SPECTRAL PROPERTIES OF ANNEALED (Fe\textsubscript{x}Al\textsubscript{1-x})\textsubscript{2}O\textsubscript{3} GELS WITH APPLICATIONS TO MARS. Richard V. Morris, Code SN4, NASA-JSC, Houston, TX 77058 and Howard V. Lauer, Jr., LEMSCO, Houston, TX 77058.

Introduction. Characteristics of the reflectance spectra of the martian bright regions are a weak absorption edge extending from the visible to the near-IR and a weak band minimum near 0.87 um (e.g., 1). The edge and the band are generally attributed to ferric iron, but the actual mineralogies of the absorbing phases are not known. The position of the band is consistent, but the position and shape of the absorption edge are not consistent, with spectra for crystalline hematite (e.g., 2). In (3) and (4) it was found that certain amorphous plagioclase and poorly crystalline compounds are characterized by generally featureless ferric absorption edges, and it was suggested that the dominant ferric-containing phases on Mars are amorphous.

The optical properties of solid solutions containing ferric oxides and oxyhydroxides are not well understood but are clearly relevant to the interpretation of martian spectral data. It seems unlikely that ferric oxide and oxyhydroxide polymorphs, if present on Mars, are formed there under conditions which would yield the chemical and phase purity of the synthetic powders that are often used as the basis for phase identification. We are studying the spectral properties of the system Fe\textsubscript{x}O\textsubscript{3}-Al\textsubscript{2}O\textsubscript{3}-H\textsubscript{2}O as a function of the degree of crystallinity as determined by Mossbauer and X-ray analyses. This system was selected for two reasons: (a) Al substitution for ferric iron can occur during terrestrial weathering (5) and similarly may occur on Mars; and (b) some data on the spectral, Mossbauer, and X-ray properties of this system are available in the literature. Discussed in this paper are our results for an Al-rich (Fe\textsubscript{x}Al\textsubscript{1-x})\textsubscript{2}O\textsubscript{3} gel annealed at several temperatures.

Methods. The gel was synthesized by precipitation from sulfate salt solutions having Fe/Al = 0.05 using methods patterned after (6, 7). After air drying, separate aliquots were annealed at 100°, 500°, and 920°C to change the water content and/or degree of crystallinity. The H\textsubscript{2}O contents were determined using the procedure of (8). The spectral, Mossbauer, and X-ray data were acquired on a Cary-14 spectrophotometer (with an integrating sphere), an Elscint Mossbauer spectrometer, and a Pickey X-ray diffractometer, respectively.

Results and Discussion. The Mossbauer spectra of the annealed samples of the gel are all quadrupole doublets. The quadrupole splittings (QS) are 0.79, 1.22, and 0.57 mm/s and the average halfwidths (HW) are 0.53, 0.74, and 0.47 mm/s for the 100°, 500°, and 920°C samples, respectively. The larger values of QS and HW for the samples annealed at 100° and 500°C as compared to the one annealed at 920°C imply a relatively more highly distorted and variable local environment for ferric iron in the former relative to the latter. These results correlate with the X-ray data. The 100° and 500°C samples are amorphous to X-rays, and the 920°C sample is crystalline with the corundum structure. As expected, the amount of bound H\textsubscript{2}O also negatively correlates with annealing temperature; the concentrations are about 23, 9, and 1 wt.% for the 100°, 500°, and 920°C samples, respectively.

The reflectivity data are shown in Fig. 1. The bands near 1.4 and 1.9 um are due to H\textsubscript{2}O. The spectra of the 100° and 500°C samples are characterized by a ferric absorption edge extending from approximately 0.35 to 0.80 um with a feature near 0.45 um and by a shallow ferric band longward of the edge. The band minimum for the 100°C sample is near 0.91 um, and the one for the 500°C sample is at a shorter wavelength but not well defined. In contrast,
the spectrum of the $920^\circ C$ sample has, in addition to the absorption edge, numerous well-defined crystal field bands whose positions are consistent with other spectra of ferric-doped corundum (9, 10). On the basis of the Mossbauer and X-ray data, the lack of a well-developed band structure for the $100^\circ C$ and $500^\circ C$ samples is due to the highly variable local environment which acts to smear out the spectral lines. For the $920^\circ C$ sample, long range order is present and so are the spectral bands. With available data, it is not possible to tell whether the observed spectral properties of the $100^\circ$ and $500^\circ C$ samples are due to ferric iron uniformly distributed throughout the samples or to local concentrations of ferric iron. It is possible, for example, that their spectral properties are due to some ferric oxide or oxyhydroxide polymorph so fine-grained (e.g., superparamagnetic) that it escaped direct verification by both the X-ray and Mossbauer techniques.

The absorption edges of spectra of the $100^\circ$ and $500^\circ C$ samples and the martian bright region spectra are similar in position and shape, including the bend at 0.45 um. Because of this correspondence, we agree with other studies (3, 4) that amorphous, ferric-containing materials are likely important constituents of the martian bright regions. Unfortunately, this conclusion is probably not compositionally restrictive because a wide variety of compositions is likely to form suitable amorphous materials. Evidence for this is the similarity in spectra but not in composition for the amorphous materials examined in this study and in (3).

A problem for interpreting the Martian spectra entirely in terms of amorphous materials like the ones studied here is the band near 0.87 um. Perhaps precipitation of incipient hematite within the amorphous material satisfies the spectral constraints, but this and other ideas require study.