non discussed in the first part of this Letter. At high frequencies, on the other hand, the velocity correlations neglected here will certainly become important.

The hydrodynamic regime at small q requires a special consideration. We find for small q a mode $\Omega_q = Cq$, where $MC^2 = (n\kappa_T)^{-1}$, which is driven by the isothermal rather than the adiabatic modulus. As a consequence, our equations are valid outside of the hydrodynamic domain, $q > \omega_H/C$, where ω_H is a hydrodynamic relaxation frequency due to viscosity, thermal conduction, etc. In the dense liquid, the dispersion law will, of course, be relatively insensitive to the changeover of regions, since $\kappa_T/\kappa_S \simeq 1$.

Finally, we remark that if the correlation function is characterized by that of a hard-core fluid it is easy to show that (9) and (21) become

$$S(q) = [S(Q)]^{\mathrm{HC}}/\{1+\tilde{v}^{\mathrm{att}}(q)[S(q)]^{\mathrm{HC}}\} \tag{25}$$

and our stability condition (13) reduces to that discussed in Chap. IV of Ref. 1. Here

$$\tilde{v}^{\mathrm{att}}(q) = n\int v(r)\, g^{\mathrm{HC}}(r)\, e^{i\vec{q}\cdot\vec{r}}\, d^3r. \tag{26}$$

In addition, we note that to our knowledge the relation to the virial (which is also true in the quantum theory) has never been observed and therefore the necessity of the term $\partial g(r)/\partial n$ in (21) has been overlooked. Therefore one expects significant modifications beyond the previous estimates of the small-q behavior also in the electron correlation problem.[10]

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Polarized Local-Mode Absorption of Aligned H^-H^-, D^-D^-, and H^-D^- Pairs in Alkali Halides*

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Aligned U-center pairs (containing H^- and D^- ions) were produced by a reaction of interstitial H_2, D_2, and HD molecules with optically aligned M centers. The study of their local-mode spectra revealed several new bands in the infrared. From the polarization of these local modes in aligned systems, the observed bands can be clearly assigned to the different optically active vibrations of the ⟨110⟩-oriented pair centers.

Substitutional H^- ions (U centers) in pure alkali halides give rise to a threefold-degenerate local-mode absorption in the infrared. This system (and its isotopic counterpart D^-) has been very extensively studied both experimentally and theoretically, and has become the most simple and well-understood example for systems exhibiting local modes in a cubic (O_h) potential.[1] In this regard, its role can be compared with that of the F center for the understanding of a localized electron in an O_h lattice potential. In this latter case, much more specific and informative studies became possible, when success was achieved in associating F centers into pairs (M) and trimers (R) as well as to foreign cations (F_A), in optically aligning these complexes, and in studying their anisotropic properties with polarized light.[2] For the U centers, comparable techniques for preparing specific complexes of reduced symmetry and selected alignment have not been available so far. In the following we describe a new technique which is based on the close interrelation of *U* and *F* centers and which produces aligned *U*-center pairs on adjacent ⟨110⟩ anion sites, allowing the study of their local modes with polarized light.

U centers can be converted by uv or x irradiation at room temperature into *F* centers.[3] In this process the hydrogen leaves the anion site, which becomes occupied by the *U*-center electron forming an *F* center. The mobile ejected H atom recombines quickly with another hydrogen forming a stable interstitial molecule. Though these H_2 molecules are mobile in the lattice near room temperature, they cannot recombine with the *F*-center system, which is found to be stable over long periods similar to additively colored systems. If, however, the *F* centers are aggregated into *F*-center pairs (*M* centers), one observes a spontaneous decay of these *M* centers at room temperature over a period of some hours.[4] As the *F*-center pair binding is thermally stable up to about +100°C, it is evident that the interstitial hydrogen must be responsible for the observed *M* decay. The conclusion can be drawn that the mobile H_2 molecules, while being unable to react with isolated *F* centers, can react with *F*-center pairs. In this latter process, the strong H_2 molecular binding need not be broken, because an H^-H^- pair on adjacent ⟨110⟩ anion sites can be formed.

Based on this idea, the following production process for *U*-center pairs was attempted: Crystals with high *U*-center concentration $[(3\text{-}7)\times10^{18}\ \mathrm{cm}^{-3}]$ were cleaved into thin slabs (~1 mm), which were x irradiated at room temperature converting a large fraction (~30-50%) of the *U* centers into *F* centers. By optical irradiation into the high-energy side of the *F* band a uniform $F\rightarrow M$ conversion could be achieved (typical optical density values in the *M* band for each crystal slab were about 2 to 4). When no alignment was planned, this system was kept at room temperature until the *M* centers had reacted with the hydrogen and disappeared. Afterwards, a new $F\rightarrow M$ conversion and *M* annealing could be repeated. Several crystal slabs treated in this way were clamped together and inserted into a He cryostat for infrared-absorption measurements.

Figure 1 shows the local-mode absorption of such a system at various stages. The initial spectrum displays the (off-scale) *U*-center local mode at 502 cm^{-1} and its phonon sideband at 565 cm^{-1}. In addition, some very small bands which do not occur in a low-density *U*-center system appear on both sides of the local-mode line. During the first two stages of the crystal treatment (x-ray–induced $U\rightarrow F$ and optically induced $F\rightarrow M$ conversion) this spectrum changes little,

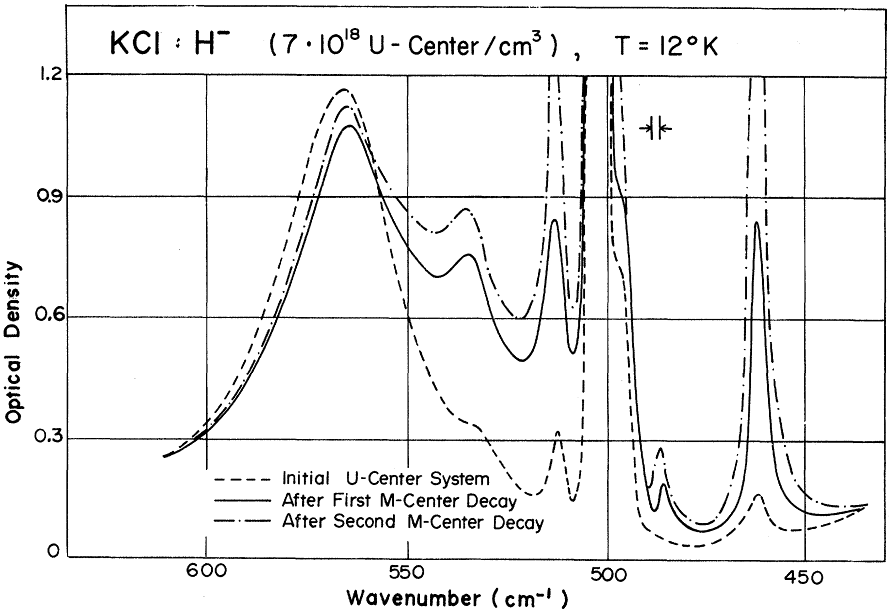

FIG. 1. Infrared-absorption spectra of a KCl crystal with high *U*-center concentration before and after two subsequent treatments leading to the production of H^-H^- pairs (see text).

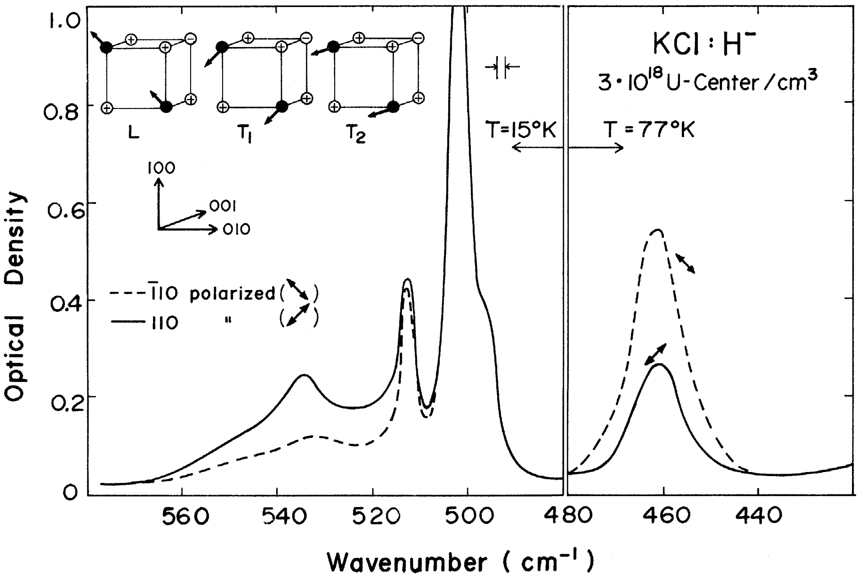

FIG. 2. Absorption spectrum of KCl:H$^-$ after production of aligned H$^-$H$^-$ pairs (with preferential [$\bar{1}$10] orientation as indicated in the upper left-hand corner), measured for [$\bar{1}$10]- and [110]-polarized light incident in a [001] direction. The phonon sideband of the H$^-$ local mode at 565 cm^{-1} has been subtracted. The band at 463 cm^{-1} was measured at liquid-nitrogen temperature in order to avoid errors from improper resolution.

apart from the phonon sideband changes, as a result of the induced variation in the U-center concentration. A very drastic change, however, takes place after the thermal annealing of the M centers at room temperature (Fig. 1, solid curve): Strong absorption increases occur in the region of the initially present small bands at 463, 512, and 535 cm^{-1}. Repetition of the $F \rightarrow M$ conversion and M annealing again produces a similar increase. Many experiments with varying concentration and temperature treatment conditions showed that the three bands at 463.5, 512.5, and 535 cm^{-1} always developed in the same proportion, while the weaker absorptions at 487 and 494 cm^{-1} appeared in varying proportions.

From the six expected nondegenerate local modes of the H$^-$H$^-$ pair in C_{2v} symmetry, the three out-of-phase modes will be infrared inactive because of the exact cancelation of the vibrating dipole moments. The three optically active in-phase vibrations of the coupled H$^-$ ions will be polarized in the longitudinal (L) and the two transverse (T_1 and T_2) directions of the pair, as sketched in the insert of Fig. 2. A clear assignment of these symmetries to the observed bands was achieved by experiments with aligned H$^-$H$^-$ systems. In these experiments the optically formed M centers were immediately cooled to liquid-nitrogen temperature and irradiated for long periods with [$\bar{1}$10] polarized light of 496 mμ. A large rate of M reorientation, even with very high concentrations of centers, could be achieved, using a method involving increased intermediate $F_2{}^+$-center production. This technique will be described elsewhere.[5] By subsequent thermal reaction of the H$_2$ moleucles with the aligned M-center system, a H$^-$H$^-$-pair system with an alignment similar to that of the M-center system can be expected. In the experiment of Fig. 2 an excess of [$\bar{1}$10]-oriented M centers, i.e., H$^-$H$^-$ pairs as indicated in the insert, was produced. Studying this system with light incident in an [001] direction, one expects for the L mode an increased absorption for [$\bar{1}$10]-polarized light as compared with [110] light, and the opposite behavior for the T_1 mode. This behavior is indeed observed in Fig. 2 for the bands at 463.5 and 535 cm^{-1}, assigning them without doubt to the L and T_1 mode of the [$\bar{1}$10] pair, respectively.

In this geometry the T_2 mode should show no dichroism but only a reduced relative size due to the pair alignment: This is observed for the 512.5-cm^{-1} band, suggesting its assignment to the T_2 mode. To test this assignment explicitly, the stack of crystal slabs was turned by 90° about the [100] direction and measured with light incident in the [0$\bar{1}$0] direction, as sketched in the insert of Fig. 3. In this geometry the T_2-mode absorption is expected to be stronger for [001]-polarized light as compared with [100] polarization. This behavior is found for the 512.5-cm^{-1} band, definitely assigning it to the T_2 mode.

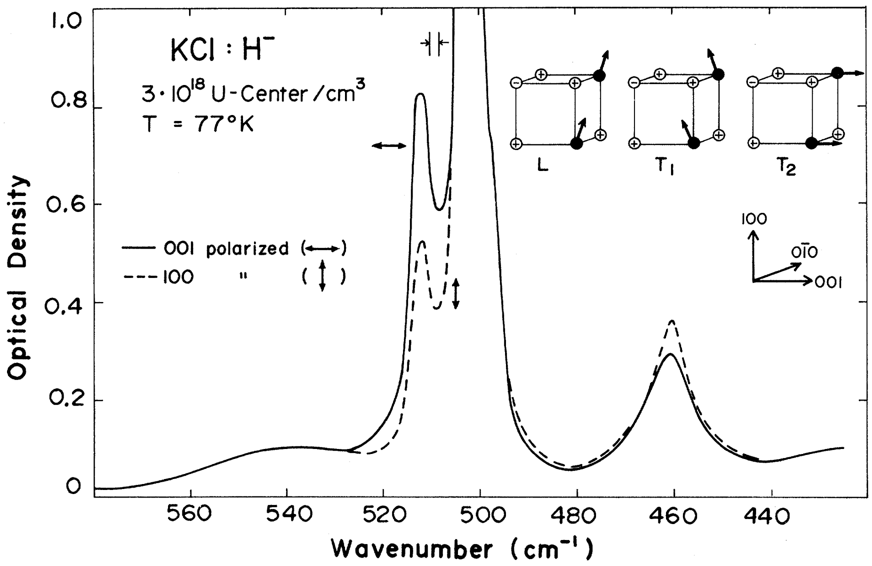

FIG. 3. Absorption spectrum of the same crystal system as in Fig. 2 turned by 90° around the [100] direction, measured for [001]- and [100]-polarized light incident in a [$0\bar{1}0$] direction, measured at liquid-nitrogen temperature. The H^- phonon sideband is again subtracted.

(The L and T_1 mode show, as expected in this geometry, only a very small dichroism). The L- and T_2-mode absorption at 463 and 512 cm^{-1} become extremely narrow at low temperatures ($\Delta\omega < 2$ cm^{-1}), beyond the resolution limit of the instrument, just as for the H^- local mode. In astonishing contrast to this, the T_1 mode at 535 cm^{-1} stays very broad ($\Delta\omega \approx 20$ cm^{-1}) even at low temperatures, indicating a very different broadening mechanism.

Using U centers with D^- ions for the same production process, aligned D^-D^- pairs were also produced and studied with polarized light in the region around the D^- local mode at 359 cm^{-1}. A similar three-band absorption structure at 331.5, 375.5, and 368 cm^{-1} was found, which from polarized experiments in aligned systems could be assigned to the L, T_1, and T_2 modes, respectively. The frequency ratio of the L, T_1, and T_2 modes for H^-H^- and D^-D^- pairs is therefore 1.40, 1.39, and 1.42, respectively, values which are very close to the observed ratio 1.40 of the isolated H^- and D^- modes and to $\sqrt{2}$.

Using different amounts of hydrogen and deuterium gas for the production of the initial U-center system, mixed pairs of aligned H^-D^- pairs could be created by the same production method too. These pairs were found to give rise to new bands in both the H^- and D^- local-mode regions. In the mixed pairs the amplitudes of the H^- and D^- vibrations are different, so that the dipole moments for the out-of-phase vibrations of the two ions no longer cancel as in the case of the homonuclear pairs; therefore these vibrations become infrared active too.

A more detailed account of the D^-D^-- and H^-D^--pair spectra as well as of the measurements of U-center pairs in several other alkali halides will be presented soon, together with a theoretical treatment of the pair modes. Raman experiments, aimed at the detection of the infrared-inactive—but Raman-active—H^-H^- and D^-D^- local modes are in preparation.

Following the same general idea outlined here, experiments are in progress in which H^- interstitials (produced by uv irradiation at low temperatures) are thermally annealed, recombining with specially perturbed anion vacancy sites which have been "prepared" and aligned by optical and thermal techniques. It seems feasible with this method to "rebuild" many of the locally perturbed F configurations (like the F_A centers) as corresponding H^- or D^- centers and to study their local modes.

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Continuous and Discontinuous Semiconductor-Metal Transition in Samarium Monochalcogenides Under Pressure

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Resistivity and lattice-constant measurements under high pressure on SmS show that a $4f \rightarrow 5d$ electronic transition in SmS occurs discontinuously at 6.5 kbar at room temperature, whereas such a transition takes place continuously over a broad pressure range in SmTe and SmSe. The pressure-induced semiconductor-to-metal transition in the Sm chalcogenides and their pressure-volume relationship are consistent with the conversion of Sm^{2+} to Sm^{3+}. Optical-absorption measurements in these materials correlate well with the resistivity data under pressure. The semiconductor-to-metal transition in Sm chalcogenides appears to fit the model recently proposed by Falicov and Kimball for a system with a localized state and a conduction band.

We recently reported the occurrence of a continuous semiconductor-to-metal transition in SmTe,[1] due to $4f$ electron delocalization induced by high pressure. In this Letter we report the discovery of a discontinuous $4f \rightarrow 5d$ electron delocalization in SmS. Both the resistivity and the lattice constant abruptly decrease at 6.5-kbar pressure at 293°K, without any change in the crystal structure. The discontinuity in the lattice constant at this pressure is consistent with the conversion of Sm^{2+} to Sm^{3+}. The occurrence of continuous and discontinuous semiconductor-metal transition in Sm monochalcogenides presents an entirely new situation from both theoretical and experimental points of view.

Samarium sulfide was prepared by a reaction of high-purity sulfur with Sm in a quartz tube and a subsequent melting in a tantalum tube, under high vacuum. The material on cooling was well crystallized, but polycrystalline, with large single-crystal regions. X-ray powder photographs confirmed both the NaCl structure and the lattice constant (5.97 Å) appropriate to SmS.[2] For resistivity as well as optical studies single crystals were used.

The material had low resistivities, in the range 0.01 to 0.001 Ω cm (at 1 atm) and when scratched or polished acquired a golden yellow color on the surface.[3] Four-lead resistivity measurements were made with bar samples. Indium metal provided excellent ohmic contacts. Resistivity measurements under pressure were carried out in isoamyl alcohol as pressure medium. Figure 1 shows the resistance as a function of pressure at 293°K. There is an abrupt decrease in resistance at 6.5 kbar which evidently represents a discon-

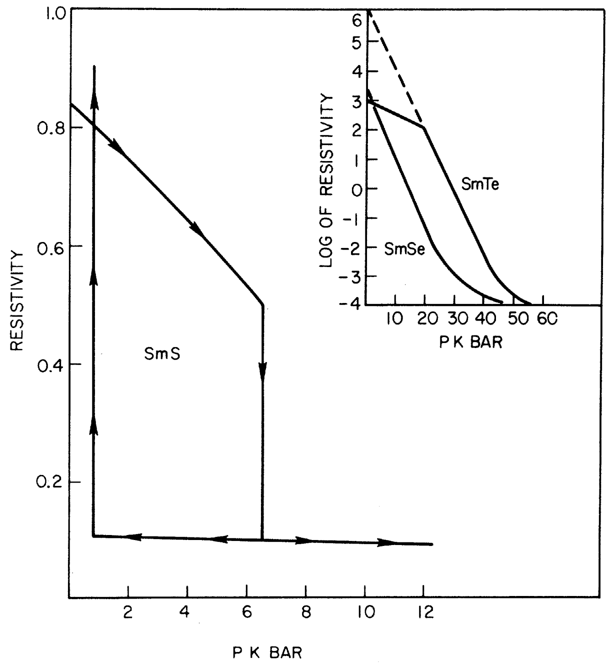

FIG. 1. Normalized resistivity versus pressure for single crystal SmS. The actual resistivity at pressures greater than 6.5 kbar is ~3–4×10^{-4} Ω cm. See text. The data for SmTe and SmSe are shown in the inset.