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CHEMICAL PROBES OF METAL CLUSTER STRUCTURE -
Fe, Co, Ni, and Cu*

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Abstract

Chemical reactivity is one of the few methods currently available for investigating the geometrical structure of isolated transition metal clusters. In this paper we summarize what is currently known about the structures of clusters of four transition metals, Fe, Co, Ni, and Cu, in the size range from 13 to 180 atoms. Chemical probes used to determine structural information include reactions with H₂(D₂), H₂O, NH₃ and N₂. Measurements at both low coverage and at saturation are discussed.

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MASTER

INTRODUCTION

This paper will summarize recent advances in the determination of the geometrical structures of neutral metal clusters (M_n , $n < 200$) for four metals in the first transition series: iron, cobalt, nickel and copper. It is hoped that by examining a series of clusters of closely related metals the important parameters that determine their structure can more easily be discerned. The general problem of determining cluster structure arises primarily from the fact that most methods of cluster production result in a wide distribution of cluster sizes, making the usual spectroscopic techniques (X-ray and electron diffraction, photoelectron spectroscopy, EXAFS, etc.) difficult to apply, especially for neutral clusters. A second difficulty is that magic numbers, which are generally seen in mass spectra of rare gas¹ and alkali² clusters and which often have structural implications, are not found for the transition metals. Chemical probes of cluster structure are thus important if only for the virtual lack of alternative methods.

The chemical probe method involves both the adsorption of weakly bound atomic and molecular adsorbates on cluster surfaces (from single molecules up to saturation levels), and the determination of the rate constants for reactions of more strongly bound species. The broad distribution of cluster sizes poses no problem, since mass analysis is sufficient to separately identify the reaction of each individual cluster. In fact, it is the relative reactivity of clusters within a distribution of cluster sizes that often provides the structural information. The chemical probe method also has the advantage of being sensitive to the presence of isomers. The disadvantage of the method is the possibility that the chemical interactions between the clusters and the adsorbed molecules may actually alter the very structure one is trying to determine.

At low adsorbate coverages, cluster structure can be probed by measuring the size dependence of the cluster- $H_2(D_2)$ reaction rate and of the equilibrium adsorption of H_2O , NH_3 , and N_2 molecules. At high coverages, saturation studies have been performed with $H_2(D_2)$,

NH₃, and N₂. An essential element in these studies is an understanding of the nature of the sites on cluster surfaces where these reagents bind. Experiment³ and theory⁴ indicate that both H₂O and NH₃ prefer to bind in the atop position to the most exposed sites on the cluster (atoms having the lowest metal-metal coordination), while H(D) prefers bridge or multiatom sites⁵. Our studies suggest that at high N₂ coverages, each metal atom on a cluster's surface can bind at least one N₂ molecule. This paper will present examples of the structural implications of all these studies for clusters sizes ranging from 13 to 180 atoms.

EXPERIMENTAL

Chemical reactions are studied in a flow-tube reactor (FTR)⁶, using helium carrier gas. The clusters are made from isotopically pure metal targets by laser vaporization^{6b} in a flow tube upstream of the FTR. By keeping the flow-tube diameter small (3 mm) and the helium pressure low (10-20 Torr), the metal atom density decreases rapidly along the flow tube and, as a result, cluster growth terminates and the clusters cool to the ambient wall temperature before the clusters enter the FTR. Chemical reagents can be introduced into the FTR at two locations, giving reaction times of ~0.8 and ~0.15 msec. The cluster source and FTR can be heated or cooled, allowing measurements from -150 °C to +150 °C. The clusters and any reaction products pass out of a 1 mm dia nozzle at the end of the FTR, are internally cooled in the nozzle expansion, and are formed into a molecular beam. The clusters are then photoionized by appropriate excimer lasers 37 cm downstream of the FTR and mass analyzed in a time-of-flight (TOF) mass spectrometer.

RESULTS

(a) 13-20 atoms

The structure of clusters in this size range can often be inferred from adsorbate uptake measurements⁷. Plots of the average number

of molecules adsorbed vs the reagent pressure (on a log scale) can provide information on the number of adsorption sites on a cluster's surface. This is illustrated in Fig. 1, where the uptake of N_2 is shown for Ni_{13} , Ni_{14} , and Ni_{19} . The data show a rapid uptake of N_2 at low pressures where the reaction is dominated by kinetics (N_2 molecules adsorb, but do not desorb, in the FTR), and then a more gradual uptake of N_2 that is characteristic of reaction equilibrium between the clusters and the N_2 gas. At higher pressures the plots show plateaus, which indicate the number of N_2 molecules that saturate the clusters, i.e., that fill the clusters' surface N_2 binding sites. In the case of Ni_{13} , the saturation at 12 N_2 molecules suggests that each surface atom binds one N_2 molecule, since a 13-atom cluster is expected to have one central atom and thus have 12 surface atoms. While this result (and a similar one for Co_{13}) does not say much about the structure of 13-atom clusters, such is not the case for other cluster sizes.

Figure 2 shows mass spectra of nickel and cobalt clusters saturated with nitrogen at low temperatures, in the size range from 13 to 22 atoms. It has been argued⁸ that at room temperature Ni_{19} occurs as a double icosahedron and cobalt as an octahedron, based on their saturation coverages of ammonia (12 NH_3 molecules for Ni_{19} and 6 for Co_{19}). The spectrum in Fig. 2 as well as the uptake data in Fig. 1 show that at $-80^\circ C$ Ni_{19} saturates with the adsorption of 17 N_2 molecules, consistent with the double icosahedron (which has 17 surface atoms). This cluster has 12 sites on the 6-atom caps at either end of the cluster (where the 12 NH_3 molecules bind), plus 5 additional sites around the waist of the cluster. The octahedron, in contrast, would be expected to take up 18 molecules (since it has only one internal atom). The uptake plots for Ni_{18} and Ni_{17} are also consistent with a double icosahedron with one and two atoms removed.

$Co_{19}(N_2)_m$ shows no evidence for saturation at $m = 17$, so it would not appear to be a double icosahedron. The sudden appearance in Fig. 2 of a broad distribution of products at Co_{18} suggests that a change of structure is occurring or that several structures are present. Kinetics data⁹ on the reaction of Co_n with D_2

at $-100\text{ }^{\circ}\text{C}$ show plots of $\ln(\text{cluster ion signal})$ vs deuterium pressure that are non linear for $n = 18, 19$, and 21 , suggesting two or more structures are present at low temperatures (room temperature data, in contrast, show linear rate plots). The relatively high level of N_2 coverage on Co_{18-20} suggests that cluster structures based on the octahedron (19 atoms with one inside) or the tetrahedron (20 atoms with none inside) are present. A minimum in the degree of adsorption of Ar and Kr on Co_{20} observed by Knickelbein¹⁰ and a minimum in N_2 adsorption at low N_2 pressures for Co_{19} and Co_{20} would suggest close-packed structures with only (111) faces, of which the 19-atom octahedron and the 20-atom tetrahedron are examples. (Close-packed bulk surfaces show weaker binding for the rare gases¹¹ as well as smaller sticking probabilities for H_2 .¹²) The D_2 kinetics data suggest that the occurrence of multiple structures increases as the temperature of the cluster source decreases.

The saturation of Ni_{14} at 14 N_2 molecules (Figs. 1 and 2) and Co_{14} at 13 molecules (Fig. 2) suggests that these clusters have different structures. The Ni_{14} structure is likely one based on a tetrahedral core, so that all atoms are exposed, while the Co_{14} cluster could have a closed 13-atom shell (fcc, hcp, or icosahedral) with an additional atom on the surface. In the case of cobalt, however, there is clear evidence for a change in structure accompanying the addition of nitrogen. The Co_{14} cluster first saturates with the adsorption of two N_2 molecules and then at higher nitrogen pressures converts to the $\text{Co}_{14}(\text{N}_2)_{13}$ product. The structure of the bare Co_{14} cluster has not been determined. The $\text{Ni}_{15}(\text{N}_2)_m$ cluster shows a clear bimodal distribution in m in Fig. 2, indicating the presence of two structures. Spectra recorded at other N_2 pressures indicate that the cluster saturating at $\text{Ni}_{15}(\text{N}_2)_{16}$ appears to form first, but is converted to $\text{Ni}_{15}(\text{N}_2)_{14}$ (possibly the 15 atom bcc closed shell) at high N_2 pressures.

Clusters of iron and copper do not adsorb nitrogen sufficiently strongly to show saturation. Studies of ammonia adsorption on copper show no evidence of a plateau at $\text{Cu}_{19}(\text{NH}_3)_6$, indicating that Cu_{19} does not form as the fcc octahedron. While Cu_{19} might be the double icosahedron, the weaker adsorption strength of NH_3 on copper

prevents the development of a plateau at $\text{Cu}_{19}(\text{NH}_3)_{12}$. Studies of the reaction of iron clusters with hydrogen¹³, ammonia^{6a}, and water^{6a}, as well as ionization potential measurements¹⁴, suggest that iron cluster structure changes between Fe_{18} and Fe_{19} , and that Fe_{19} may have two structures. Based on the trends observed from copper through cobalt, we would expect one of these structures to be the 19-atom octahedron.

(b) 20-50 atoms

Cluster structures in this size region are largely unknown. Measurements of the clusters' ionization potentials^{14,15} (or ionization efficiencies) and rates of reaction with $\text{H}_2(\text{D}_2)$ often show significant changes at certain cluster sizes, which most likely reflect changes in structure. These changes occur most clearly for iron at Fe_{23} ¹³, and for cobalt at Co_{38} ⁹. For the entire region from Ni_{22} through Ni_{44} , but not above this region, there are frequent and significant changes in the ionization potentials^{15a} suggesting that there may be many different nickel cluster structures in this region. For copper, significant changes in ionization potentials with size are observed^{15b}, but these are largely associated with electronic shell structure, and effects of changes in geometrical structure are not as easily seen. Copper clusters do, however, show a clear change in ionization efficiency at Cu_{42} , suggesting a change in structure there.

Several nickel clusters in the 20- to 50-atom size range show particularly weak adsorption for certain adsorbates. Ni_{28} , for example, has a clear minimum in the uptake of rare gases as well for nitrogen and water. The weak adsorption for the rare gases suggests a structure with only (111) closed-packed faces. Figure 3 shows a possible 28-atom cluster of this form. The cluster consists of interpenetrating 19-atom octahedra. The mass spectra of $\text{Ni}_n(\text{NH}_3)_m$ in the $n = 28$ region are also consistent with this structural assignment. Adding a metal atom to the 28-atom cluster, or removing one (the four corner atoms are the most weakly bound) would be expected to provide an additional NH_3 binding site, and the $\text{Ni}_n(\text{NH}_3)_m^+$ spectrum shows just this behavior. Another cluster that

shows a minimum in rare gas uptake is Ni_{40} . A possible structure for Ni_{40} , which is analogous to that for Ni_{28} is also shown in Fig. 3.

In the 19- to 34-atom size region evidence is found for polyicosahedral structure¹⁶ when iron, cobalt, and nickel clusters are saturated with ammonia¹⁷. Polyicosahedral clusters at 19, 23, 26, 29, 32, and 34 atoms all have 12 obvious binding sites for NH_3 , and iron clusters show saturation at 12 for just these six clusters. Ammoniated cobalt and nickel clusters appear to have polyicosahedral structure only for the smaller clusters in this series (cobalt through Co_{29} and nickel through Ni_{26}).

(c) 55-150 atoms

The size region from 55 to 150 atoms has been examined for all four metals with the ammonia and water probes. The only structural determinations made so far suggest icosahedral structure. Closed icosahedral shells or subshells tend to show minima in the saturated adsorption of ammonia, and closed (sub)shell-plus-one-atom clusters tend to show maxima in the equilibrium adsorption of a single water molecule. Based on the H_2O results, nickel clusters show clear evidence^{3a} of icosahedral structure from Ni_{50-105} , while copper clusters show such evidence only in the range from 70 to 95 atoms. Cobalt clusters, on the other hand, show only weak evidence, and iron shows none at all. For ammoniated clusters the evidence points to icosahedral structure over a wider size range, from 50 to 116 atoms for both both cobalt and nickel, but not for iron. For copper, the weakness of the cluster-ammonia bond does not permit unambiguous determination of ammonia saturation. Analogous results for fully hydrogenated clusters of cobalt and nickel show evidence for icosahedral structure over a larger size region than for the bare clusters, suggesting that hydrogenation (like ammoniation) tends to increase the relative stability of the icosahedral structure.

Nickel clusters, whether bare, ammoniated, or hydrogenated, do not show evidence of icosahedral structure at 147 atoms, where the third shell closing would occur. Heating the clusters to elevated temperature, however, produces a conversion to icosahedral

structure for the hydrogenated clusters and for the ammoniated clusters. This is illustrated by the mass spectra in Fig. 4 for the hydrogenated clusters. The telltale sign of icosahedral packing would be the appearance of a strong peak due to $\text{Ni}_{148}\text{H}_2\text{O}^+$, a cluster having the H_2O bound to the single atom located on the surface of the 147-atom closed shell. At 20 °C there is no evidence of such a peak in Fig. 4, although peaks at $\text{Ni}_{126}\text{H}_p^+$, $\text{Ni}_{132}\text{H}_p^+$, and $\text{Ni}_{138}\text{H}_p^+$ appear, which are all expected for icosahedral packing. At 85 °C (and increased water pressure), however, a clear $\text{Ni}_{148}\text{H}_p\text{H}_2\text{O}^+$ peak (as well as several higher $\text{Ni}_n\text{H}_p\text{H}_2\text{O}^+$ peaks) appears, indicating a conversion to icosahedral structure. If the last 2 cm of the FTR is cooled to 20 °C, the 147-atom cluster is converted back to the alternate non-icosahedral structure, but the higher $\text{Ni}_n\text{H}_p\text{H}_2\text{O}^+$ peaks remain. These results suggest that between $n = 138$ and $n = 147$, the structure of hydrogenated nickel clusters is not icosahedral. The evidence also suggests that icosahedral structure returns at some point above $\text{Ni}_{147}\text{H}_p$, since a clear peak at $\text{Ni}_{179}\text{H}_p\text{H}_2\text{O}^+$ is seen in the annealed spectrum corresponding to the 178-atom capped icosahedron (not shown in the figure). It is likely that the change in structure that occurs prior to $\text{Ni}_{147}\text{H}_p$ locks in the alternate structure, and that annealing the clusters at elevated temperature is required to bring the larger clusters back to their equilibrium (icosahedral) geometry. In a like manner, icosahedral features are not seen for the nonhydrogenated Ni_{147} cluster, although heating to elevated temperature also converts Ni_{147} to an icosahedral structure, as has been demonstrated by the ammonia probe^{3a}.

The loss of icosahedral structure near the third shell closing is of considerable interest, since it imposes an important constraint on the nickel-nickel interaction potential. The experimental results suggest that adding the last few metal atoms, presumably to the apex sites of the icosahedron, introduces considerable strain in the surface bonding, leading to a destabilization of the icosahedral structure relative to some alternate structure, perhaps the fcc 147-atom closed shell. Although this has not been found in cluster calculations using Lennard-Jones pair potentials¹⁸, it is apparently a feature of the metal-metal interactions characteristic of the nickel system. Model

metal-metal interactions characteristic of the nickel system. Model potentials that predict structures other than icosahedral should be investigated.

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Figure Captions

1. Plots of the uptake of nitrogen by Ni₁₃, Ni₁₄, and Ni₁₉ clusters. The ordinate is the average value of m for the species Ni _{n} (N₂) _{m} ⁺ seen in the mass spectra and the abscissa is the ammonia pressure in the flow-tube-reactor (FTR). The nitrogen is added to the port giving a 0.8 msec reaction time and the FTR temperatures are given in the figure.

2. Time-of-flight mass spectra of nickel and cobalt clusters at equilibrium with nitrogen at the FTR temperatures and nitrogen pressures given below each spectrum.

(3) Models of 28- and 40-atom clusters having only close-packed faces.

(4) Time-of-flight mass spectra of hydrogenated nickel clusters in the presence of a small pressure of water. In the upper spectrum, the cluster source and flow-tube-reactor (FTR) are at 20 °C and only residual water is present. In the middle spectrum, both the source and FTR are at 85 °C and a small flow of water is added to the reactor to give a water pressure of 1.4 mTorr. In the lower spectrum, only residual water is present and the cluster source and FTR are kept at 85 °C, except for the last 2 cm, which are cooled to 20 °C. Peaks corresponding to clusters that adsorb water strongly are shaded black.

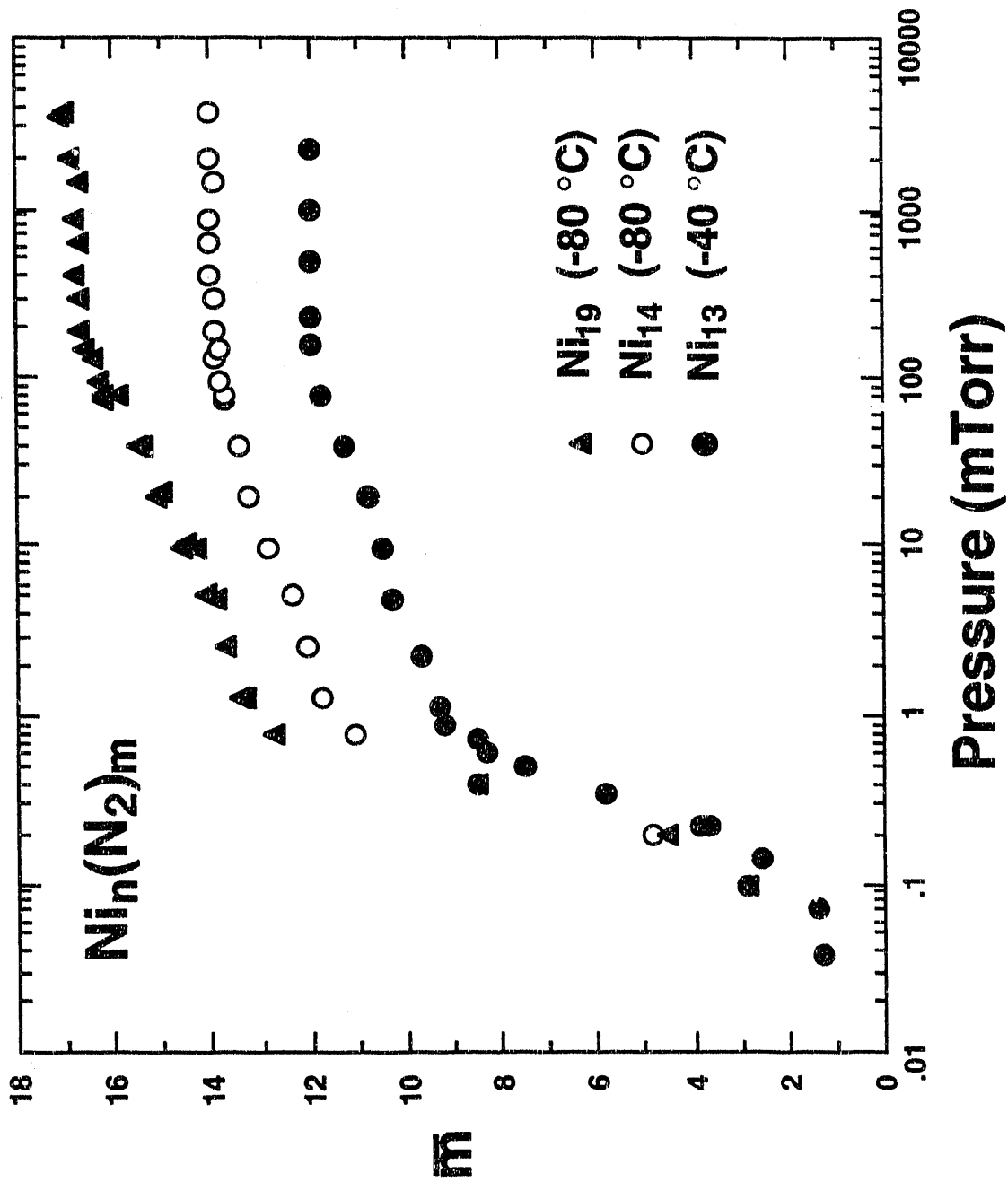
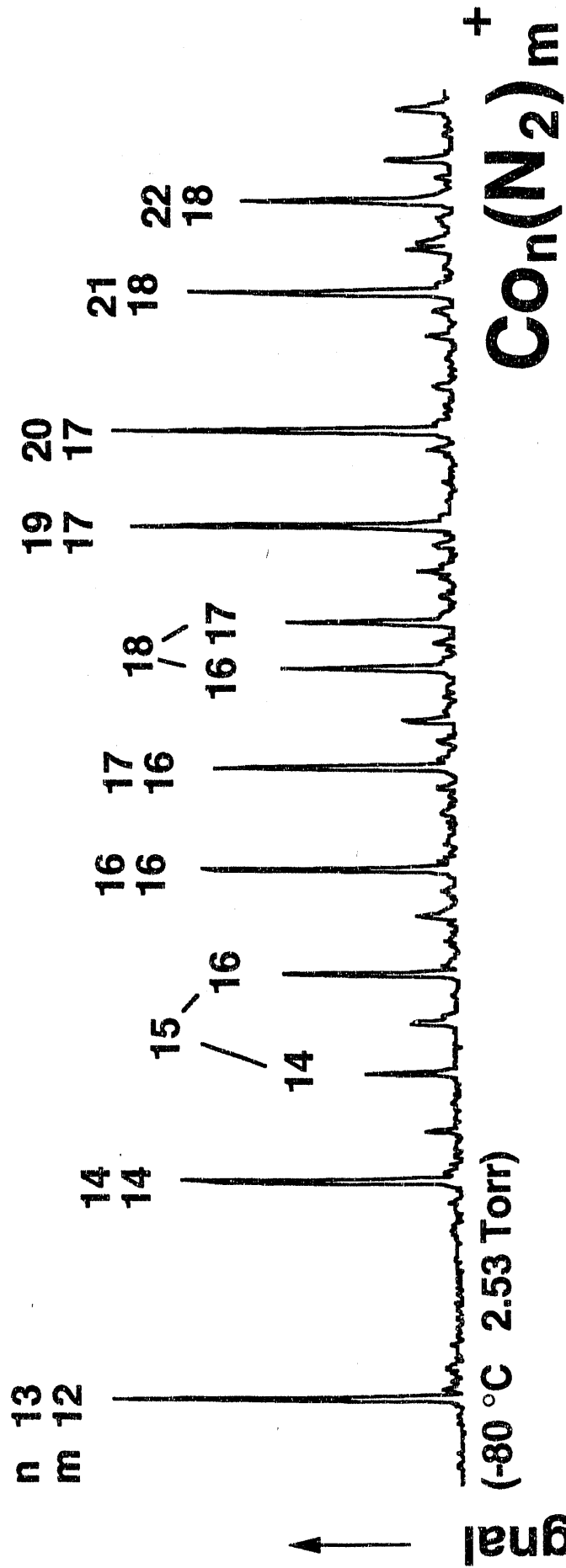
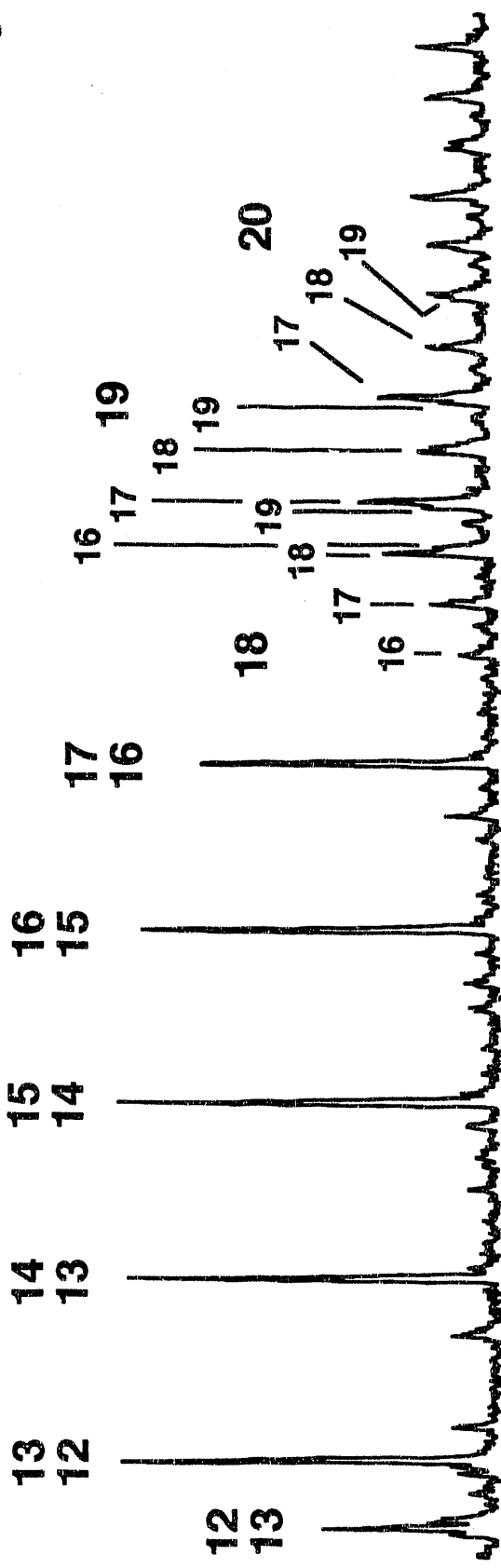


Fig. 1

$Ni_n(N_2)_m^+$

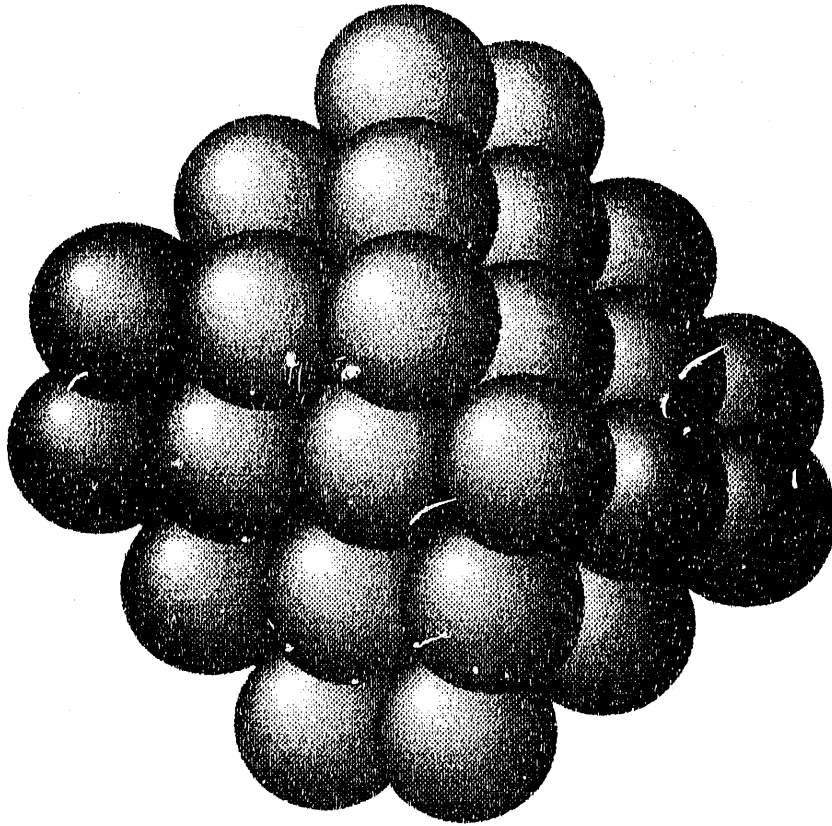


(-80 °C 2.53 Torr)

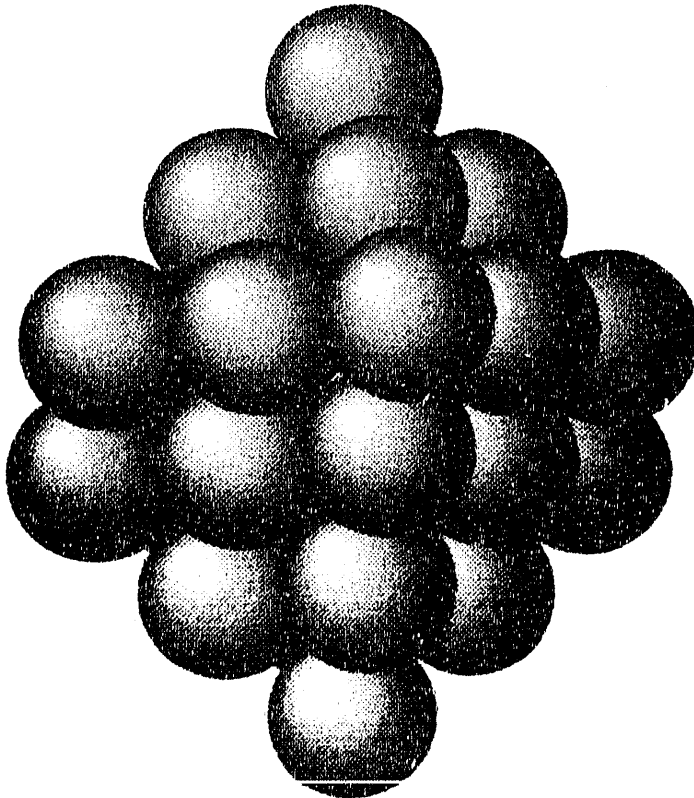


Time →

Fig. 2



Ni₄₀

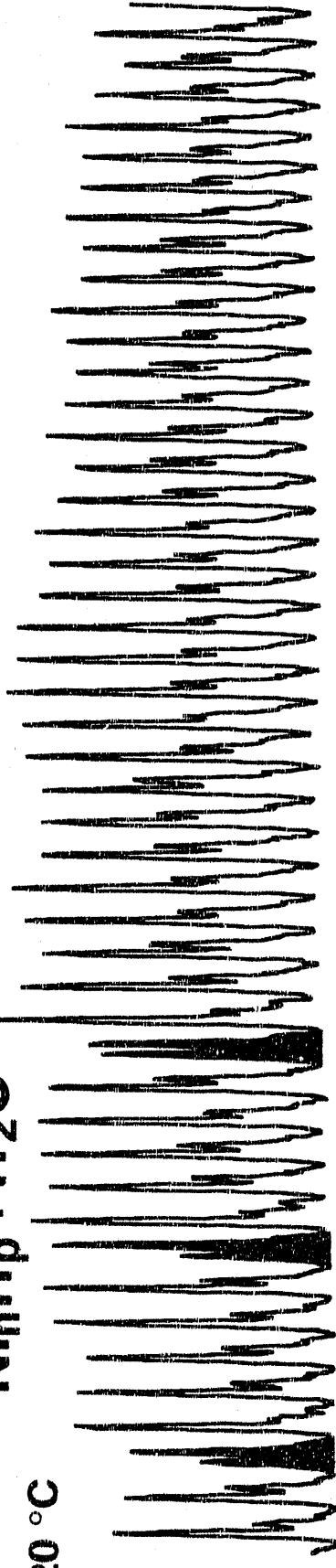


Ni₂₈

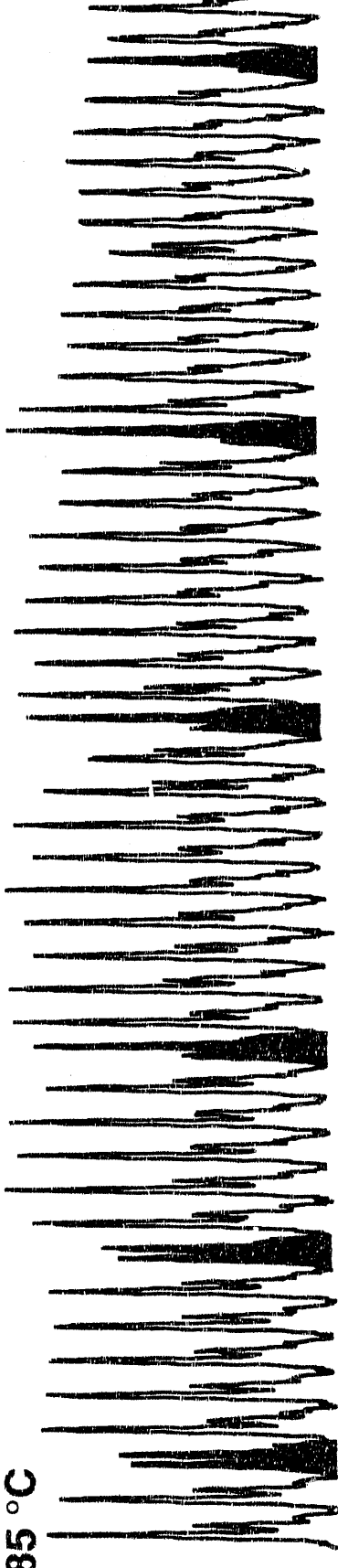
Fig. 3

Ni_nH_p + H₂O

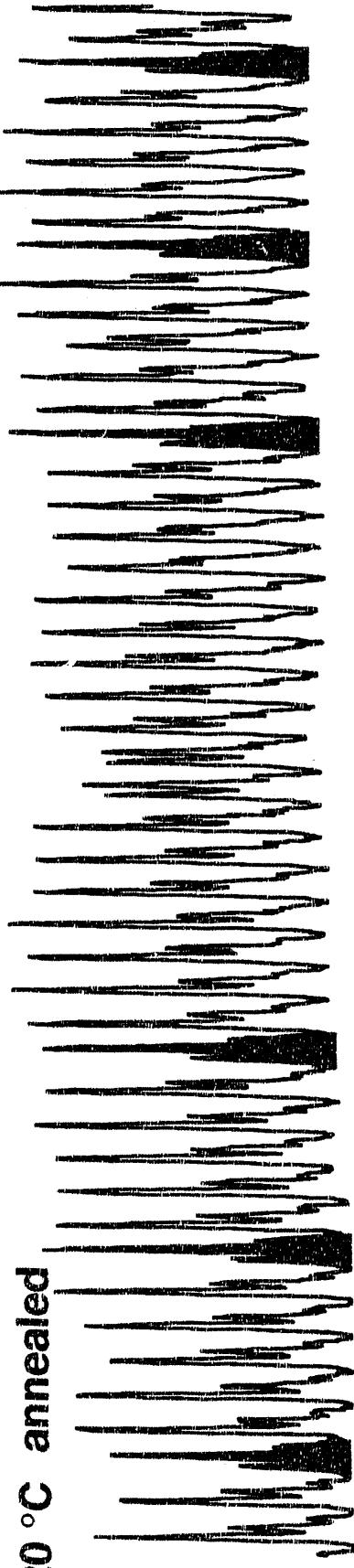
20 °C



85 °C



20 °C annealed



Time →

Fig. 4

END

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