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Studies of Alloys by X-ray Absorption Spectroscopy

Fine structure exhibits the effect of alloying on the absorbing atom's electronic structure.

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It has been known since the early 1920's that the way a compound modifies the electronic structure of an atom is manifested by the x-ray spectrum of that atom. Because a quantitatively rigorous theory to explain the intensity, shape, and energy dependence of x-ray spectra has not as yet been developed, experimental measurements in organic and inorganic compounds have been limited to fingerprinting the x-ray spectra of atoms having known valencies and coordinations with the aim of identifying these atoms when they are encountered in an unknown matrix. In the case of pure metals, the emergence of the band theory of solids, in the early 1930's, gave reason to hope that a more rigorous theory to explain the spectra of metals might be at hand. Although some successful interpretations and correlations of x-ray spectra with band models of pure metals were reported, the few attempts made to extend these procedures to alloys led to inconclusive results. Continued efforts to improve theoretical band models of metals and certain of their alloys, however, recently have spurred new attempts to utilize these models in the interpretation of x-ray spectra. A novel procedure for correlating band-model calculations with the x-ray spectrum—a modification of procedures previously proposed—makes it possible to deduce the electronic structure of the absorbing atom in an alloy. This augurs the ability to characterize the bonding of metal atoms in alloys and to study alloy properties dependent on interatomic forces. In fact, some apparently successful correlations have already been reported.

The characteristic x-ray emission spectrum of an atom is usually produced by bombardment of the atom either with electrons or with x-rays. In the latter process, called fluorescence, an incident x-ray photon is absorbed by an atom provided the photon has sufficient energy to eject an electron from the atom. When such an electron has been ejected from, say, the *K* shell, the atom is said to be in the *K* excited state. This higher energy state of the atom is not stable, hence one of the outer electrons "falls" into the vacancy created in the *K* shell. Energy is conserved in this process when the atom emits an x-ray photon whose energy is exactly equal to the difference between the atom's energy before the emission process and its energy after it. From this it follows that an atom whose electrons have unique energies gives rise to a characteristic x-ray spectrum. It also follows that the emission spectrum should reflect the distribution, among the available energy levels, of the electrons present in an atom. As is well known, the allowed energy levels can be described in terms of the shells (*K, L, M,* and so on) and symmetries (*s, p, d,* and so on) of the electron orbitals.

By comparison, the x-ray absorption spectrum of an atom depends on what happens to the electron ejected from the atom by the absorbed energy quantum. In *K* absorption processes, it is evident that some minimum energy is required to eject a *K* electron. This is the work that must be done to overcome the binding energy of the electron and to move it into the first available higher-energy unoccupied orbital. X-ray photons whose energy is less than this amount are not absorbed by the atom, so the atomic absorption coefficient has a relatively small value for such energies. When the energy of the incident x-ray photons just equals this minimum value, a sharp rise in the absorption coefficient takes place, called the *K* absorption edge. Obviously, if there is a succession of discrete energy levels in an atom to which the ejected electron can transfer, then there should arise a succession of discrete maxima in the absorption curve at corresponding energies. Thus the fine structure appearing in the immediate vicinity of the x-ray absorption edge exhibits the distribution of normally unoccupied electron orbitals in the atom.

To summarize, x-ray emission spectra correspond to electron transitions from filled orbitals to the momentary vacancy created in an inner shell. They display the energy distribution of occupied orbitals. X-ray absorption spectra correspond to transition of the ejected electron to higher-energy unoccupied orbitals, so they display the distribution of normally empty energy levels. Formally, the transition prob-

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ability can be calculated according to quantum mechanics (*1*) from the matrix element

$$\int \psi^*_0(r) r \, \psi_1(r) d\tau \qquad (1)$$

whose magnitude depends on the value of the wave function of the final state $\psi_1(r)$ and the complex conjugate of the wave function of the initial state $\psi^*_0(r)$ at each point r. In the simplest case, Eq. 1 leads to the well-known selection rules which require that a K electron, having s-type symmetry, can undergo transitions only to an orbital having p-type symmetry. In more complicated cases, the exact form of the wave functions is not known, so the transition probabilities can be calculated only approximately.

Absorption Spectroscopy

For a number of reasons, x-ray emission spectra are more difficult to obtain experimentally and to interpret theoretically than x-ray absorption spectra (*2*). Consequently, the present discussion is limited to exploring the electronic structure of atoms by means of absorption spectroscopy to deduce the energy distribution of unoccupied orbitals. In the case of metals, the inner electrons are localized in each atom and occupy orbitals whose energy and spatial extent are little different from what they would be in an isolated atom. The outer or valence electrons, on the other hand, occupy orbitals that overlap each other rather extensively, so that it is more convenient to think of quasi-continuous energy bands than of discrete valence-electron levels (*3*). As an example, consider an isolated copper atom in which the K, L, and M shells are completely filled and its one valence electron occupies an s orbital in the N shell. (The N shell is the 4th shell, so this is properly denoted a $4s$ orbital.) When the atoms are brought together to form copper metal, not only do the $4s$ orbitals overlap in neighboring atoms but the $3d$ orbitals in the M shell do also. In fact, the next highest and normally empty $4p$ orbitals overlap both the $4s$ and the $3d$ orbitals, so that the relative energies of these various orbitals are somewhat jumbled. The most convenient way to describe this situation is in terms of what is called the density-of-states curve, which represents the number of orbitals available at each allowed energy value. Such a curve was recently redetermined for copper by G. A. Burdick (*4*); it is shown in Fig. 1, top. As may be seen, the $4s$ states overlap in energy the $3d$ states, which, at higher energies, are also admixed with $4p$ states.

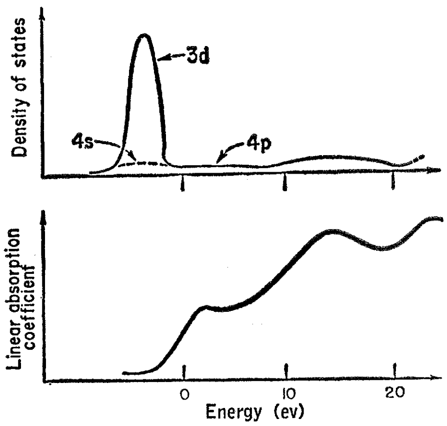

Fig. 1. Density-of-states curve and the K absorption spectrum of copper. [After Burdick (*4*)]

The distribution of the valence electrons in copper metal is such that the lower-energy states are occupied first, with the result that all the states shown in Fig. 1, up to the energy E_0, called the Fermi level, are filled, while all those states whose energy exceeds E_0 are normally empty (*5*). It is not surprising, then, to find that the K absorption coefficient of copper shown in Fig. 1, bottom, rises abruptly at E_0 as the ejected K electron undergoes transitions to the lowest-energy empty states. For energies exceeding E_0 by about 4 electron volts there is a decline in the admixture of $4s$ and $4p$ states. Because the selection rules based on Eq. 1 require that the ejected $1s$ electron undergo transitions only to states having p-type symmetry, a slight decline is produced in the absorption coefficient at these energies, followed by a rise as the higher-energy states assume successively more $4p$ character. The second maximum in the absorption curve corresponds to transitions to empty $5p$ orbitals, and so forth. With slight modification to allow for the more recent calculation of Burdick, this model follows the interpretation first proposed by Beeman and Friedman (*6*) on the basis of the then-prevalent energy-band model as calculated by Krutter (*7*) and Slater (*8*).

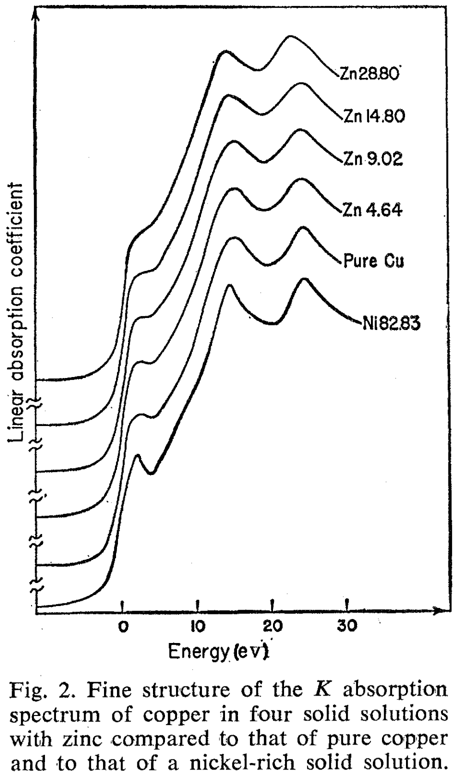

Fig. 2. Fine structure of the K absorption spectrum of copper in four solid solutions with zinc compared to that of pure copper and to that of a nickel-rich solid solution. Concentrations are given in atomic percent (atoms of zinc or nickel per 100 atoms present). The zero along the energy scale marks the Fermi energy E_0. [After Yeh and Azároff (*14*)]

Alloys of Copper

In extending their interpretations to alloys of copper with nickel, Friedman and Beeman (*9*) assumed that the absorption fine structure would represent the density-of-states distribution in the alloys. Since nickel and copper have identical crystal structures, and really differ only in that nickel has one less electron (and a correspondingly lower mass and charge on the nucleus), the so-called rigid-band model predicts that the density-of-states curve for copper-nickel solid solutions is virtually identical to that for copper except that the Fermi level shifts to lower energies to coincide with the decreased number of valence electrons present to fill the available states. The K absorption spectrum of copper in copper-nickel alloys was indeed found to resemble the K absorption spectrum of pure copper. What apparently surprised Friedman and Beeman, however, was the finding that the absorption spectrum of nickel in the alloy resembled the spectrum of pure nickel rather than that of copper in the alloy; they had expected the two spectra to have similar fine structures representative of the alloy. A similar surprise was recently expressed by Clift, Curry, and Thompson (*10*), who observed that the M emission spectra of copper and of nickel retain the forms characteristic of the pure metals throughout the entire range of alloy compositions.

A somewhat modified interpretation was recently proposed by Azároff and Das (*11*). Since the x-ray absorption (or emission) process takes place within a single atom, it should not be surprising that the spectrum typifies the atom rather than its environment. The principal modifications that the surrounding atoms introduce are slight shifts in the energy values of the orbitals or changes in their occupation or in their spatial distribution. If this view is correct, then the band-model calculation is useful for determining the relative energy levels, symmetries, and occupation probabilities for an "average" atom in the alloy. The x-ray spectrum, however, is made up of the superposed spectra of individual atoms, each of which is typical of the instantaneous electronic structure of the excited atom. For example, the *M* emission spectra of copper and nickel exhibit the density of occupied $3d$ states in each atom, so the line intensities emitted by their alloys should be directly proportional to the atomic ratios, since, in the alloys, the $3d$ density of nickel changes by less than 6 percent and that of copper remains unchanged. This is exactly what Clift, Curry, and Thompson (*10*) observed and why they could, as they reported, reproduce alloy emission curves by suitably proportioned superpositions of emission curves from pure copper and pure nickel.

The significance of this interpretation becomes more evident when the *K* absorption curves of copper alloys are examined. Consider, for example, solid solutions of copper with zinc. When zinc is added to copper, the rigid-band model implies that the additional $4s$ electron of zinc should be equally shared with copper atoms (*12*). Thus, as more and more zinc is alloyed with copper, an increasing number of copper atoms will have, in effect, two $4s$ electrons at the instant they are struck by the incident x-ray beam. Since this means that the number of empty $4s$ orbitals available to a *K* electron ejected from a copper atom is decreased, the first maximum in the absorption curve (Fig. 1) should decline in prominence (*13*). That this is indeed what happens can be seen quite clearly in Fig. 2, in which the copper absorption curves of four alloys are compared to the absorption curve of pure copper (*14*). The lowermost curve in Fig. 2 shows how the first absorption maximum increases when a large amount of nickel is alloyed to copper (*11*). This increase results because almost half the copper atoms have now "lost" their $4s$ electrons, which, according to the rigid-band model, have been "transferred" to the lower-energy, empty $3d$ orbitals of nickel.

Alloys of Nickel

From the foregoing discussion, one might expect that the density-of-states curve for nickel would resemble that for copper (Fig. 1), with the difference that the decreased electron-to-atom ratio would cause the Fermi level to move to a lower energy. This turns out to be exactly correct. As demonstrated by a number of physical measurements which are in agreement with theoretical estimates, E_0 lies just below the top of the $3d$ band, so that there are 9.4 electrons in $3d$ orbitals and 0.6 electron in $4s$ orbitals in an "average" nickel atom. The *K* absorption curve of nickel, therefore, resembles that of copper except that the absorption edge is shifted to lower energies. The first maximum now represents transitions to the empty $3d$ and $4s$ states, which have some admixed *p* character, and it is somewhat less pronounced than the maximum at the edge in copper. When the empty $3d$ states become gradually filled, as the result of alloying increased amounts of copper to nickel, the model proposed by Azároff and Das predicts that the first absorption maximum should decline. Such a systematic decline actually has been observed (*11*), although its magnitude is less prominent than the accompanying rise of the maximum in the absorption edge of copper (Fig. 2, bottom curve).

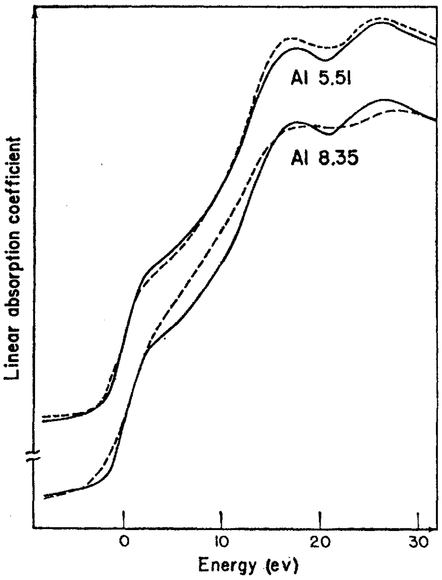

Fig. 3. Fine structure of the *K* absorption spectrum of nickel in two nickel-aluminum solid solutions (dashed curves) shown relative to that of pure nickel (solid curves). Concentrations are given in atomic percent. [After Das and Azároff (*16*)]

As a final example, consider the alloys of nickel with aluminum. Up to 21 atomic percent (atoms of nickel per 100 atoms present) of aluminum can be added to nickel in the alpha solid-solution region of this binary system. Since aluminum has three valence electrons ($3s^23p^1$), according to the rigid-band model, the empty $3d$ orbitals of nickel in these alloys should be filled three times as fast as they are in copper-nickel solid solutions. An apparent transfer of about two electrons per nickel atom added previously had been deduced from magnetic saturation measurements by Crangle and Martin (*15*). One would expect, therefore, that the first maximum in the nickel absorption curve of the nickel-aluminum system would decline twice as fast, per solute atom added, as the corresponding maximum in the nickel-copper system. The actual curves obtained (dashed lines) are shown in Fig. 3 for two different compositions. The absorption curve for pure nickel is also shown (solid curves). This curve is included purely for reference purposes, so that the fine-structure variations in the alloy curves (dashed) can be discerned more readily in each case. As may be seen in Fig. 3, although a decline in the first maximum is clearly apparent in the curve for the alloy of lower aluminum content (5.51 atomic percent), this decline is replaced by an increased absorption at slightly higher energies as the aluminum content is increased. From this, two conclusions can immediately be drawn: the rigid-band model predicting valence-electron sharing does not seem to hold for nickel-aluminum solid solutions, and the nature of the interatomic interactions changes with composition in the solid-solution range.

To understand the rise in absorption exhibited by the lower curve of Fig. 3 it is necessary to realize that the addition of aluminum to nickel causes the valence-electron orbitals of aluminum atoms to overlap those of neighboring nickel atoms. This leads to a kind of admixing of valence orbitals which is more closely related to that occurring in covalent bonding than to that typical of a metallic bond. As a result, the number of unoccupied orbitals having p-type symmetry in the vicinity of nickel atoms increases with increasing aluminum content. It reaches its maximum value (Fig. 4) in the ordered intermetallic phase Ni_3Al, in which each aluminum atom is surrounded by 12 nickel atoms. Note that, although the x-ray spectra clearly demonstrate the absence of the electron sharing that would be expected from the rigid-band model, they do not contradict the deductions made from magnetic saturation measurements (*15*), since the latter merely require that the number of unpaired electrons decline progressively. If the proposed explanation of covalent-like bonding in nickel-aluminum solid solutions is correct, then the apparent loss of two unpaired $3d$ electrons of nickel per aluminum atom added can be explained as resulting from the formation of a corresponding number of electron-pair bonds.

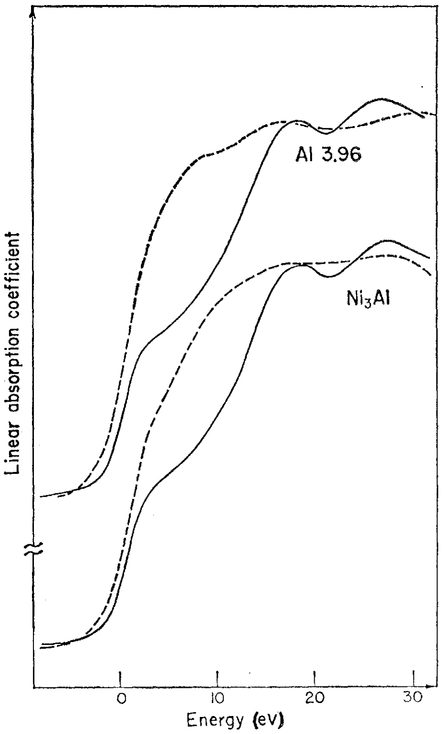

Fig. 4. Fine structure of the K absorption spectrum of nickel in two nickel-aluminum alloys (dashed curves) shown relative to that of pure nickel (solid curves). Concentrations are given in atomic percent. [After Das and Azároff (*16*)]

Relation to Alloy Properties

The foregoing results have been presented in order to demonstrate that the x-ray absorption spectra of alloys change characteristically when the electronic structure of the absorbing atom changes. Under favorable conditions, interpretation of the observed fine structure can be relatively exact, whereas in a less favorable case it is somewhat more speculative. The foregoing is true despite the fact that it is not at present possible to carry out a theoretical synthesis of an absorption curve even for pure metals because of the uncertainties in formulating the transition probabilities with the aid of Eq. 1. For alloys this problem is further complicated by uncertainties regarding the correct band model. Nevertheless, as long as one deals with one-parameter systems—for example, solid solutions in which the principal change is an alteration of lattice constants with composition—it is possible to make direct comparisons with theoretical models. In such systems there is no reason to expect pronounced changes in the amount of overlap between the wave functions of the initial and final states. This means that changes in the fine structure which result from alloying are caused by changes in the number of empty orbitals available for the ejected electron in an atom rather than by a change in kind. Exceptions may occur when the nature of the empty orbitals changes —for example, when neighboring atoms alter the symmetry and spatial extent of the valence orbitals. Again, the observation of systematic changes caused by varying one parameter (the composition) allows correlation with theoretical models. Although, in the absence of a rigorous theory, it is not possible to make quantitative predictions, the nature of interatomic interactions in solids is sufficiently well understood by now to allow empirical corroboration of reasonable models. Thus there is a need to explore a large number of alloy systems in order to substantiate any models proposed and to relate them to other experimental observations.

It is well known that in alloys, as in other solids, the electronic structure of the atoms determines the interatomic bonding and various physical and mechanical properties. It is now becoming evident that the details of the electronic structure can be established from x-ray spectra, despite many difficulties. An unexpected demonstration of the sensitivity of x-ray spectroscopy was found in the alpha solid-solution region of the nickel-aluminum system. In the course of preparing a series of alloys of differing compositions, it was found that the solid solutions containing aluminum at concentrations of 3 to 4 atomic percent were exceptionally brittle as compared to the malleable solid solutions outside this range. After careful reexamination of all preparatory stages it was found that the brittle alloys could be reproduced consistently. Examination of their nickel K absorption spectra showed that these spectra resemble very closely the spectra of covalently bonded nickel in Ni_3Al (Fig. 4) and are quite unlike the other solid-solution spectra (Fig. 3). It has been suggested (*16*) that this phenomenon is associated with an ordering process in the alloy similar to that observed in certain dilute ferromagnetic alloys (*17*).

In essence, it was proposed that the aluminum atoms "order" themselves in the solid solution by becoming as widely dispersed as possible. To test this hypothesis, the brittle alloys were reheated to just below their melting points and quenched rapidly so as to prevent the ordering process. This heat treatment made them quite malleable, a result which confirmed the validity of the initial postulate. In fact, it has proved possible to alter several such samples back and forth by successively quenching and annealing them. Both their hardness and their x-ray spectra change in a manner suggesting that some kind of order-disorder phenomenon is present (*18*). Additional studies of such ordering phenomena in dilute solid solutions are needed, but it is already clear that a correlation exists between the characteristic changes noted in the absorption-edge fine structure and the mechanical properties of such alloys. Doubtless many more correlations will become apparent as successively more alloy systems are investigated. Although such correlations, at present, must be mainly qualitative, it is hoped that the continued accumulation of clear-cut models may stimulate the necessary theoretical developments.

References and Notes

1. The discussion of quantum-mechanical calculations and the band theory is limited to what is called the one-electron approximation, which, although based on a somewhat oversimplified model, has proved itself quite adequate for semiquantitative comparisons in the case of metals.
2. The experimental difficulties with electron bombardment are numerous, while x-ray fluorescence has not been used sufficiently to provide the basis for a complete evaluation. Moreover, theoretical interpretations of x-ray emission spectra are hampered by self-absorption in the emitter, by multiple ionization processes, and by radiationless transitions.
3. In true metals, valence electrons are virtually "free" to move in an external electric field, hence they are also the electrons contributing to conductivity. It is quite common, therefore, to speak of valence-conduction electrons in metals.

4. G. A. Burdick, *Phys. Rev.* **129**, 138 (1963).
5. Strictly speaking, this statement is true only at 0°K. Whereas a slight redistribution of electrons near E_0 takes place at room temperature, this effect is small enough to be negligible for present purposes; it is responsible for the slope's deviating from the vertical in the absorption curve at E_0.
6. W. W. Beeman and H. Friedman, *Phys. Rev.* **56**, 392 (1939).
7. H. Krutter, *ibid.* **48**, 664 (1935).
8. J. C. Slater, *ibid.* **49**, 537 (1936).
9. H. Friedman and W. W. Beeman, *ibid.* **58**, 400 (1940).
10. J. Clift, C. Curry, B. J. Thompson, *Phil. Mag.* **8**, 593 (1963).
11. L. V. Azároff and B. N. Das, *Phys. Rev.* **134**, A747 (1964).
12. This is the literal picture of the rigid-band model as first developed by the independent efforts of N. F. Mott, E. C. Stoner, and J. Jones. More recent theories, particularly those developed by J. Friedel, cast doubt on how literally one may interpret this model on an atomic scale. Whether the "extra" valence electron of the added zinc atom is "shared" with adjacent copper atoms because an empty copper 4*s* orbital overlaps a filled zinc 4*s* orbital (or whatever the process) is irrelevant provided the final effect is to reduce the number of empty 4*s* orbitals in or at copper atom sites.
13. The reader who may wonder how transitions $1s \rightarrow 4s$ are possible is reminded that the copper 4*s* states at energies just above E_0 have a considerable admixture of *p*-type symmetry.
14. H. C. Yeh and L. V. Azároff, *Appl. Phys. Letters* **6**, 207 (1965).
15. J. Crangle and M. J. C. Martin, *Phil. Mag.* **4**, 1006 (1959).
16. B. N. Das and L. V. Azároff, *Acta Met.* **13** 827 (1965).
17. G. G. E. Low and M. F. Collins, *J. Appl. Phys.* **34**, 1195 (1963).
18. H. H. V. Narasimhamurty and L. V. Azároff, in preparation.
19. The investigations discussed in this article, which were carried out at Illinois Institute of Technology, were supported in part by the Metallurgy Division of the Office of Naval Research and by a grant from the National Science Foundation.

The Search for Extraterrestrial Life

Present knowledge does not permit the conclusion that, if life ever existed on Mars, it is now extinct.

N. H. Horowitz

The discovery of life on another planet would be a monument to our age. Not only would it be an unparalleled technological achievement, but it would be a momentous scientific event that would enlarge our view of nature and ourselves and provide unique evidence bearing on the origin of life. In this article, I am going to discuss the coming search for life on Mars. Venus, our other close neighbor among the planets, has been excluded from consideration, for the time being at least, because its high surface temperature—in the neighborhood of 400°C—seems incompatible with life or, for that matter, with much organic chemistry of any kind. The planets of the solar system beyond Mars are out of reach for the present.

The Martian Environment

I have given the reason for thinking that if life ever existed on Venus, it does so no longer. What can be said about Mars? We can say that although the situation is not brimming with hope, neither is it hopeless. The Martian environment is a harsh one by terrestrial standards. The mean temperature is −55°C, compared to +15°C for the Earth. The atmosphere is thin and very dry; it contains carbon dioxide and a small amount of water vapor, but no detected oxygen. Owing to the low density of the atmosphere and the absence of a magnetic field, the surface of Mars is bombarded by cosmic rays and solar radiation in an almost unattenuated form, as O'Gallagher and Simpson have recently pointed out (*1*). Finally, the Mariner IV photographs give the definite impression that Mars is geologically a dead planet whose surface has been undisturbed by anything except meteorite impacts for a very long time and which lacks the great variety of ecological habitats that characterize the Earth (*2*).

This is all very depressing news for biologists, but if I have learned anything during 6 years of association with the space program, it is that people with manic-depressive tendencies should stay out of it. Our knowledge of planetary environments is still fragmentary, and one's subjective estimate of the likelihood of finding life on Mars is liable to undergo violent fluctuations from time to time as new data accumulate. The fact is that nothing that we have learned about Mars—in contrast to Venus—excludes it as a possible abode of life. Martian temperatures are not very different from those of Antarctica, where a varied microbial life, and even a few flowering plants and invertebrate animals, have been found (*3*). Although the mean temperature on Mars is low, the seasonal and diurnal fluctuations are great, and temperatures as high as 25°C have been measured near the equator.

Radiation Flux on Mars

The ionization produced at the surface of Mars by cosmic rays is several hundred times greater than that found on the Earth, which is shielded by 1033 grams of atmosphere per square centimeter, but it is still far below a level that could be considered hazardous for life—even a slowly reproducing form of life. The dose rate calculated from O'Gallagher and Simpson's estimate of the ion density at or near the Martian surface is about 20 millirads per day, whereas the mean lethal dose for a typical bacterium (*Escherichia coli*) is in the neighborhood of 5000 rads. A greater potential hazard is posed by the solar far-ultraviolet light which, according to a recent report (*4*), penetrates to the Martian surface. Wavelengths in the neighborhood of 2600 angstroms are highly lethal for unprotected cells. On the

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The author is professor of biology at the California Institute of Technology and chief of the Bioscience Section, Jet Propulsion Laboratory, Pasadena, California. This article is based on a talk given at the dedication of the Laboratory for Astrophysics and Space Research, University of Chicago, 13 October 1965.