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Exploration of the structural and chemical rearrangements at the vaporizing surface leads to a better control of the rate of sublimation.

Studies of sublimation mechanisms are carried out to uncover the reaction steps by which atoms break away from their neighbors in the crystal lattice and are removed into the gas phase. Detailed understanding of these steps should allow us to control vaporization, increase or suppress its rate by suitable adjustment of the conditions of sublimation.

Most previous studies of sublimation were carried out under conditions of equilibrium between the solid and vapor in order to obtain thermodynamic data (vapor pressure, enthalpy, free energy) for the vaporization reaction. Vaporization experiments of this type, however, do not yield information about the reaction path. Little attention has been paid to studies of the kinetics of vaporization which are carried out far from equilibrium and should provide information about the mechanism of sublimation. These investigations have been carried out only recently on a relatively small number of solids in a few laboratories.[1]

I shall discuss here some of the principles and techniques of sublimation kinetics studies and describe our present physical picture of the vaporization process. Finally, I shall discuss investigations of the sublimation mechanisms of four solids which may be taken as representatives of larger groups of materials.

Consider the vaporization of one crystal face of a monatomic solid A(solid). If we assume that the overall vaporization reaction is $A(solid) \underset{k'}{\overset{k}{\rightleftarrows}} A(vapor)$, the net rate of vaporization, J, can be expressed as

$$J(\text{moles/cm}^2\text{sec}) = k(A)_s - k'(A)_v \qquad (1)$$

where k and k' are the rate constants for vaporization and condensation, respectively, $(A)_s$ is the concentration of molecules in the surface sites from which vaporization proceeds and $(A)_v$ is the vapor density. For studies of the kinetics of vaporization the condensation rate, $k'(A)_v$, must be smaller than the rate of sublimation, $k(A)_s$. In such investigations the evaporation rate of the solid is measured under non-equilibrium

conditions, most frequently in vacuum.[1] For sublimation into vacuum or as it is frequently called, "free vaporization," the rate of condensation can be taken as zero and Eq. (1) can be simplified to, $J_v(\text{moles/cm}^2\text{sec}) = k(A)_s = k_o(A)_s \exp(-E^*/RT)$ where k_o is a constant related to the frequency of motion of vaporizing molecules over the energy barrier, E^*, R is the gas constant and T is the temperature.

The maximum theoretical rate of vaporization from the surface, J_{max}, would be attained at a given temperature if the solid were in dynamic equilibrium with the vapor $[k(A)_s = k'(A)_v]$. Under these conditions the net rate, J, is zero. Such conditions may be studied however, by carrying out the vaporization experiment in a cell (Knudsen cell) with a very small orifice through which one may "sample" the vapor phase without significantly perturbing the solid-vapor equilibrium. Thus, from equilibrium (Knudsen cell) studies one can determine the maximum evaporation rate of most substances. The vacuum sublimation rate, on the other hand, may have any value depending on the mechanism of vaporization but its upper limit is that which is obtained under dynamic equilibrium conditions at a given temperature. It is customary to express the deviation of the vacuum evaporation rate, J_v, from that of the maximum equilibrium rate, J_{max}, in terms of the evaporation coefficient, α, which is given by $\alpha(T) = J_v(T)/J_{max}(T)$.[1] We shall see that the vacuum evaporation rate for some substances can be equal to the maximum rate ($\alpha(T) \simeq 1$) while for others it can be orders of magnitude smaller than the maximum rate ($\alpha(T) \ll 1$).

There is strong experimental evidence[2,3] indicating that the surface of the solid is heterogeneous, one can distinguish several atomic

positions which differ in the number of neighbors surrounding them. Figure 1 depicts some of these positions. Atoms in these different surface sites have different binding energies. Vaporization is considered to be a multi-step process in which atoms break away from a kink site, may diffuse on the surface until they are ready to vaporize most likely from an adsorbed state. This simple sequence of reaction steps becomes more complicated if the surface atoms or ions must undergo rearrangements such as association, dissociation or charge transfer prior to desorption from the vaporizing surface.[1] The rate of any one of these reaction steps may control the overall sublimation process. Certain solids may vaporize by two different reaction paths which can operate simultaneously at different surface sites.[4]

During vaporization the structure of the surface adjusts itself to the particular conditions of sublimation as to attain optimal vaporization rate. During these rearrangements in the surface structure there is an initially transient evaporation rate.[5] After a short induction period however, a steady state vaporization rate is obtained which can then be maintained at a given temperature.

Studies of sublimation mechanisms may be divided into two categories. (1) Chemical studies which are carried out to uncover the chemical rearrangements (association, dissociation charge transfer) which take place during vaporization, and (2) studies of surface topology which reveal the surface structure (arrangement and concentration of atomic steps, ledges, dislocations, etc.) to give the optimum sublimation rate under different experimental conditions. The sublimation of substances

which undergo marked chemical rearrangements during vaporization is, in general, controlled by the rate of a chemical reaction which takes place at a particular surface site. For solids which do not undergo marked atomic rearrangements during sublimation the surface structure plays a more dominant role in determining the rate of vaporization.

Studies of sublimation mechanisms should, in general, be carried out using "stable" single crystal surfaces.[1] (The surface area of a "stable" crystal face remains constant throughout the vaporization.) The use of polycrystalline samples can lead to serious difficulties of interpretation of the experimental results.[6] The measuring techniques are of two types, (1) total weight loss measurements which are carried out using vacuum microbalance techniques.[7] Such studies give reliable absolute evaporation rates but do not provide information about the composition of the vapor. (2) The vapor composition and its temperature dependence can be monitored using a mass spectrometer.[8] This technique should certainly be used if the vapor is composed of more than one species. This way the vapor constituents are identified and their activation energies of vaporization determined separately. Mass spectrometric measurements, in general, yield only relative evaporation rates. Preferably, both of these techniques should be used to obtain complete information about the sublimation mechanism.[4,8] Since sublimation is an endothermic reaction, heat has to be supplied to the vaporizing surface continuously in order to avoid surface cooling. For the same reason vacuum sublimation studies should be restricted to temperatures at which the flux of vaporizing molecules is small to avoid introducing any temperature gradient between

the bulk of the crystal and its vaporizing surface (approximately $J \leq 5 \times 10^{-5}$ moles/cm^2 sec).[1] Studies of the velocity distribution of the vapor fluxes indicate that thermal equilibrium between the solid surface and the vaporizing molecules can be easily maintained.[9]

From measurements of the vacuum evaporation rates at different temperatures using one face of a clean single crystal one can determine the activation energy of vaporization. These data however, do not tell us the mechanism of the vaporization reaction. Suitable complimentary experiments should be performed to uncover the reaction steps which control the desorption rate of the vaporizing species. Here I list some of the experiments which, for certain solids, were found useful in identifying the reaction steps of the complex vaporization reaction.

1. Sublimation rate measurements using crystals doped with impurities.[4,10]

2. Study of the sublimation rate of crystals with defects (vacancies, dislocations) in excess of their steady state concentration.[11,12]

3. Sublimation rate measurements as a function of the surface concentration of the vaporizing species.[13]

4. Measurement of the sublimation rates in a temperature range where phase transitions occur or in the presence of a liquid phase.[14,15]

5. Illumination of the vaporizing surface by light of suitable wavelength and intensity.[16]

It should be noted that as the conditions of sublimation are changed the rate controlling reaction step may change as well. Thus, the evaporation rate, $\alpha(T)$, the activation energy or even the vapor composition can differ from that observed during vacuum vaporization of the clean single crystal surface.

I shall now discuss studies of the sublimation mechanisms of sodium chloride, silver, arsenic and cadmium sulfide single crystal surfaces. The first two solids show evaporation rates which, under suitable conditions, are nearly equal to the maximum rate. Arsenic and cadmium sulfide however, are representatives of a large group of solids, which undergo marked chemical rearrangements during sublimation. These materials have sublimation rates which are appreciably smaller than the maximum equilibrium rate.

Sublimation Mechanism of Sodium Chloride

The sublimation mechanism of sodium chloride has been investigated using the (100) face of the single crystal in the temperature range 450-650°C.[8] The sodium chloride vapor is composed of mostly monomer (NaCl) and dimer (Na_2Cl_2) molecules with the dimer concentration increasing with increasing temperature (5-30 mole%).

The activation energies of vaporization of the monomer and dimer molecules under conditions of vacuum vaporization were found to be $E^*(NaCl) = 52.6$ kcal/mole of vapor and $E^*(Na_2Cl_2) = 62.1$ kcal/mole of vapor[4,8] nearly equal to the equilibrium heats of sublimation [$\Delta H_v(NaCl) = 52.1$ kcal/mole of vapor, $\Delta H_v(Na_2Cl_2) = 59.5$ kcal/mole of vapor].[17] It was found that the vacuum evaporation rate is dependent on the dislocation density in the clean single crystals. Samples with low, approximately $\sim 10^6$ dislocations per cm^2 have showed evaporation rates one-half of that of the maximum evaporation rate (Fig. 2). Other crystals which were strained to introduce high dislocation densities (approximately $10^7 cm^{-2}$) vaporized with the maximum rates (Fig. 2).[11] The activation energies of vaporization and the relative concentrations of monomer and dimer sodium chloride

molecules in the vapor remained unchanged for the different dislocation density crystals. When the samples were doped with approximately 200 parts per million of calcium, the vacuum evaporation rate of the (100) face decreased markedly to about one-tenth of the maximum rate of sublimation (Fig. 2). Also, the activation energies of vaporization have increased by several kilocalories for the doped crystals. Calcium enters the sodium chloride crystal lattice as a divalent ion and simultaneously excess sodium ion vacancies are created. Monovalent ion impurities, Br^-, OH^-, O_2^-, on the other hand, had no apparent effect on the sublimation rates of sodium chloride single crystals.

These observations provide a great deal of information about the mechanism of sublimation of sodium chloride and of other alkali halides. Increasing the dislocation density seems to proportionately increase the concentration of surface sites (kinks in ledges) from which vaporization can proceed. This is a surprising result, for most other solids which have been investigated show a constant evaporation rate (after a short induction period) at a given temperature, independent of the dislocation density. It appears, that, for alkali halides the mean free path, (X), of molecules away from ledges is short, they must vaporize near the ledges so that surface diffusion cannot play an important role in the vaporization reaction. The mean free path can be estimated by the equation, $X = a \exp(E^*_{des} - E^*_{diff})/2kT$ where $\underline{a}$ is the interatomic distance E^*_{diff} and E^*_{des} are the activation energies of surface diffusion and of desorption from the free surface, respectively. Calculations[18] give $X \approx a$, thus, of the order of a few lattice spacings. The lack of any appreciable surface diffusion inhibits the establishment of a steady state ledge

concentration for the low dislocation density crystals. Therefore, greater ledge density and kink concentration could be created around dislocations. This gives rise to an increase in the sublimation rate with increasing dislocation density.

The observation that the ratio of monomer (NaCl) and dimer (Na_2Cl_2) molecules remains constant for the different dislocation density crystals even though the total evaporation rate changes markedly indicate that there is no equilibrium on the surface between these two species.[4,8] Their reaction paths which lead to sublimation appear to be independent of each other. This result gives additional evidence for the short residence time of the adsorbed molecules on the vaporizing surface prior to desorption into vacuum.

The marked decrease of the sublimation rate for calcium doped crystals indicates that the removal of a sodium chloride molecule from a surface site became the rate controlling step in the presence of neighboring divalent ions or sodium ion vacancies.

Several complementary vaporization studies have been carried out using other types of alkali halide crystals in different laboratories.[19,20]

Sublimation Mechanism of Metals

The vapor of most metals is composed of dominantly monatomic gaseous species. Vaporization studies using single crystal metal surfaces are scarce, they have been carried out only recently using silver[21] and zinc[22] surfaces. The results indicate that the evaporation rates, after a short induction period, reach the maximum sublimation rate within the accuracy of the experiments. Also, the activation energy for vacuum vaporization was found to be equal to that of the heat of sublimation determined from

equilibrium vapor pressure measurements ($E^* \simeq \Delta H_v$). It appears that equilibrium can be established in all of the surface reaction steps which lead to vaporization and that the desorption of metal atoms from the vaporizing surface requires no extra activation energy. Oxygen was found to increase the evaporation rate of silver.

If we assume that the surface area of the vaporizing crystal face is equal to the geometrical surface area, such a large vacuum evaporation rate, J_{max}, implies that every surface atom should be available for sublimation with equal probability. This, of course, is very unlikely considering the heterogeneous nature of the surface (many different atomic sites with varying atomic binding energies). Closer inspection of the metal surfaces (using electron microscope) reveals, however, a considerable roughness thus, markedly increased surface area. The larger total surface area with respect to the geometric area could make it possible that only a fraction of the total surface atoms, which are in suitable atomic positions and have sufficient energy, would vaporize per unit area and the maximum sublimation rate could still be maintained. Melville[23] and others[24] have shown that no matter how rough the surface becomes the evaporation rate may never be larger than the maximum sublimation rate from a crystal with the smooth, geometrical surface area (for a condensation coefficient near unity).

At the onset of the vaporization experiments the sublimation rates were reported to be lower for both zinc and silver single crystals and only slowly approached the higher steady state rate at a given temperature. It appears that during this induction period the vaporizing surface area or the concentration of surface sites from which sublimation occurs gradually increase until the limiting maximum rate is obtained.

Hirth and Pound[25] have derived an equation for the evaporation rate of monatomic solids using a model with a probable series of surface reaction steps. For "small" crystals the maximum sublimation rate was predicted for their model crystal. For "large" low index crystal planes a limiting evaporation rate which is one-third of that of the maximum rate was obtained from their theory due to the limiting velocity of ledge motion. So far, there is no experimental confirmation of this latter result. It is possible that due to the imperfect structure of real crystal surfaces which always contain a large concentration of ledge sources (like dislocations) the maximum evaporation rate will be obtained in steady state for metal crystals of any size. More experiments using clean metal single crystal surfaces have to be carried out to ascertain the sublimation mechanism of monatomic solids.

We have seen that clean single crystals of sodium chloride, silver, and zinc show nearly maximum sublimation rates under proper experimental conditions and activation energies which are approximately equal to that of the equilibrium heat of sublimation. For these clean materials the structure of the vaporizing surface (dislocations, step or ledge concentrations) plays a dominant role in determining the sublimation rate. Impurities of certain types, when introduced in the crystal lattice, could also markedly change the vaporization characteristics (calcium in sodium chloride, oxygen in silver). It appears, however, that for these materials equilibrium can be achieved in all of the surface reaction steps and that desorption of the vaporizing species from the solid surface requires no additional activation energy. We shall see below that this is certainly not the case for the sublimation of solids which undergo pronounced chemical changes such as association or dissociation upon vaporization.

Sublimation Mechanism of Arsenic

The vaporization of polycrystalline and single crystal arsenic has been studied by Brewer and Kane[14] and by Rosenblatt[5] in the temperature range of 270-370°C. The vapor over the rhombohedral crystal is composed of dominantly tetrahedral gaseous molecules (As_4). Evaporation studies using the (111) crystal face revealed vacuum evaporation rates which were five to six orders of magnitude smaller than the maximum sublimation rates ($\alpha = 5\times10^{-5}$ at 277°C). The activation energy of vaporization is $E^* = 43.8$ kcal/mole of vapor while the equilibrium enthalpy of sublimation is much lower ($\Delta H_v^o = 33.1$ kcal/mole of vapor). Low dislocation density crystals show initially low evaporation rates which gradually rise to reach a higher steady state value. Studies of the surface topology revealed that most of the vaporization occurs from shallow triangular pits which appear at the point of emergence of spiral dislocations. The rate of vaporization increases as the pits grow until they intersect. Once the whole surface is covered by pits constant vaporization rate is obtained.

The evaporation rate of arsenic can be increased by orders of magnitude in the presence of liquid thallium which is placed in intimate contact with the vaporizing surface.[14] It appears that the formation of As_4 molecules is catalyzed by the presence of the liquid metal.

The sublimation characteristics of antimony[5] and red phosphorus[14] were found to be similar to that of arsenic.

These experimental results appear to be consistent with the mechanism that the slow reaction step in the vaporization process is associated with

the formation of the tetrahedral As_4 molecule at a kink on a spiral ledge [4 As(surface) $\rightarrow$ As_4(surface)]. These adsorbed molecules then diffuse rapidly on the surface and are subsequently desorbed into vacuum.

As in any complex multi-step reaction it is expected that changing the conditions of the experiment can change the reaction rate. The greatly enhanced vaporization rate of arsenic in the presence of a liquid metal (thallium) shows this clearly. Sublimation catalysis has been also observed for other solids such as gallium nitride[26] and gallium arsenide.[26a] Both of these compounds show markedly increased sublimation rates in the presence of liquid gallium. This effect may be due to the dissolution of the vaporizing crystal in the liquid metal thus, providing an alternate reaction path for sublimation.[14]

It is interesting to note that for sodium chloride crystals the steady state evaporation rate was dependent on the initial density of dislocations while for arsenic the same steady state evaporation rate was reached at a given temperature regardless of changes in dislocation density (after a short induction period). This difference in vaporization behavior is thought to be due to the much shorter mean free path for surface diffusion of sodium chloride ion pairs as opposed to arsenic molecules.

Sublimation Mechanism of Cadmium Sulfide

There are large groups of substances which dissociate to their atomic constituents or molecular aggregates of their constituents. For diatomic substances of this type the dominant vaporization reaction can be written as AB(solid) $\rightarrow$ A(vapor) + $\frac{1}{y}$ B_y(vapor) where y = 1, 2, or 4 in

most cases. If the vaporizing substance retains a nearly constant composition during vacuum vaporization the sublimation is "congruent." Some of the congruently vaporizing dissociating materials exhibit partly ionic character (NH_4Cl,[27] ZnO,[28] CdS[1]) or more covalent bonding (SnO_2,[29] GaN,[26] GaAs[26a]). The vaporization kinetics of these materials have been investigated. I shall discuss the sublimation mechanism of only one of these substances, cadmium sulfide which has been investigated in detail.

The vapor emanating from the (111) face of the hexagonal cadmium sulfide single crystal is composed of dominantly cadmium atoms (Cd) and diatomic sulfur molecules (S_2). The vacuum evaporation rate is approximately an order of magnitude smaller ($\bar{\alpha} \leq 0.1$) than the maximum sublimation rate in the temperature range, 650-800°C. The activation energy of vaporization is $E^* = 50.3$ kcal/mole of solid, much smaller than the heat of sublimation, $\Delta H_v^o = 75.2$ kcal/mole of the vaporizing solid.[1] [It should be noted that E^* can be either larger or smaller for the rate limiting sublimation step than the equilibrium heat of sublimation since the rate of the slow reaction step depends on the product, $k(A)_s$ and not on k alone. Thus, even if $E^* < \Delta H_v^o$ either the surface concentration of vaporizing species or the pre-exponential factor might be small and can make that particular vaporization step rate determining.] In order to explore the mechanism of sublimation of cadmium sulfide several studies were carried out.

(a) The vaporizing surface was illuminated by light of greater than band gap energy [$E_{gap}(25°C) = 2.41$ eV] in order to increase the charge carrier concentration (holes and electrons) at the surface of the semiconductor

crystal.[16,30] For high resistivity crystals the vacuum evaporation rate was found to increase linearly with light intensity.

(b) Cadmium sulfide crystals were doped with copper and then vaporized.[10] Copper is an acceptor in CdS which reduces the free carrier concentration of the pure crystals by orders of magnitude. It was found that copper doping reduced the vacuum evaporation rate by more than 50% from that of the evaporation rate of the undoped sample.

(c) The crystals were doped with excess cadmium or sulfur.[12] These treatments have reduced the initial evaporation rates of both cadmium and sulfur doped crystals by almost an order of magnitude with respect to the undoped crystal at the same temperature. The excess cadmium or sulfur, however, diffuses out of the crystal during vaporization. When all of the excess crystal constituents are removed and the crystal attains its steady state composition the evaporation rate undergoes a sharp transient and returns to the higher steady state rate characteristic of the undoped samples.

(d) The surface concentration of the vaporizing species were varied by using an atomic beam of cadmium or a molecular beam of sulfur which were allowed to impinge on the vaporizing surface at a given temperature.[13] It was found that the evaporation rate of cadmium sulfide is proportional to the -1/2 power of the sulfur flux and independent of the cadmium flux incident on the vaporizing surface.

From these experiments the detailed mechanism of vaporization of cadmium sulfide can be deduced.[1] It is apparent that the concentration of charge carriers, electrons, and holes play an important role in

determining the sublimation rate. The vaporization reaction steps which can be deduced from the available experimental data are (1) diffusion of excess cadmium or sulfur from the bulk of the crystal to the vaporizing surface, (2) electron transfer to convert the cadmium ions at the surface to neutral atoms, (3) hole transfer to neutralize the sulfur ions at the surface, (4) association of sulfur atoms, (5) desorption of diatomic sulfur molecules and (6) desorption of cadmium atoms.

Under conditions of vacuum sublimation for undoped crystals the reaction steps (2) and (3) are indistinguishable and rate limiting. For sulfur and cadmium doped crystals step (1) controls the rate. For copper doped samples, step (2) is the possible slow step.

It is interesting to note the self-correcting vaporization process of cadmium sulfide. The crystal composition which produces the optimum evaporation rate at a given temperature is established when steady state sublimation rate is reached. Any deviation from this solid composition decreases the rate and is self-corrected by the out-diffusion of the excess during vaporization. Similar results were obtained for oxygen doped zinc oxide crystals as well.[28] This self-correcting composition change indicates that although the compound dissociates upon vaporization the vaporization of cadmium and sulfur species are not independent but must be controlled by the same slow reaction step at the vaporizing surface.

Most of the oxides (Al_2O_3, Ga_2O_3, SnO_2, etc.) vaporize dissociatively while remaining congruent during the vaporization. For all these substances the vacuum evaporation rates are markedly smaller than the maximum rates which were determined from equilibrium vaporization studies.

Several oxides exhibit a marked discontinuity in the evaporation rate at the melting point where the rates show a sudden (three-fold) increase as the crystal lattice collapses.[15]

Noncongruent Vaporization

Substances which belong to this group of solids have constituents with greatly different evaporation rates. Thus, the solid composition may change markedly during vaporization. This kind of vaporization process indicates that the compound constituents vaporize by independent reaction paths.[31] A large fraction of the metal nitrides, carbides, borides, and silicides vaporize in this manner.

Compounds of the IIIA-VA elements of the periodic table exhibit an interesting transition from congruent to noncongruent vaporization. These compounds vaporize dissociatively; both gallium nitride and arsenide appear to vaporize congruently although the presence of liquid gallium droplets are readily discernible on the surface of the gallium arsenide crystals. Boron nitride on the other hand shows noncongruent vaporization. Solid boron condenses at the vaporizing surface and further vaporization is limited by the out-diffusion of nitrogen through the boron layer.[31] So far, studies of the sublimation mechanisms which lead to noncongruent vaporization have not been reported.

Summary

Sublimation rate studies which are carried out far from equilibrium provide information about the mechanism of sublimation. The activation energy of sublimation is obtained from measurements of the vacuum evaporation rate of single crystal surfaces as a function of temperature.

Complementary vaporization studies are carried out to uncover the reaction steps leading to the desorption of the vaporizing species. The rates of vacuum sublimation of solids which undergo marked chemical rearrangements (association or dissociation) upon vaporization are lower ($\alpha \ll 1$) than the maximum equilibrium sublimation rate. For these solids a particular chemical reaction is the rate controlling vaporization step. Solids which do not exhibit appreciable structural rearrangements during sublimation may have vacuum evaporation rates equal to that of the maximum rate. For clean materials of this type the structure of the vaporizing surface (dislocations, atomic steps, ledge concentrations) plays a more dominant role in determining the rate of vaporization. Once the reaction steps which lead to sublimation are known the sublimation rates can be changed by orders of magnitude by a suitable adjustment of the conditions of sublimation (addition of impurities, illumination, introduction of dislocations, vacancies, etc.).

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FIGURE CAPTIONS

Fig. 1 Model of a surface depicting atoms in the following positions: (a) in surface, (b) kink, (c) at ledge and (d) adsorbed on the surface.

Fig. 2 Vaporization rates of clean NaCl single crystals with different dislocation densities and of calcium doped samples.

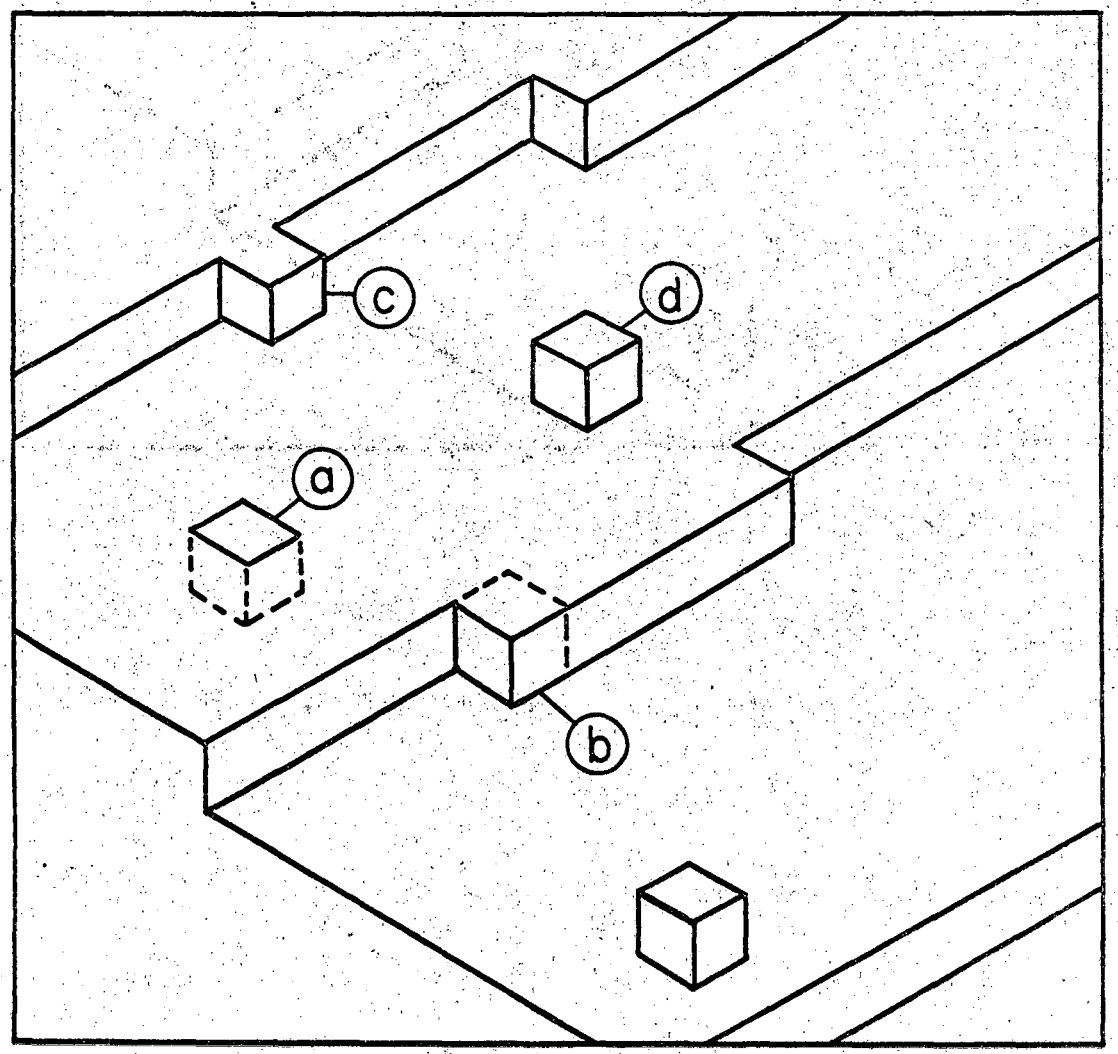

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Fig. 1

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Fig. 2