

and tilts similar to values in an elastic half space. But, as time progresses, the deformation changes as a result of the relaxation of the shear modulus in the lower half space, as shown in Fig. 2a; the surface displacement spreads out away from the surface break, and the change with time of displacement at fixed points on the surface shows complicated patterns.

The duration of the slow transient deformation is characterized by the relaxation time constant τ for both screw and edge dislocations, given by the ratio of the viscosity η of the viscoelastic asthenosphere to the shear modulus μ_1 of the elastic lithosphere,

$$\tau = \alpha\eta/2\mu \quad (1 < \alpha < 10)$$

Our models show that, if the asthenosphere is indeed viscous (and the lithosphere elastic), then crustal earthquakes with sufficiently deep faults should be followed by measurable postseismic deformation. The most spectacular example of such deformation was obtained after the Nankaido, Japan, thrust type earthquake (magnitude 8.2) of 20 December 1946.

In Fig. 2a we compare the results computed from a selected edge dislocation model (dip, 30°; depth, 0.75 of the crustal thickness) with the observed coseismic and postseismic deformation along a profile perpendicular to the surface break, reproduced from Kanamori (4). The computed and the observed initial coseismic vertical displacements are quite similar, both showing a zone of great uplift next to the fault and a broad zone of subsidence further away. The theoretical postseismic vertical displacement is obtained by subtracting the initial displacement from the final one, and the observed postseismic displacement is obtained from changes in beach levels during the 17-year period since the earthquake.

The similarity between the two postseismic curves is striking. In both most of the postseismic recovery takes place in the broad region of initial subsidence, and in both the amplitude of recovery is of the same order of magnitude as the initial amplitude of subsidence. This indicates that the postseismic deformation of the Nankaido earthquake results in all likelihood from viscous adjustments in the lower crust or the upper mantle of the earth.

In Fig. 2b we compare computed displacement time functions at selected points with observed vertical displace-

ments measured at beaches on Shikoku Island (4). Both displacement sets show the initial, coseismic displacement followed by slow added deformation, and both sets show large, similar variation of these shapes over small horizontal distances.

The decay time τ for the observed deformation is of the order of 5 years. Taking an average crustal shear modulus $\mu_1 = 8 \times 10^{11}$ dyne/cm², $\tau = 1.6 \times 10^8$ seconds, and $\alpha = 5$, we obtain the viscosity $\eta = 5 \times 10^{19}$ poise. This value is in gratifying agreement, though not identical, with estimates based on very long viscous rebound from crustal loading in Fennoscandia and North America. The amplitude of the observed transient deformation indicates roughly a 50 percent relaxation of the shear modulus of the asthenosphere.

Because it is more difficult to measure horizontal displacements than vertical displacements, the data on relaxation after large strike slip earthquakes are rare. Nevertheless, several resurveys in Japan were probably precise enough to detect postseismic deformation although none was found. It is possible, therefore, that strike slip faults inherently fail to break to sufficient depth in the lithosphere to allow measurable postseismic deformation. Thrust faults, in contrast, probably break through almost the entire lithosphere.

The agreement between the postseis-

mic data and the model, based on the current concepts of plate tectonics, provides not only an attractive explanation for postseismic deformation of shallow large earthquakes but also a new and independent confirmation that the asthenosphere behaves viscously, even over short periods of time. Careful monitoring of deformation after large earthquakes may provide a new tool for studying the upper mantle and may help to unravel the poorly understood physical processes responsible for its overall rheology.

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Ordered Lattice Defects in Colored Fluorite: Direct Observations

Abstract. *Ordered arrays of defect aggregates in the (111) planes of natural fluorite have been observed by transmission electron microscopy. The intense blue coloration observed in corresponding sample areas after 200-kilovolt electron microscopy confirms the conclusion that these are color-center aggregates and, conversely, that color centers are primarily responsible for fluorite coloration.*

The color and fluorescence of natural fluorite (CaF₂) have been the subject of many investigations over a period of more than a half century. Early summaries of fluorite studies indicated that the varying color of fluorite in deposits in the United States, South America, and Europe could be due to included organic matter or rare-earth compounds deposited on the surfaces of growing crystalline deposits (1). In a study of the ultraviolet absorption spectra of fluorite Titley and Damon (2) observed a strong absorption band at 3050 Å, and they ascribed a marked variation in the degree of

absorption to a variable concentration of defects in the crystal structure. More importantly, Titley and Damon ascribed the absorption (coloration) characteristics to color centers similar to those outlined for the alkali halides in the classic papers by Seitz (3, 4).

The notion of color centers in minerals has been advocated by a number of investigators (5, 6), but, to my knowledge, there have been no reports of direct observations of any associated defect structure. Even in the review of Seitz (4), there were no reported incidents of direct observations of color centers in alkali halides, or of associ-

ated defect clusters which have been proposed to result by color-center aggregation (4).

The results reported here indicate that color centers or color-center aggregates are responsible for fluorite coloration, and direct observations of such centers have been made for the first time with the use of the transmission electron microscope.

The fluorite samples used in this study were collected at Bingham, New Mexico (Blanchard group mines), south of highway 380 in southeastern Socorro County. Samples actually examined in this study included uncolored (clear) fluorite, light- to dark-blue fluorite, and pink to purple fluorite. All samples examined showed color bands or color-band concentrations, with the fragments cleaved along the {111} or {001} crystal planes. Samples were examined in an optical metallograph in reflected and transmitted light, and samples that were to be examined in a transmission electron microscope were prepared by crushing small pieces on a polished stainless steel support plate placed on a paper towel so that small flakes just barely observable in reflected light could be recovered. The samples were carefully broken so that small fragments cleaved along the {111} planes; selected cleavage fragments were examined in an electron microscope (Hitachi-Perkin Elmer H.U. 200 F) operated at 200 kv with a goniometer tilt stage.

Numerous unexplained defect and related contrast features were observed in the fluorite samples, and few observations were made of dislocations which could be readily identified in the classical sense, that is, on the basis of established diffraction contrast theory (5). However, in all the colored samples examined, a mosaic contrast feature was observed which intensified and developed with increased exposure to the electron beam. Small fragments cleaved from heavily colored samples exhibited this contrast feature, and the density of the mosaic increased with an increase in color density. Samples prepared from uncolored (clear) fluorite sometimes exhibited noticeable mosaic contrast which, after sufficient exposure to the electron beam, was observed to intensify. This contrast feature was observed to have a definite crystallographic regularity in bright-field electron micrographs, and associated selected-area electron diffraction patterns were observed to contain reg-

ular superlattice reflections in addition to the expected CaF_2 reflections associated with diffraction from a (111) surface orientation. During extended periods of observation in a region along the edge of a fluorite {111} cleavage fragment, considerable activity was observed in the regular structure developed. The structure was observed to grow, and recognizable defect aggregates appeared. These were crystallographically oriented, and entire defect aggregates were observed to move from one location to another. Rapid movement of isolated defect aggregates caused sharp shifts in the image as if large dislocations swept the area, after which the perfection of the array of defects was enhanced. These

features are illustrated in Fig. 1. Figure 1a shows a bright-field electron micrograph of the ordered defect array, and a portion of this image is shown enlarged in Fig. 1b. The defects are obviously aggregates since their mean image diameter is roughly 100 Å and their mean distance of separation in the linear image array is 200 Å. The symmetry directions of the defect array as shown in Fig. 1a are coincident with the (224) directions of the CaF_2 (111) pattern shown in Fig. 1c. However, all the observed diffraction spots in Fig. 1c can be consistently indexed on a cubic unit cell with lattice parameter $a_s = \sqrt{3}a_0$ where a_0 is the CaF_2 lattice parameter (5.463 Å). There is a systematic coincidence of

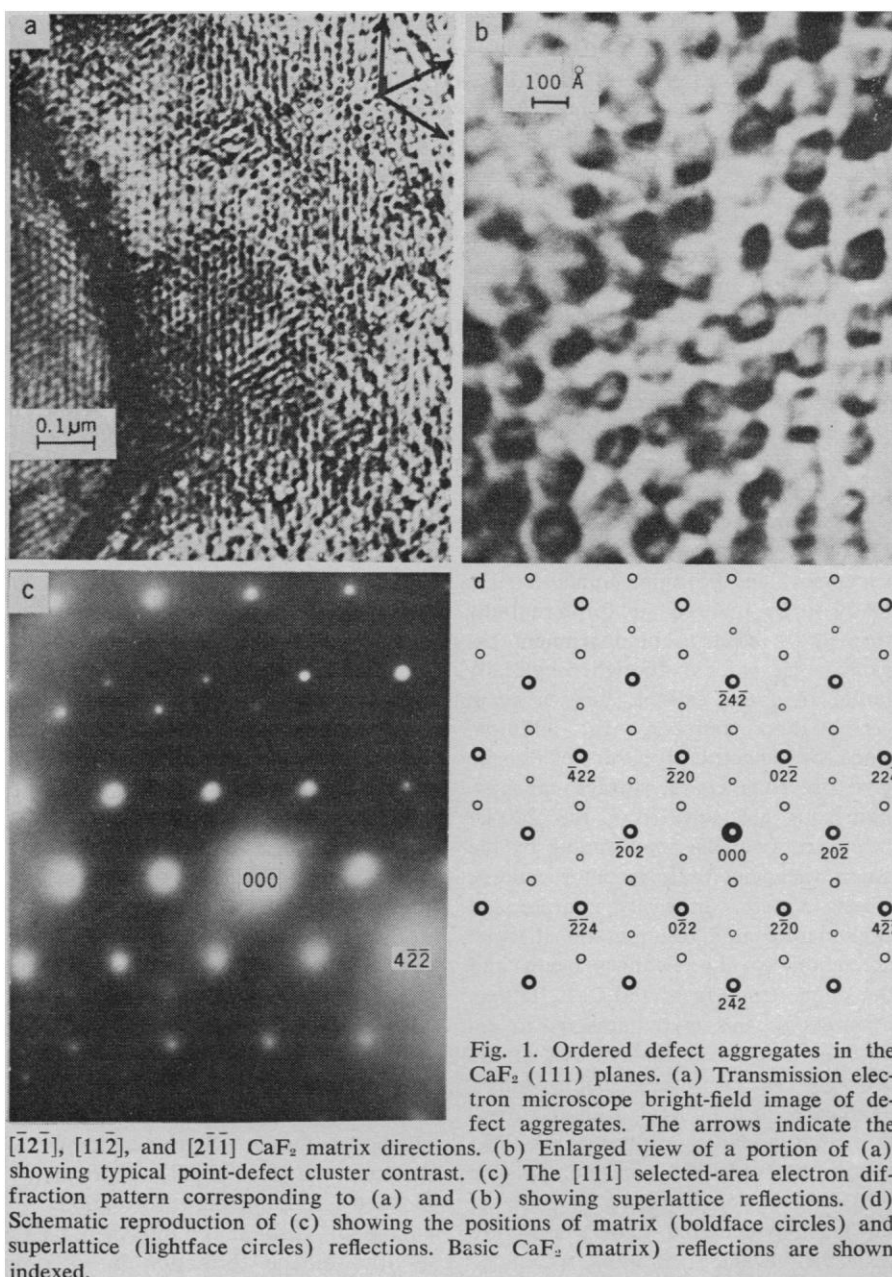
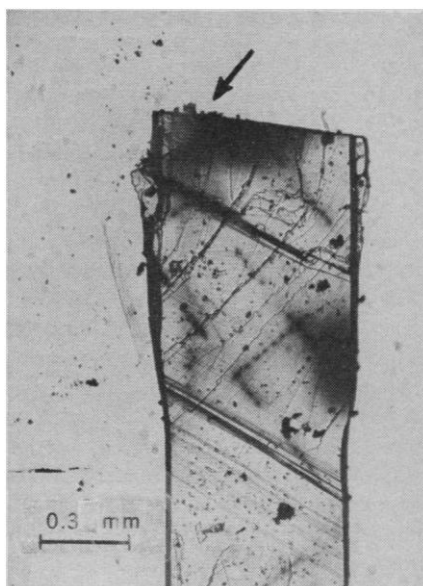


Fig. 1. Ordered defect aggregates in the CaF_2 (111) planes. (a) Transmission electron microscope bright-field image of defect aggregates. The arrows indicate the $[12\bar{1}]$, $[11\bar{2}]$, and $[2\bar{1}1]$ CaF_2 matrix directions. (b) Enlarged view of a portion of (a) showing typical point-defect cluster contrast. (c) The $[111]$ selected-area electron diffraction pattern corresponding to (a) and (b) showing superlattice reflections. (d) Schematic reproduction of (c) showing the positions of matrix (boldface circles) and superlattice (lightface circles) reflections. Basic CaF_2 (matrix) reflections are shown indexed.

Fig. 2. Optical micrograph showing blue coloration in the area of Fig. 1a (arrow) after electron microscopy.



superlattice and CaF_2 matrix reflections, as noted in the schematic diffraction net of Fig. 1d. On looking at the superlattice pattern, one can see that the defect symmetries indicated by the arrows in Fig. 1a are coincident with the $\langle 220 \rangle$ directions of the superlattice.

Because of the very small size of the sample fragments examined, little identifiable color was observed. Nearly all samples appeared completely colorless. However, after examination in the electron microscope, distinct and intense blue-colored regions were observed in the samples. Figure 2 shows the region of the sample from which the images and the selected-area electron diffraction pattern of Fig. 1 were obtained, illustrating the associated coloration. It is apparent that 200-kv electron-beam irradiation of the fluorite has induced additional defects and defect agglomeration, and that the defect agglomeration is directly responsible for the residual coloration. This seems to be a clear implication of color centers in natural fluorite, analogous to the results reported by Seitz on alkali halides (4).

The CaF_2 structure can be visualized as a cubic array of F^- ions with Ca^{2+} ions at every other body-centered position. Fluorite is therefore intrinsically a calcium-vacancy-defect structure. However, Frenkel defects (or F^- vacancies) in the anion sublattice are likely to be favored and preferentially formed by electron bombardment because the anions, though physically larger than the cations, have a small coordination number. In addition, since the dielectric properties of fluorite give rise to a charge-storage capacity, numerous electrons from the 200-kv beam are available for trapping by the anion vacancies to form color centers. These centers can easily migrate and agglomerate as a result of the thermal activation of the electron beam and the open structure of the CaF_2 lattice.

Although this study appears to report the first direct observations of the ordering of vacancy (color-center) aggregates in a mineral, I should mention that vacancy ordering has also been observed in nonstoichiometric NiAl which was found to be a defect CsCl (body-centered cubic) structure with the vacancies forming triangular

arrangements in the (111) plane (6). The investigation reported here shows that electron microscope observations of an ordered defect aggregate superlattice array, presumably color-center aggregates, are directly associated with the observed coloration in fluorite. These results appear to be the first

direct observations of color-center aggregates and the first direct evidence of color-center activity in a colored mineral system. These results will be presented in greater detail elsewhere (7).

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Ethane Evolution: A New Index of Lipid Peroxidation

Abstract. *Homogenates of mouse liver and brain at 37°C spontaneously formed lipid peroxides and simultaneously evolved ethane. α -Tocopherol, a lipid antioxidant, blocked ethane formation. When mice were injected with carbon tetrachloride (a liquid prooxidant for liver), the animals produced ethane. Ethane evolution in vivo was stimulated by prior administration of phenobarbital and it was diminished by prior injection of α -tocopherol. These data suggest that ethane production may be a useful index of lipid peroxidation in tissue homogenates and in intact animals.*

There is widespread belief that lipid peroxidation may be a factor in certain forms of tissue pathology, particularly under the extreme conditions of experimental vitamin E deficiency (1). Recknagel and co-workers have presented evidence for peroxidation of microsomal lipids during CCl_4 poisoning in experimental animals (2) and in humans (3). We now report that the spontaneous formation of lipid peroxides in homogenates of mouse tissue shaken in air at 37°C is accompanied by evolution of ethane, a hydrocarbon gas. In *in vivo* studies, administration of CCl_4 to mice provoked ethane evolution. Since α -tocopherol (vitamin E, a lipid antioxidant) blocked spontaneous formation of ethane *in vitro* and diminished CCl_4 -induced ethane formation *in vivo*, it

appeared that lipid peroxidation was linked to the formation of the hydrocarbon gas.

Homogenates of mouse liver and brain were prepared in nine volumes of ice-cold isotonic saline buffered with phosphate at pH 7.4 (4). Samples (10 ml) were incubated in air with shaking at 37°C in 25-ml Erlenmeyer flasks that had been sealed with rubber caps (5). Samples (0.5 or 1.0 ml) of air atmosphere were removed with a gas-tight plastic syringe, equipped with a side-venting needle (6). These samples were analyzed immediately by gas chromatography (7). Lipid peroxidation was evaluated with the 2-thiobarbituric acid reaction, which measures malonaldehyde evolved as a breakdown product of peroxidized lipids (8).

For *in vivo* studies, five mice were