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X-ray absorption studies of the electronic structure of nickel–copper catalysts

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X-ray absorption threshold resonances associated with L_{III} and L_{II} absorption edges, which are attributed to excitation of electrons from 2p core levels to unoccupied d-states in the valence band, were investigated for a series of nickel–copper alloys of widely differing compositions. The catalysts were alloys in the form of metal powders with surface areas of the order of 1 m^2/g. When the resonances for such samples are determined from measurements of the intensity of emission of electrons from the samples (i.e. by the so-called "electron yield" detection method), one can avoid experimental artifacts arising from the sample "thickness effect" encountered in X-ray transmission or fluorescence measurements. Edge resonances can then be determined reliably for metal powders. It was observed that copper had only a small attenuating effect on the resonances of nickel in the catalysts. The effect was smaller by an order of magnitude than that predicted by the rigid-band model of the electronic structure of nickel–copper alloys. The results provide strong support for earlier conclusions of others about the limitations of the rigid-band model.

Keywords: X-ray absorption of Ni–Cu; electronic structure of alloy catalysts

1. Introduction

Shortly after World War II, studies of the catalytic properties of metal alloys were considered by a number of scientists to provide a promising approach for probing into the so-called "electronic factor" in catalysis by metals [1–4]. One type of alloy which attracted much attention in this regard was a combination of a metal from Group VIII of the periodic table with a metal from Group IB, e.g., nickel–copper.

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For many reactions, including hydrogenation, dehydrogenation, and hydrogenolysis of hydrocarbons, the Group VIII metals are active catalysts, while the metals of Group IB are relatively inactive [5]. In terms of the energy band theory of electrons in metals, the former possess d-bands with states which are not completely occupied by electrons while the latter have filled d-bands. According to an early model of the electronic structure of a Group VIII + Group IB metal alloy, there is a single d-band which becomes increasingly filled as the amount of the Group IB metal increases [6,7]. The application of this model, known as the "rigid-band" model, to nickel–copper alloys leads to the prediction that the d-band becomes completely filled at a composition of approximately 60 at% copper. According to the model, the ferromagnetism characteristic of nickel and nickel-rich alloys should disappear at this composition, as is observed experimentally [8–10].

For a long time, the rigid-band model of the electronic structure of nickel–copper alloys was widely accepted, largely because of its success in the interpretation of the ferromagnetic behavior of the system. However, questions about the validity of the model were eventually raised as a consequence of the results of various types of experiments [11–17]. For example, the studies of Seib and Spicer [15–17] on the photoemission of electrons from single-crystal samples of nickel–copper alloys suggest the presence of two separate energy bands for nickel and copper, the relative intensities of which simply reflect the relative amounts of the two components present. Such results appear to be more consistent with a model of the electronic structure in which there is minimal sharing of electrons between the two types of metal atoms [18–21].

Photoemission studies provide information on the filled electronic states of the nickel–copper alloys. Of more direct interest for the ferromagnetic and catalytic properties of the alloys is the number of unfilled electronic states, in particular, the number of unoccupied d-states. Studies of the intensities of the absorption threshold resonances at L_{III} and L_{II} absorption edges provide a way of obtaining this information. The resonances are due to excitation of electrons from 2p core levels to unoccupied d-states in the valence band [22]. Cordts et al. [23] have made such studies of three nickel–copper foils with different compositions and concluded that the copper had no effect on the intensities of the L_{III} and L_{II} resonances of the nickel, in marked disagreement with the rigid-band model of the electronic structure of the alloys. These workers obtained their absorption spectra via transmission measurements, and it was necessary to correct for the sample "thickness effect" [24–26] in arriving at their conclusions. While this is certainly a reasonable procedure, there is an alternative method of obtaining the absorption spectra which avoids such a correction. It is known as the "total electron yield" detection method and involves the measurement of the intensity of emission of electrons from the sample accompanying the absorption process [27]. The emission occurs as one of the modes of atomic

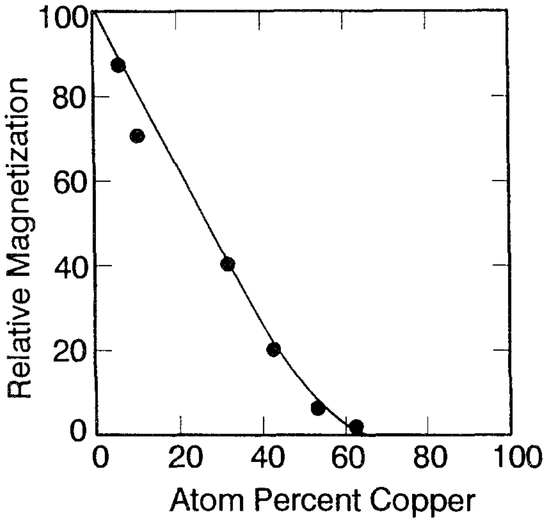

Fig. 1. Magnetization of nickel–copper alloys as a function of composition [10]. The points represent data of Sinfelt et al. [10] on nickel–copper catalysts in the form of metal powders, the curve represents data of Ahern et al. [9] on metallurgical specimens.

de-excitation in the filling of the core level vacancies created by the original absorption of X-ray photons by the atoms.

In view of the great interest in the nickel–copper system in fundamental studies of the action of bimetallic catalysts [2,4,10,28–30], we decided to investigate the L_{III} and L_{II} absorption threshold resonances of a series of nickel–copper alloys with the use of a total electron yield detector. The alloys were powders which had previously been the subject of an extensive catalysis study [10]. A preliminary account of the X-ray absorption spectroscopy studies has appeared in ref. [31].

2. Experimental

The nickel–copper catalysts were powders with surface areas of the order of 1 m^2/g. Actual values of the areas ranged from 0.63 to 1.46 m^2/g, as reported in a paper from this laboratory some twenty years ago [10]. Details of the method of preparation of the alloys, and of their characterization by adsorption, X-ray diffraction, and magnetic measurements are given in the same paper. Fig. 1 summarizes the results of the magnetic measurements taken from the paper. The ordinate of the figure is the magnetization of the alloy relative to the magnetization of pure nickel. The points represent data on the alloy powders, while the curve is derived from data reported by Ahern et al. [9] for metallurgical samples. The two sets of data exhibit excellent agreement, showing a decline in magnetization with increasing copper content until the ferromagnetism disappears at a composition of approximately 60 at% copper.

The X-ray absorption data were obtained at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory on beamline U-1 with apparatus developed for soft X-ray absorption spectroscopy [32]. In a typical experimental run, the nickel–copper sample was inserted in the apparatus and then exposed to hydrogen at a pressure of 2.5 Torr at 760 K for 30 min to ensure that it was completely reduced. After reduction, the sample was heated to 785 K and maintained at this temperature for 5 min while it was being evacuated to a pressure of approximately 1×10^{-7} Torr. While still under evacuation, the sample was cooled to 150 K for measurement of a spectrum. The pressure during the measurements was about 1×10^{-8} Torr. The X-ray absorption was monitored by measuring the total emission of electrons (commonly called the "total electron yield") from the sample. The emission is proportional to the X-ray absorption.

3. Results

Our analysis of the X-ray absorption data on the nickel and nickel–copper powders involved the following procedure. In an original spectrum (i.e. a plot of total electron yield in arbitrary units versus X-ray energy), the point of inflection in the L_{III} edge of nickel is taken as the zero point in the energy scale. This corresponds to an absolute X-ray energy of 855 eV [33]. A value for the increase in electron yield over the range of energy spanning the L_{III} and L_{II} edges of nickel is then obtained by subtracting the yield in the pre-L_{III} edge region (−50 to −20 eV) from the yield in the post-L_{II} edge region (30–50 eV). We refer to this increase as the Ni $L_{III}L_{II}$ absorption jump. Similarly, a value for the Cu $L_{III}L_{II}$ absorption jump is obtained by subtracting the electron yield in the post-L_{II} edge region of Ni (30–50 eV) from the yield in the post-L_{II} edge region of Cu (110–130 eV). The complete spectrum is normalized to the Ni $L_{III}L_{II}$ absorption jump. Since X-ray absorption is proportional to electron yield, normalization of the spectrum produces a plot of normalized absorption vs energy. A typical spectrum is shown in fig. 2 for a nickel–copper alloy containing 52% Ni (atomic percent). The spectrum shows the L_{III} and L_{II} absorption edges of both nickel and copper. The nickel edges exhibit absorption threshold resonances, frequently called "white lines" [34], whereas the copper edges do not.

In fig. 2 the normalized Ni $L_{III}L_{II}$ absorption jump is represented by the two-headed arrow labelled Ni. Likewise, the normalized Cu $L_{III}L_{II}$ absorption jump is represented by the two-headed arrow labelled Cu. A similar arrow designated Ni + Cu shows the combined absorption jumps for the two components. As can be seen from the figure, the relative lengths of the nickel and

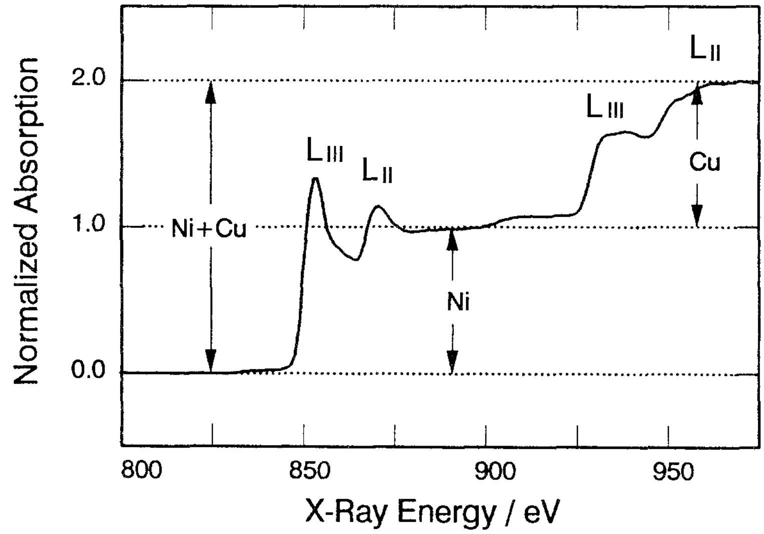

Fig. 2. X-ray absorption spectrum for a nickel–copper catalyst with a molar composition of 52% Ni, 48% Cu in the region encompassing the L_{III} and L_{II} absorption edges of the two components. The complete spectrum is normalized to the nickel $L_{III}L_{II}$ absorption jump represented by the length of the two-headed arrow labelled Ni. The arrow labelled Cu represents the $L_{III}L_{II}$ jump for copper, while that labelled Ni + Cu is the sum of the $L_{III}L_{II}$ jumps for the two components.

copper arrows are in good agreement with the known composition of the alloy (the respective changes in absorption coefficients across the $L_{III}L_{II}$ absorption jumps, characteristic of nickel and of copper, are the same to within 3% [35]). Moreover, the overall bulk compositions of all of the alloy samples are consistent with the relative magnitudes of the $L_{III}L_{II}$ absorption jumps for the nickel and the copper, as shown by the data in fig. 3. The ordinate of the figure is the ratio of the absorption jump for copper to the combined jumps for the two components. The ratio corresponds closely to the atomic fraction of copper in the alloy over the whole range of composition.

When an X-ray absorption spectrum on a sample is obtained by a measurement of the total emission of electrons therefrom, it is well known that the depth of escape of electrons from the sample is limited. Because there is much evidence attesting to marked differences between the surface and bulk compositions of nickel–copper alloys due to surface enrichment by copper [10,36,37], one might have been concerned that an X-ray absorption spectrum obtained by the electron yield method on such an alloy would not be representative of the overall bulk composition of the material. Since such a result is not observed, it appears that the region of composition different from that of the bulk is very thin compared to the escape depth, perhaps including only the outermost layer of atoms.

In a quantitative comparison of the intensities of the absorption threshold resonances at the L_{III} and L_{II} edges of nickel in a nickel–copper alloy with

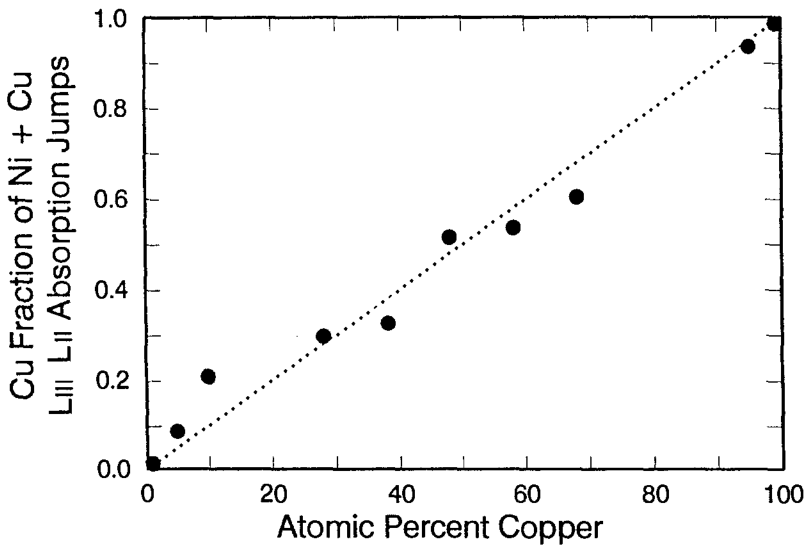

Fig. 3. Demonstration that the data on $L_{III}L_{II}$ absorption jumps (i.e. jumps including both L_{III} and L_{II} edges) for the components of nickel-copper alloys are consistent with data on alloy compositions. The ordinate of the figure is the ratio of the $L_{III}L_{II}$ absorption jump for copper to the sum of the $L_{III}L_{II}$ jumps for nickel and copper.

those in the pure nickel sample, it is necessary to align the overall spectra very carefully with respect to both the absorption and energy scales to ensure that the resonance features are properly resolved. This is particularly important when the differences in resonances are very small. We employ a three-step procedure in making such a comparison. In one step, the pre-L_{III} edge regions for the nickel from −50 to −20 eV, where the normalized absorptions are close to zero, are fitted to each other by a simple vertical shift of one spectrum relative to the other. In another step, the normalized absorptions in the post-L_{II} edge regions from 30 to 50 eV are fitted to each other by applying a scaling factor to one of the spectra. The factor is then applied to the entire spectrum, including the regions encompassing the absorption threshold resonances at the L_{III} and L_{II} edges of nickel and of copper as well. It corrects for differences introduced in the original normalizations of the spectra being compared. In the final step, the regions between −20 and +30 eV (spanning the L_{III} and L_{II} edges of nickel) are aligned with each other by a simple horizontal shift (i.e. energy shift) of one spectrum relative to the other. The shift aligns the points of inflection at the L_{III} edges of nickel and tends to minimize the difference between the integrated intensities of the two spectra being compared in the energy range indicated. In general, the energy shifts are a few tenths of an electron volt.

A spectrum (solid line) in the region of the L_{III} and L_{II} edges of nickel for a nickel-copper alloy containing 52% Ni is compared with a similar spectrum

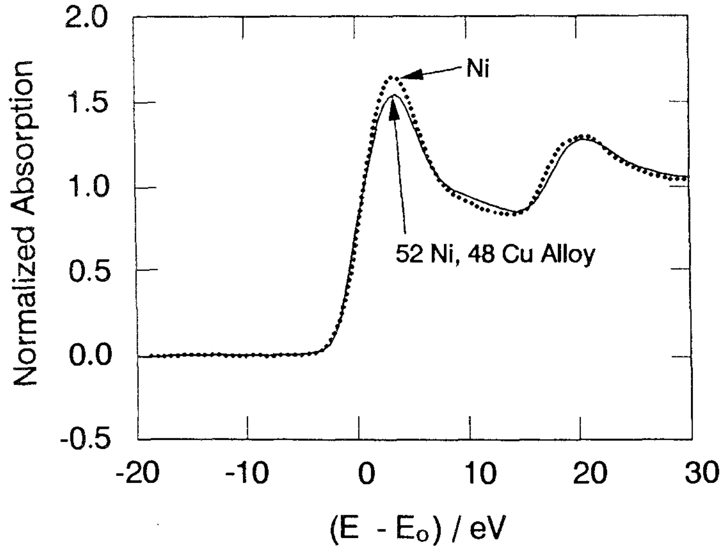

Fig. 4. Comparison of X-ray absorption spectrum for a nickel–copper alloy containing 52% Ni (solid line) with that for pure nickel (broken line) in the region of the L_{III} and L_{II} absorption edges of nickel. The point of inflection in the abruptly rising part of the L_{III} edge of nickel is taken as the zero point in the energy scale.

(broken line) for a pure nickel powder in fig. 4. The resonances for the nickel in the alloy are slightly less intense than those for the pure nickel. The attenuating effect of the copper is small and is more evident at the L_{III} edge than at the L_{II} edge.

The L_{III} and L_{II} edges of copper are simpler than those of nickel because of the absence of the pronounced peaks at the absorption thresholds. They have the appearances of simple steps and are due to excitations of electrons from 2p core levels of the copper atoms to continuum states external to the atoms. The steps can be approximated by arctangent functions, which in turn have a theoretical basis [38]. The more complex L_{III} and L_{II} edges of nickel exhibit peaks superimposed on the steps. The peaks, or white lines [34], are indicative of absorption threshold resonances due to excitation of electrons from 2p core levels to unfilled d-states in the valence band. When resolved from the step function at the edge, such a resonance has a Lorentzian line shape [39].

To make a determination of the fractional decrease in unfilled d-states resulting from the addition of copper to nickel in an alloy, we need to have a method of isolating the Lorentzian function characterizing the absorption threshold resonance of pure nickel. We employ a method described by Lytle [40] with a modification suggested by Cordts et al. [41]. Since copper is the element immediately following nickel in the periodic table, the assumption is made that the step functions constituting the L_{III} and L_{II} edges of copper can be used to approximate the step functions included in the L_{III} and L_{II} edges of nickel. By

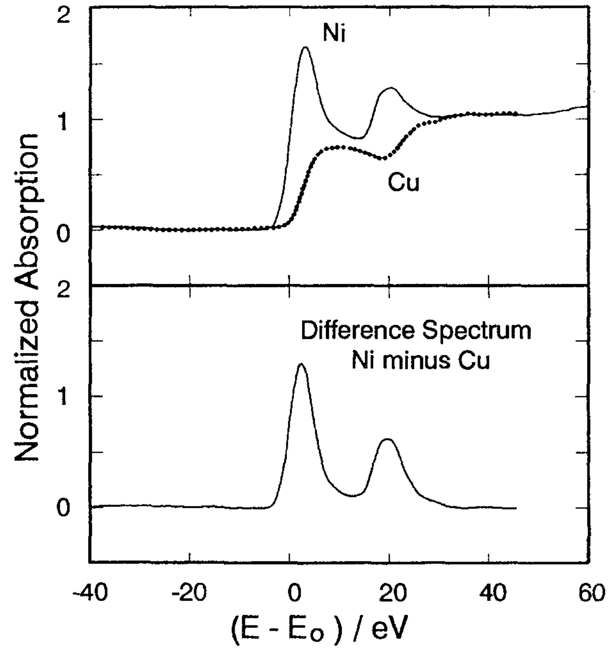

Fig. 5. Extraction of the spectral component representing the L_{III} and L_{II} absorption threshold resonances of nickel from the observed X-ray absorption spectrum of the pure metal, assuming that the L_{III} and L_{II} edges of copper can be substituted for the underlying step functions in the corresponding edges of nickel. In the upper field, the solid line is the spectrum for pure nickel while the broken line is the spectrum for pure copper. The latter is positioned so that the point of inflection in the L_{III} edge is aligned with the maximum in the peak at the L_{III} edge of nickel. The zero point in the energy scale is located at the point of inflection in the nickel L_{III} edge. The difference spectrum obtained by subtracting the broken line from the solid line is shown in the lower part. It is assumed to represent the L_{III} and L_{II} absorption threshold resonances of nickel.

subtracting the spectral area encompassing the L_{III} and L_{II} edges of copper from the corresponding area for nickel, we then isolate the spectral features associated with the absorption threshold resonances at the L_{III} and L_{II} edges of nickel. In making the subtraction, we align the energy corresponding to the point of inflection in the steeply ascending region of the L_{III} edge of copper with the energy corresponding to the maximum of the peak in the nickel L_{III} edge. As discussed by Cordts et al. [41], this procedure serves to align the two components of the spectrum with respect to the Fermi energy. The alignment is shown in the upper part of fig. 5, and the difference spectrum constituting the absorption threshold resonances at the L_{III} and L_{II} edges of nickel is shown in the lower part.

For each of the nickel–copper alloys, we compare the spectral region encompassing the nickel L_{III} and L_{II} edges with the corresponding spectral region for pure nickel in the manner which was illustrated in fig. 4 for the alloy containing 52% Ni. The spectral area for the alloy is then subtracted from that for the pure

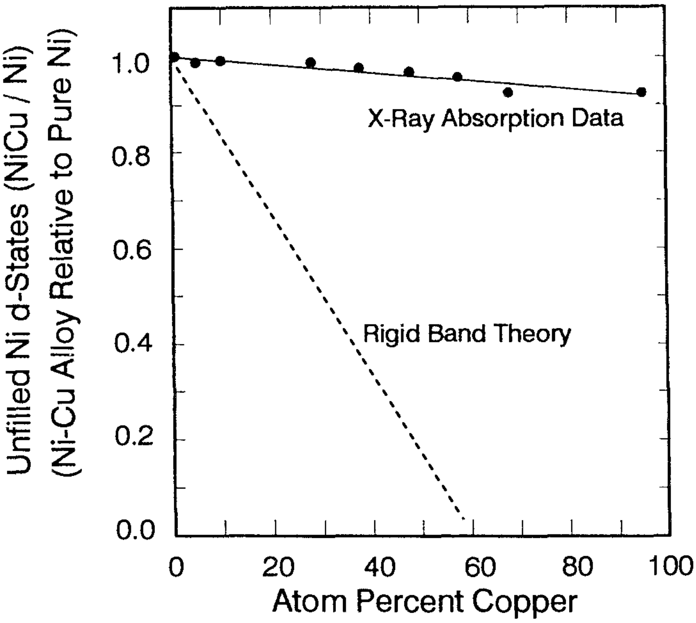

Fig. 6. Electronic structure of nickel–copper alloys as a function of alloy composition. The ordinate represents the number of unfilled nickel d-states per nickel atom relative to the number for pure nickel. The solid line through the data points was derived from X-ray absorption data. For comparison, a prediction based on the rigid-band model of the electronic structure is shown as the broken line.

nickel and the resulting difference is normalized to the spectral area shown in the lower part of fig. 5 for the combined L_{III} and L_{II} absorption threshold resonances of pure nickel. This normalized quantity is taken as the fractional decrease in the number of unfilled d-states of nickel as a consequence of its association with copper in the alloy. The number of unfilled Ni d-states for a Ni–Cu alloy relative to the number for pure Ni is shown as a function of alloy composition in fig. 6 (the solid line through the data points). For comparison, the prediction of the rigid-band theory of the electronic structure is shown as the broken line in the figure. The measured effect is an order of magnitude smaller than the predicted one.

4. Discussion

The results of the X-ray absorption spectroscopy studies reported in this paper provide clear evidence that the rigid-band theory of the electronic structure of binary alloys of a Group VIII metal and a Group IB metal cannot be applied satisfactorily to nickel–copper alloys. Measurements of intensities of absorption threshold resonances at L_{III} and L_{II} absorption edges provide a direct way of probing the number of unfilled d-states of nickel atoms in the alloys. The systematic investigation of such resonances for a number of nickel–copper alloys over a broad range of composition has yielded results on electronic structure which can be compared quantitatively with those predicted by the rigid-band theory. The measured decrease in the number of unfilled nickel d-states when nickel is alloyed with copper is an order of magnitude smaller than predicted. Our conclusions are in excellent accord with the views of a number of earlier investigators who raised questions about the validity of the rigid-band theory [11–21,23].

Despite the evidence opposed to the rigid-band theory, there is still interest in the theory for historical reasons. At the time the theory was originally proposed, more than a half-century ago [6], its simplicity and spectacular success in accounting for the magnetic properties of nickel–copper alloys led to its widespread acceptance by solid state physicists. In the field of heterogeneous catalysis, it had a major influence for many years on the thinking of catalytic scientists regarding the electronic factor in catalysis by metals. While the theory has not proved to be correct regarding the electronic structure of nickel–copper alloys, and has therefore not provided a rigorous basis for the use of such alloys to probe the electronic factor in catalysis, it has nevertheless been a vital stimulus in the development of present ideas concerning these issues.

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