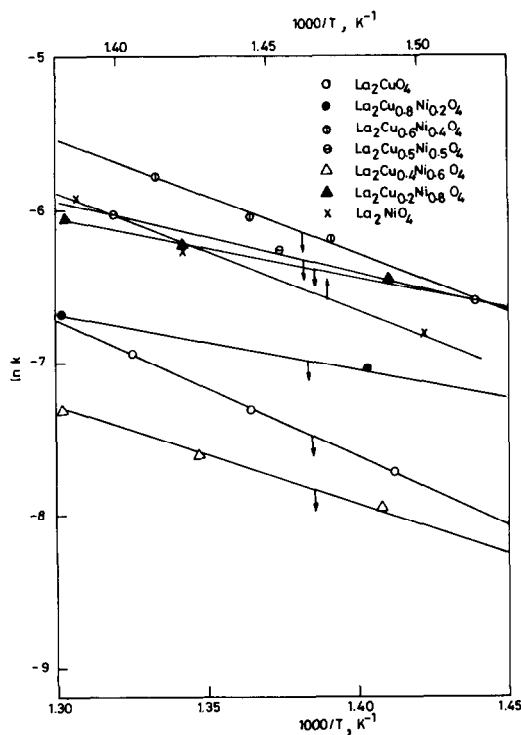


FIG. 2. Arrhenius plots for the decomposition of N₂O on La₂Cu_{1-x}Ni_xO₄ solid-solution series at 50 Torr pressure.

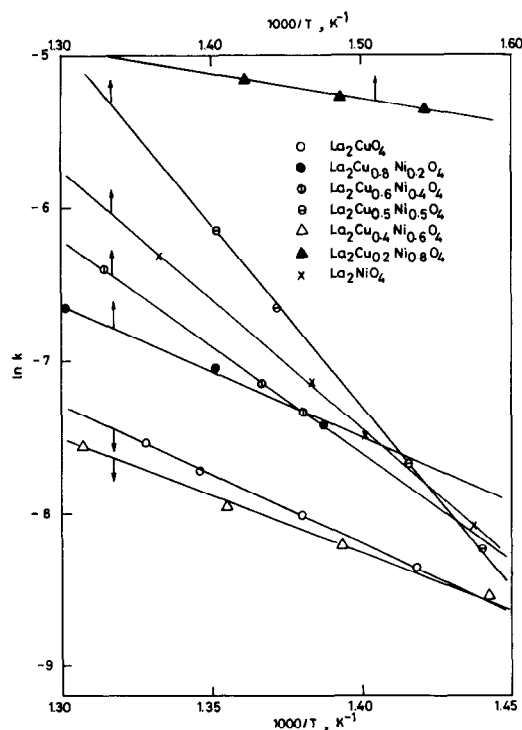


FIG. 3. Arrhenius plots for the decomposition of N₂O on La₂Cu_{1-x}Ni_xO₄ at 200 Torr pressure.

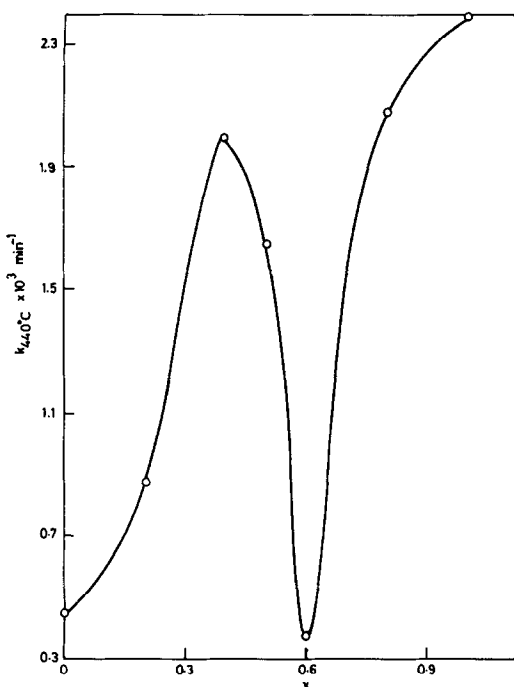


FIG. 4. Variation of rate constant at 440°C with composition (50 Torr data) in $\text{La}_2\text{Cu}_{1-x}\text{Ni}_x\text{O}_4$.

few attempts made in this direction employing extended Hückel theory method were without much success.

It is clear from Figs. 4 and 5 that, with the introduction of Ni^{2+} into the lattice of La_2CuO_4 the activity increases rapidly up to $x = 0.4$. The initial increase in the activity with the introduction of Ni^{2+} , can be attributed to an increase in the localized interactions. As the nickel ion is substituted in the place of Cu, the interaction of N_2O molecule with the surface is modified by the presence of partially filled d -manifold (d^8) and hence the decomposition tends to be facile on nickel-substituted systems. Although this observation is generally true, the absence of a systematic variation in the values of rate constant or activation energy along the series instigated further examination.

An explanation has been offered on the basis of a solid-state polaron hopping mechanism to account for the complex variation of the catalytic activities with a change in

Cu/Ni ratio. Austin and Mott (22), invoked polaron hopping mechanism to explain the electronic conduction properties of transition metal oxides like NiO and TiO_2 . The conduction band in these oxides is narrow and is essentially constituted by an overlap of $d_{x^2-y^2}$ (or d_{z^2}) orbitals of transition metal ions with the $2p$ orbitals of oxygen. Pomonis and Vickerman (23) have extended this concept to explain the catalytic behavior of solid solutions formed between transitional and nontransitional metal oxides like $\text{Al}_{2-x}\text{Cr}_x\text{O}_3$, $\text{MgAl}_{2-x}\text{Cr}_x\text{O}_4$, etc. Several workers (24–30) have employed oxide solid-solution catalysts in an attempt to understand the mechanism of operation of complex catalyst systems. In all these cases, the undoped catalyst possessed low activity which increases rapidly up to a particular concentration of the dopant, and after that a fall is noticed. A similar variation has been noticed in the present investigation and is represented in Fig. 4.

It has already been argued that in the present solid-solution system, localized interactions are of paramount importance with activation of N_2O on these surfaces. By way of introducing the polaron hopping mechanism in understanding complex variation of the activity, one can clearly visual-

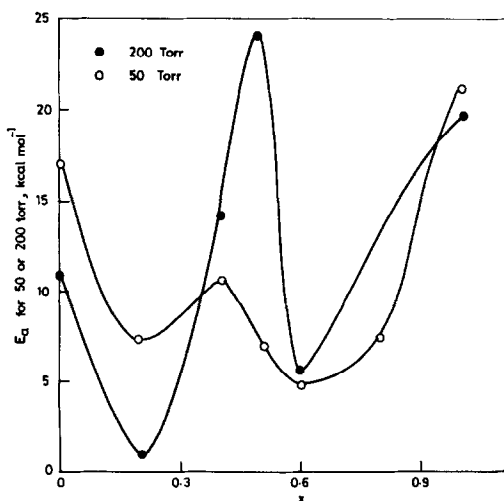
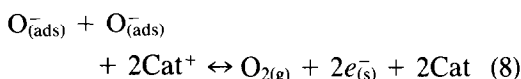
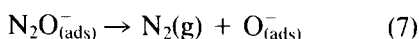
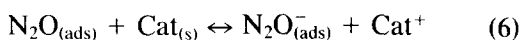
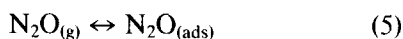


FIG. 5. Correlation between the Cu/Ni ratio and the E_a at 50 and 200 Torr in $\text{La}_2\text{Cu}_{1-x}\text{Ni}_x\text{O}_4$.

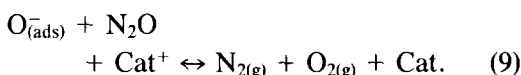
ize the operation of these interactions in the context of surface processes underlying the decomposition reaction.

A polaron consists of a *d*-electron under the influence of the polarized region of the crystal. Goodenough (33) has reported that in the case of La₂CuO₄ the bands are very narrow and consequently the effective mass of the polaron (or simply the *d*-electron) will be very large. A polaron with these dimensions is called a small polaron and its energy is equivalent to the energy required to polarize the host lattice. The small polarons can hop from one polarization well to the other, provided the thermal fluctuations of the lattice ensure that the energies of the neighboring wells are equal. When the dopant ions (Ni²⁺) are far apart, the charge clouds do not interact appreciably and the activation energy will be high, as in the case of initial substitution of nickel in La₂CuO₄ lattice. However, with the increasing additions of Ni²⁺ the possibility of these ions existing in neighboring wells will increase and the polaron essentially becomes nonlocalized. Thus, before a critical concentration of the dopant ions is reached, the localized interactions affect the activation of N₂O.

The decomposition of N₂O is known to proceed through the following route on many perovskites, like oxides (31):



or



Step (6) involves the generation of an electron-deficient site (Cat⁺) which can be filled in one of two ways: (i) electron donation by the adsorbed species (steps 8 or 9) or (ii) transfer of electrons from the bulk to the

surface. The electron that moves into the vacant site obviously will be that electron which experiences the lower activation barrier.

In the samples with low concentrations of Ni²⁺, the charged clouds would not overlap appreciatively, and consequently the Cat⁺ will be neutralized by the electron from the adsorbed species. However, at the critical concentration of the dopant ions, both these paths start competing with each other and this results in electron collision. Hence, a further activated step has to be introduced into the desorption process which in turn lowers the activity. This would account for the drop in the activity beyond [x = 0.4] in the present series. Finally, beyond this critical point, the activity rises with further doping. Although the vacant sites created in these samples have to be acquired from the bulk transport phenomenon, the activity can still increase with the substitution because of the fact that the number of effective sites on the surface is continuously increasing. This is also reflected in the values of frequency parameter, ln A (Table 2). Thus the arguments presented above explain the complex variation of rate constant for the N₂O decomposition as a function of composition at any given temperature.

Physicochemical Correlations

The catalytic reaction studies on a series of isostructural, isocompositional systems have the prime motive of establishing physicochemical correlations which enables one to understand the mechanism of the reaction and the nature of the active site involved. The operation of a compensation effect has been shown (Fig. 6) in the system La₂Cu_{1-x}Ni_xO₄ at both the initial pressures of N₂O. A linear correlation between the activation energy for decomposition and logarithm of the preexponential factor indicates that the energetics of the active component are different in these series (32). This is not surprising in view of the fact that the substitution at the B site results in the

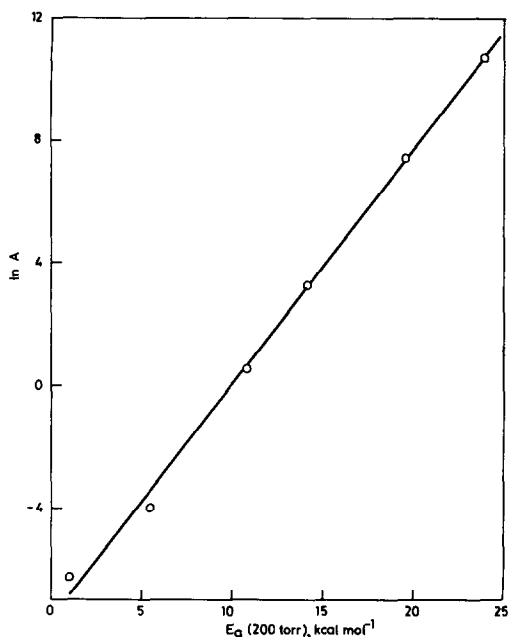


FIG. 6. Compensation effect (200 Torr initial pressure of N_2O) on $La_2Cu_{1-x}Ni_xO_4$.

heterogeneity of the surface. The implication however, is that the B -site ions are responsible for the observed activity in the series under study.

As the transition metal ions constitute the active site, it is highly probable that ex-

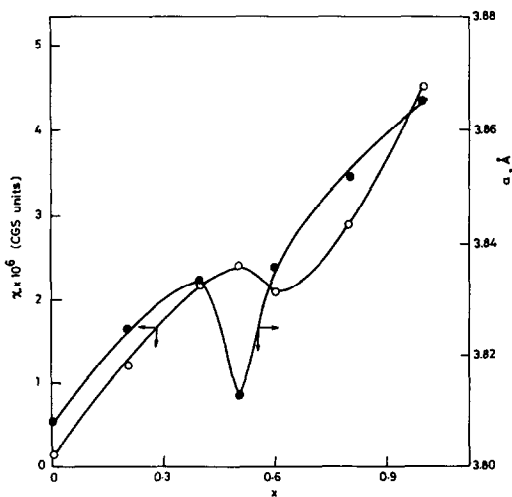


FIG. 7. Variation of magnetic susceptibility and cell parameter with x in $La_2Cu_{1-x}Ni_xO_4$.

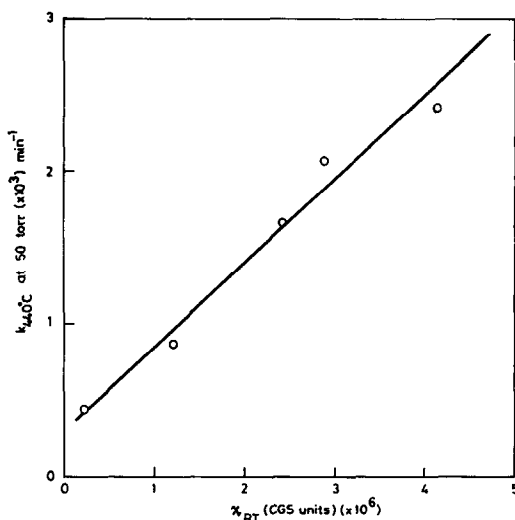


FIG. 8. Correlation between the $k_{440^\circ C}$ at 50 Torr and magnetic susceptibility in $La_2Cu_{1-x}Ni_xO_4$.

change interactions occurring between these ions are also significant in determining the kinetics of the decomposition. This aspect has already been substantiated in the previous section. A parallelism observed in the variation of the cell parameters and magnetic susceptibility with the compositional parameter (x) is depicted in Fig. 7. This implies that exchange interactions of the type cation-anion-cation are prevalent in these series and are responsible for the magnetic ordering (33). In order to extend this conclusion in electron-exchange processes such as the N_2O decomposition (where spin decoupling and the charge transfer are the essential steps involved), a correlation between the magnetic susceptibility of the samples, with the rate constant values at $440^\circ C$ and 50 Torr initial pressure was attempted and this is evidenced in Fig. 8. The linear relationship obtained clearly demonstrates the importance of spin-decoupling processes in the rate-determining step of the decomposition. This is also in accordance with the observation that on this system the kinetic data at both the initial pressures obeyed first-order kinetics. However, the strong inhibition exhibited by the product oxygen on the kinetics of de-

composition at 200 Torr initial pressure in the case of La₂Cu_{0.2}Ni_{0.8}O₄ is not clear.

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