

siderations one can estimate that the solar wind or plasma protons are scattered and absorbed within a few tenths of a micron of the surface of the solid and that each proton produces about seven displaced atoms. Thus in a few months each fresh particle of dust should be sintered to its neighbors at the points of contact. This is much less than the time required for sintering through sputtering. Nevertheless, this efficient sintering process is limited to the outermost layer of the dust. It is also continually inhibited by the impact of micrometeorites and by breaking up by larger meteorites (16). Deeper layers of the dust are sensitive only to the more energetic protons. Thus 2-Mev protons will be stopped within less than 0.1 mm of the surface of the dust layer and 10-Mev protons will not reach beyond 1 mm. The flux of protons of higher energy, even if one includes the solar flares, is relatively low, and the defects the protons produce are spread over a much thicker layer. Thus, while a sintering process under these circumstances is possible on the scale of thousands or millions of years, its efficiency is critically dependent upon the meteorite bombardment. It appears thus that radiation sintering of lunar dust may play an important role in determining the mechanical properties of the outermost lunar surface. In a quantitative comparison of all the various phenomena which affect the cohesion and formation of surface dust, the recently discussed chemical degradation (17) should also be taken into account. Evidently much careful experimental and theoretical work is needed before the whole problem of the structure of the lunar dust layer is understood.

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Intercrystalline Links in Bulk Polyethylene

Abstract. Strength-promoting intercrystalline links in polyethylene, crystallized from the melt, have been observed under the electron microscope. The links measure up to many thousands of angstroms in length (depending upon the molecular weight of the polymer) and are of the order of 100 Å in diameter. Their formation appears to be initiated by molecular chains which contact, and begin to crystallize upon, the surfaces of two or more different crystals, often some distance apart. Deposition continues until these molecular bridges are pulled taut. More molecules are laid down upon the bridges to build up the larger links, which are themselves crystalline and may well be extended-chain single crystals.

When crystallized from the melt, synthetic high polymers such as polyethylene develop spherulitic structures which consist, in the main, of chain-folded lamellar crystals (1). It is evident from the ductility and strength of these materials, however, that neighboring lamellae are probably bound by ties stronger than those provided by Van der Waals attraction between planes of molecular folds, even in the case of lamellae whose surfaces are in intimate contact. Consequently, it has generally been thought that molecular folding is not as regular in polymers crystallized from the melt as it appears to be in single crystals grown from dilute solution. Some molecules (tie molecules) participate in the growth of two or more adjacent lamellae, thereby providing relatively short molecular

links which reinforce the structure (2). We now report what we believe to be the first direct observation of intercrystalline links in a melt-crystallized high polymer. These links are much more substantial (and thus much stronger) than has been anticipated. The links have been revealed by co-crystallizing fractionated samples of linear polyethylene with $n\text{-C}_{32}\text{H}_{66}$, this hydrocarbon diluent being removed later by dissolution in xylene at room temperature to expose the skeletal structure of the high polymer.

The photograph on the cover of this issue is an electron micrograph of the boundary between spherulites grown at 95°C in fractionated polyethylene (weight = average molecular weight, $\bar{M}_w$, = 726,000) blended with 50 percent of $n\text{-C}_{32}\text{H}_{66}$. The fibrillar links, which bridge radial arms of the spherulites and also the boundary between these spherulites, measure up to 15,000 Å in length and are between 30 and 300 Å in diameter. They are a genuine growth feature and not an artifact resulting from deformation of the sample. Electron-diffraction analysis of selected areas indicates that chain molecules lie parallel to the long axes of the links, and we have reason to believe that each link may be an extended-chain single crystal.

No intercrystalline links were found in polyethylene of molecular weight 4500 and only a few relatively short links were observed in polymer of molecular weight 27,500. In fractions of higher and higher molecular weight, however, links were found in increasing profusion, and their maximum length ($l_{\max}$) obeyed the relation $l_{\max} \sim 20 (\bar{M}_w)^{1/2}$ Å. Since the average maximum dimensions of a coiled chain (the average distance between the segments furthest removed from one another) should vary as $(\bar{M}_w)^{1/2}$, this relation suggests the following interpretation of our observations.

At the appreciable supercoolings generally employed in crystallizing high polymers from the melt, chain molecules may occasionally come into contact with, and begin to crystallize upon, the surfaces of different, and often widely separated, crystals. These molecules continue to crystallize until they are pulled taut. In some manner not as yet clear (possibly with assistance from entanglements) further molecules condense upon the nuclei provided by the bridges established initially in this way.

Samples of polyethylene cocrystallized with less than 50 percent of $n\text{-C}_{32}\text{H}_{66}$ show a greater profusion of links than is found in the sample illustrated in the photograph on the cover. It is unlikely that crystallization will be drastically different in an undiluted high polymer in which, therefore, extrapolation leads us to expect an even greater number of links to be formed. Being highly oriented (in the molecular sense) and, because of their mode of formation, being firmly anchored to the crystals, these links should possess considerable strength.

It is interesting to note that, for polyethylene fractions of higher molecular weight, observed values of $l_{\max}$ are larger, by more than an order of magnitude, than root-mean-square values of the end-to-end lengths of the

participating molecules as computed statistically (3). This may indicate that polymer molecules are much more extended in the melt than in dilute solution.

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Iron Minerals Formed by a Nuclear Explosion in a Salt Bed

Abstract. *The nuclear event, Gnome, was carried out in halite in the Salado formation and yielded a varied mineral assemblage. The iron support members reacted in the salt melt and formed several iron oxide phases. The magnetite which formed during the fireball stage reached in various ways with the environment to form higher oxides and hydrated oxides.*

The Gnome event was a nuclear explosion carried out at a depth of 361 m in bedded rocksalt in the Salado formation near Carlsbad, New Mexico, on 10 December 1961. Microscopic and x-ray examination of postshot drill cores sampled in the summer of 1963 and containing device debris showed a number of minerals which were not present before the shot. We want to draw particular attention to some of the iron-containing minerals which were identified; namely, magnetite (Fe_3O_4), hematite ($\alpha\text{-Fe}_2\text{O}_3$), maghemite ($\gamma\text{-Fe}_2\text{O}_3$), goethite ($\alpha\text{-FeO}\cdot\text{OH}$), and lepidocrocite ($\gamma\text{-FeO}\cdot\text{OH}$). Of these, only hematite was positively identified as being present in the formation before the event.

The main source of iron was sev-

eral tons of structural steel which had been placed in the shot room before the event. Although the initial environment was probably conducive to chemical reduction owing to the presence of rather large amounts of paraffin, material of the walls of the room contributed to the fireball and rendered the atmosphere oxidizing: large amounts of H_2O and CO_2 were released as compared to only small amounts of H_2 and CO . It may, therefore, be assumed that magnetite, the dominant iron mineral formed, was a primary product of the reaction between metallic iron and oxygen from minerals such as anhydrite with the possible addition of water from the Salado formation.

Magnetite has been usually, but not always, associated with considerable amounts of device debris. The presence of maghemite, lepidocrocite, and goethite are undoubtedly the result of secondary reactions which occurred after the temperature had dropped considerably. Figure 1 shows the relations between some of these minerals. Lepidocrocite can be formed by the oxidation of freshly prepared magnetite in the presence of water. Its dehydration below 750°C yields maghemite (1). The conditions of direct con-

version of magnetite to hematite and maghemite have been discussed recently by Colombo *et al.* (2) and by Lepp (3). In particular, maghemite may be formed between 200°C and 500°C in the absence of hematite, and depending upon particle size and oxidation rate. Smaller particles and a large rate promote maghemite formation.

The conditions in the cavity shortly after the detonation were favorable for the formation of lepidocrocite, since a large amount of water vapor was present. Consequently, under these conditions it would appear that maghemite would not be formed by the dehydration of lepidocrocite. One might hypothesize that magnetite oxidation could occur in a salt melt containing sulfate as an oxidizing agent. The $\text{NaCl}\text{--}\text{CaSO}_4$ eutectic lies at about 740°C , and although this temperature may be reduced by the addition of K_2SO_4 and MgSO_4 (from polyhalite), temperature conditions are such that probably hematite rather than maghemite would result. If, however, lepidocrocite becomes engulfed by hot and perhaps partially fused rock, it may well become isolated from the surrounding atmosphere and become dehydrated with the formation of maghemite. In view of the violent partial cavity collapse which started within a few seconds after the explosion and which was completed within 3 minutes, such a mechanism would reasonably explain the occurrence of maghemite.

Presumably goethite is formed by an entirely different path, namely, the oxidation of solutions of iron (II) compounds. Since small amounts of austenite and α -iron were found, we propose that goethite is formed by reaction of metallic iron (i) with the melt followed by hydrolysis under the prevailing hydrothermal conditions in the cavity, or (ii) with subsurface waters since December 1961.

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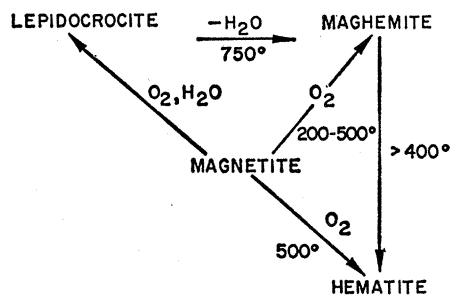


Fig. 1. Relation between iron oxides.