J. Phys. Soc. Jpn. 22, 1060 (1967).
[11]N. N. Gerasimenko, A. V. Dvurechenskii, and L. S. Smirnov, Fiz. Tekh. Poluprovodn. 6, 987 (1972) [Sov. Phys. Semicond. 6, 862 (1972)].
[12]H. Ibach, K. Horn, R. Dorn, and H. Lüth, Surf. Sci. 38, 433 (1973).
[13]J. T. P. Grant and D. Haneman, Surf. Sci. 15, 117 (1969).
[14]D. Haneman, J. T. P. Grant, and R. U. Khokhar, Surf. Sci. 13, 119 (1969).
[15]M. V. Swain, B. R. Lawn, and S. J. Burns, J. Mater. Sci. 9, 175 (1974).
[16]D. E. Eastman and W. D. Grobman, Phys. Rev. Lett. 28, 1378 (1972).
[17]L. F. Wagner and W. E. Spicer, Phys. Rev. Lett. 28, 1381 (1972).
[18]J. E. Rowe and H. Ibach, Phys. Rev. Lett. 32, 421 (1973).
[19]D. J. Miller, D. L. Heron, and D. Haneman, J. Vac. Sci. Technol. 9, 906 (1972).
[20]B. L. Crowder, R. S. Title, M. M. Brodsky, and G. D. Pettit, Appl. Phys. Lett. 16, 205 (1970).
[21]R. U. Khokhar and D. Haneman, J. Appl. Phys. 43, 317 (1972).

Multiphoton-Induced Directional Emission of Halogen Atoms from Alkali Halides*

Ansgar Schmid and Peter Bräunlich
Research Institute for Engineering Sciences, Wayne State University, Detroit, Michigan 48202, and Bendix Research Laboratories, Southfield, Michigan 48076

and

Pieter K. Rol
Research Institute for Engineering Sciences, Wayne State University, Detroit, Michigan 48202
(Received 31 July 1975)

Multiphoton-induced directional emission of halogen atoms and ions from fcc KCl, KBr, and NaCl single crystals has been observed in the [110] and [211] direction during interaction of the crystals with strong ruby laser pulses. Nonradiative decay of self-trapped excitons and subsequent replacement collision chains seem to account for this effect. Some difficulties remain with the mechanism for the previously unobserved [211] emission.

We wish to report the observation of directional emission of lattice constituents from alkali halides that are exposed to intense fluxes of photons from the visible spectrum. This phenomenon is distinctly different from the ablation of surfaces due to the characteristic hot plasma formed during optical surface breakdown. It was detected at photon fluxes one order of magnitude below the intrinsic surface breakdown threshold. It is clearly a multiphoton effect, while laser damage at the ruby frequency was found to be avalanche ionization assisted by multiphoton carrier generation[1,2]; and, finally, it is characterized by a strictly directional emission of the halogens predominantly in the form of halogen atoms. Negative ions were detected with high-gain detectors only and no positive ions were found.

The following experimental procedures were used. A well-defined pulse from a ruby laser (TEM_{00} mode, 30 nsec full width at half-maximum) was focused onto the transparent sample. Care was taken to avoid self-focusing at the higher fluxes. The sample was mounted on a temperature-controlled sample holder inside a liquid-nitrogen-trapped, oil-pumped, high-vacuum system ($\lesssim 2\times10^{-6}$ Torr) and oriented perpendicular to the direction of the laser beam (Fig. 1). High-gain microchannel plates were used for the detection of charged particles with high spatial resolution. They were arranged with respect to the sample surface so that they were facing in the crystallographic [110] and [211] directions. During and immediately after interaction of the laser pulse with the sample, well-localized emission of negative ions was observed with the detectors from KBr and KCl with a narrow angular

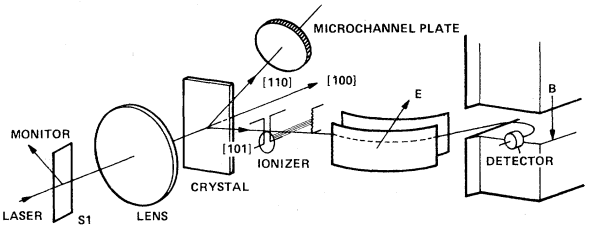

FIG. 1. Schematic of experimental arrangement.

distribution around these directions. The ionic character of the emission was established by means of conventional separation of electrons and ions in a magnetic field and by utilizing differences in the quantum yield of the microchannel plates for electrons and ions at selected kinetic energies.

Neutral species were measured with a modified miniature Mattauch-Herzog mass spectrometer.[3] Its ion source was positioned so that one of the [110] directions was intercepted (Fig. 1). A set of oppositely biased grids prevented any charged species from entering the source. In this way strong emission of neutral halogen atoms was found from KCl, KBr, and NaCl, but not from LiF, and it was established that the emission was not the result of removal of surface contaminants. In the case of KCl the chlorine emission intensity recorded by the mass spectrometer follows a fourth-order dependence on the laser peak flux indicating that a four-photon absorption process is required to trigger the emission (Fig. 2).

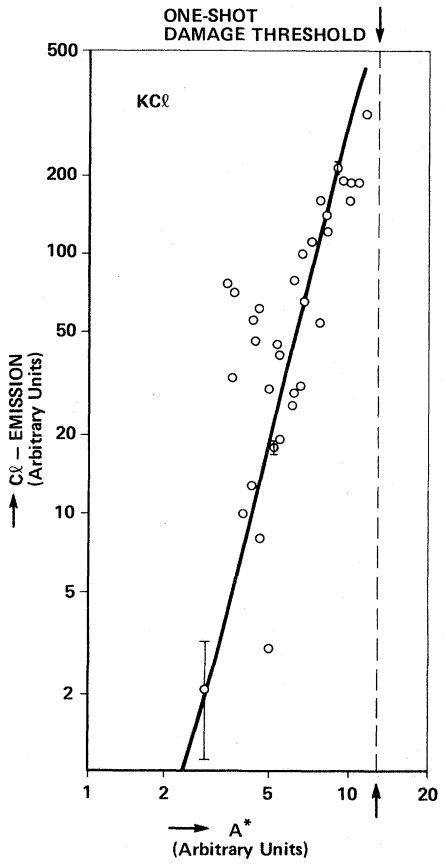

FIG. 2. ⟨110⟩ Cl-emission intensity from KCl versus ruby laser peak flux.

Similar curves were measured for KBr and NaCl. Close to the damage threshold about 10^{16} halogen atoms were removed per shot from the surfaces of the three alkali halides investigated. All experiments were performed at room temperature.

The directional character of the halogen emission is demonstrated in Fig. 3. A specially modified detector having a small hole for the passage of the laser beam was mounted 0.30 in. in front of and parallel to the (100) plane of the sample. The emission pattern consists of eight clearly visible spots representing four [211] and the four [110] directions of the sample. Because of the limited size of the detector eight additional [211] directions [63.4 deg away from the normal to the (100) plane] could not be observed. Similar patterns were found from KBr and NaCl.

No measurable alkali signals were observed with the mass spectrometer from any sample. This emission is not expected to occur in preferred directions and, therefore, the number of alkali atoms entering the ion source is considerably smaller than that of the halogen atoms. Any alkali signal was buried in the laser-induced electromagnetic noise.

The results described resemble in several aspects the observation of preferential ejection of halogen atoms from NaCl during sputtering by low-energy electrons at temperatures above 250°C by Townsend and Elliott.[4,5] A peak in the sputtering yield at 45° away from the normal to the (100) plane, measured by these authors, is taken as an indication for the occurrence of a [110] halogen atom replacement sequence, the Pooley-Hersh mechanism of defect formation.[6-8] Our measurements provide direct experimental evidence that atom collision chains propagate not only in [110] but also in [211] directions of fcc alkali halides.

The source of energy for this process is the

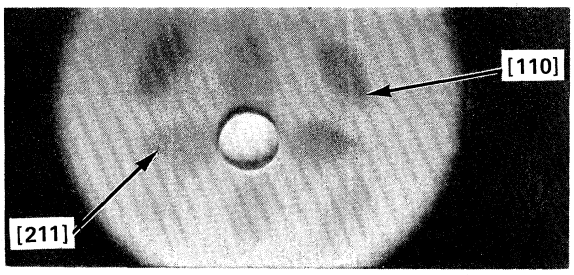

FIG. 3. Cl-emission pattern obtained from KCl during exposure to intense pulse from a Q-switched ruby laser.

nonradiative recombination of an electron with a self-trapped hole (V_k center).[6,9] The alternative possibility of initiating a halogen *ion* replacement sequence is small.[10] The threshold energies for the latter process are considerably higher than the energies available from V_k-center–electron recombination. For example, in KCl it would require 12–15 eV in kinetic energy to launch a Cl^- collision chain.[10] This is in agreement with two of our observations: (i) Four-photon absorption provides only 7.12 eV at the ruby frequency, and (ii) only a very small fraction of the ejected halogens are negative ions.

In the bulk the halogen replacement chain leads to the formation of separated F and H centers.[6-8] If the chain is launched within a few layers from the surface (a condition readily achieved with the laser excitation in transparent crystals, see Fig. 1), it will cause the ejection of halogen atoms in the direction of chain propagation. This accounts for the four [110] spots shown in Fig. 3. The observation of four equally intense [211] spots is somewhat unexpected. Apparently, the possibility of initiating a halogen-atom collision chain in these directions has not been considered previously. Clearly, the only possible low-index directions in an fcc alkali halide lattice additional to the [110] direction for the propagation of a halogen replacement sequence is [211]. The mechanism of energy transfer to the halogens in [211] directions is presently not well understood. According to Smoluchowski *et al.*[10] the Cl_2^- molecular ion vibrates as a whole around its ideal position. However, the maximum angle it forms with the [110] direction is about 5 deg. It is likely to be off its ideal position when the recombination occurs but not sufficiently to impart the kinetic energy in the [211] direction.

Once a [110] collision chain is launched it may lead to emission away from this direction through distortions of the last few outermost layers of a (100) face. Benson and Claxton[11] have calculated displacements of the ions from the unperturbed position in the last five layers. In all the crystals considered here these displacements appear to be too small to account for the spots we observed in addition to the [110] emission.

Finally, one might speculate that a different defect center may be responsible for the [211] emission. It must involve more than two halogens in order to allow for bonding and vibration in the [211] directions. An excited Cl_3^- molecule-ion should be considered as one of the possible configurations. Halogen complexes of this type are responsible for the V_2 and V_3 bands observed at low temperatures in alkali halides.[12] Nonradiative decay of a $(\text{halogen})_3^-$ molecule-ion may conceivably supply sufficient energy to launch a halogen-atom replacement sequence in a [211] direction in analogy to the Pooley-Hersh [110] replacement chain involving an excited $(\text{halogen})_2^-$ molecular ion.

The formation of excited halogen molecular ions in alkali halides by absorption of ruby photons is due to a multiphoton process. From optical absorption experiments[9,13] involving one-photon absorption, the energies required to form an exciton at liquid helium temperature are known to be 7.96 eV for NaCl, 7.76 eV for KCl, and 6.89 eV for KBr. As predicted by Wood,[14] these excitons relax promptly into a self-trapped state of V_k type. Four-photon absorption at the ruby frequency provides sufficient energy to generate V_k centers in KBr. In NaCl and KCl four-photon absorption appears to involve impurity states in the forbidden gap. Even though the experiments were performed at rms optical fields of 0.65 to 1.5 MV/cm, Stark shift and lifetime broadening are not expected to shift the exciton levels sufficiently to facilitate direct four-photon exciton generation.

Fluorine replacement chains in LiF were not observed because a multiphoton absorption process of order $N > 4$ would be necessary to generate excitons and V_k centers. The cross section becomes too small to produce detectable halogen emission at photon fluxes below the avalanche-dominated breakdown threshold.

The cross sections for four-photon exciton generation in KCl, NaCl, and KBr are not known with sufficient accuracy. From measurements performed by Aseev, Kats, and Nikolskii[15] we deduce for KCl $\sigma \leq 10^{-108}$ cm^{10} sec^{-4} which is a surprisingly high value[16] compared to results reported by Catalano, Cingolani, and Minafra[17] for photocarrier generation. At the upper limit (damage threshold) of the photon flux ($\sim 3\times10^{28}$ photons cm^{-2} sec^{-1}) this corresponds to a total generation rate of up to 10^{20} excitons per cubic centimeter per laser shot. However, as high as this value for exciton generation seems to be, the emission of up to 10^{16} halogen atoms at the maximal flux from a focal waist of 5×10^{-3} cm^2 cross sectional area indicates that many monolayers of the crystal are abladed per laser shot and that the mechanism of halogen ejection is very efficient. This in turn can be interpreted as an indication that the probability for launching a collision chain

once the V_k center is formed is very high, too.

The authors want to thank J. P. Carrico and J. Rice who made the mass spectrometer available for this work.

*Work supported by the Division of Materials Research of the National Science Foundation.

[1]N. Bloembergen, IEEE J. Quantum Electron. 10, 375 (1974).

[2]P. Braunlich, A. Schmid, and P. Kelly, Appl. Phys. Lett. 26, 150 (1975).

[3]J. P. Carrico, S. Booker, J. Rice, and E. Schaefer, J. Phys. E: Sci. Instrum. 7, 469 (1974).

[4]P. D. Townsend and D. J. Elliott, in *Atomic Collision Phenomena in Solids*, edited by D. W. Palmer, N. W. Thomson, and P. D. Townsend (North-Holland, Amsterdam, 1970) p. 328.

[5]D. J. Elliott and P. D. Townsend, Philos. Mag. 23, 249 (1971).

[6]D. Pooley, Proc. Phys. Soc., London 87, 245, 257 (1966).

[7]H. N. Hersh, Phys. Rev. 148, 928 (1966).

[8]R. E. Howard, S. Vosko, and R. Smoluchowski, Phys. Rev. 122, 1406 (1961).

[9]M. N. Kabler and D. A. Patterson, Phys. Rev. Lett. 19, 652 (1967).

[10]R. Smoluchowski, O. W. Lazareth, R. D. Hatcher, and G. F. Dienes, Phys. Rev. Lett. 27, 1288 (1971).

[11]G. C. Benson and T. A. Claxton, J. Chem. Phys. 48, 1356 (1968).

[12]J. J. Markham, *F-Centers in Alkali Halides* (Academic, New York, 1966).

[13]J. E. Eby, K. J. Teegarden, and D. B. Dutton, Phys. Rev. 116, 1099 (1959).

[14]R. F. Wood, Phys. Rev. 151, 629 (1966).

[15]G. I. Aseev, M. L. Kats, and V. K. Nikolskii, Zh. Eksp. Teor. Fiz., Pis'ma Red. 8, 174 (1968) [JETP Lett. 8, 103 (1968)].

[16]Since the focal volume in their experiment is not known with sufficient accuracy this value is only a rough estimate.

[17]I. M. Catalano, A. Cingolani, and A. Minafra, Phys. Rev. B 5, 1629 (1972).

Mechanism of Emission of Halogen Atoms from Alkali Halides

R. Smoluchowski
Princeton University, Princeton, New Jersey 08540
(Received 9 September 1975)

The emission of neutral halogen atoms from alkali halide crystals in [211] directions is explained in terms of defocusing of the usual [110] momentum produced by ionization and a short sequence of momentum transfers to a surface halogen. No replacement sequences are involved in the process.

The usual mechanism of F and H center formation by ionizing radiation in alkali halides is based on the recombination of a self-trapped hole with an electron and the ensuing dynamic replacement sequence of a neutral crowdion configuration in the halogen sublattice in the [110] direction.[1,2] If this dynamic crowdion orginates near the surface then a neutral halogen may be ejected in the [110] direction from the crystal. This has indeed been observed by Elliott and Townsend[3] using low-energy electrons and quite recently by Schmid, Bräunlich, and Rol[4] using multiphonon ruby laser excitation at room temperature. The latter authors also observed, however, a strong halogen atom emission in the [211] direction. This new phenomenon requires an explanation.

As pointed out by Schmid, Bräunlich, and Rol, the usual equilibrium distortion of an alkali halide lattice near its surface is not sufficient to account for a 30° change from a [110] to a [211] direction. The possibility of nonradiative decay of a Cl_3^- configuration, if it exists at all, is too speculative at the present time. It remains to consider the behavior of a dynamic replacement sequence near a surface. First of all, as discussed by Dienes and Smoluchowski,[5] the range of a dynamic sequence near room temperature is at best a few lattice constants, which shortens drastically the operation of the usual focusing mechanism.[6] This conclusion is in agreement with the observation that the emerging beam of atoms is perhaps as much as 30 deg wide. Also the vibrational amplitude of surface atoms could be as much as 100% higher than in the bulk[7] so that a similar spread around the [211] direction would be sufficient to permit bridging the 30° gap between the [110] and [211] directions.

Another, more likely, possibility is that the transfer of momentum from the usual [110] direc-

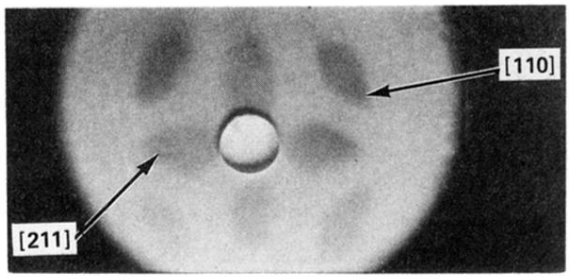

FIG. 3. Cl-emission pattern obtained from KCl during exposure to intense pulse from a Q-switched ruby laser.