CsBr. (The properties of hard RbI, KI, and KBr have not been fully investigated.) It is apparent that for LiF, NaCl, and KCl, $\delta\sigma/\sigma$ differs from $\delta K/K_s$ by 3×10^{-2} or less. For LiF and NaCl, $\delta\sigma/\sigma < \delta K_s/K_s$ and for KCl, $\delta\sigma/\sigma > \delta K_s/K_s$. As a consequence, $\delta\sigma/\sigma$ for KCl is more nearly equal to $\delta K_e/K_e$. This suggests that in KCl the mobility of edge dislocations may be more nearly rate limiting while in LiF and NaCl the screws are rate limiting. In fact, the ratio of edge to screw dislocation velocity, v_e/v_s, varies from ~50 in LiF[16] to ~10 in NaCl[17] to ~1 to 1.5 in KBr[18] (presumably v_e/v_s is similar in KCl and KBr). For CsBr, we may not have established the lowest possible $\delta\sigma/\sigma$ for hard crystals, but $\delta\sigma/\sigma$ is nearly equal to $\delta K_e/K_e$ suggesting, again, that the mobility of edge dislocations is most important. Although the difference between $\delta\sigma/\sigma$ and $\delta K/K$ (edge or screw) for LiF and NaCl is slightly outside the limits of experimental error, it is clear that the response of flow stress to pressure in hard crystals of LiF, NaCl, KCl, and CsBr could result from the change in elastic interaction between dislocations and defect hardening centers (for irradiated crystals) or other dislocations (for work-hardened crystals). The good agreement between $\delta K/K_{s,e}$ and $\delta\sigma/\sigma$ for the heavily irradiated crystals and the fact that $\delta\sigma/\sigma$ is the same for crystals hardened to a given stress by either irradiation or strain hardening, where defect tetragonality does not enter, suggest that the degree of tetragonality of the hardening defect in the irradiated crystals does not change significantly with pressure.

Note added in proof: In the text above, the flow-stress values at high pressure are not corrected for the reduced cross-sectional area of the specimen under pressure. This correction is positive, i.e., σ at 4.3 kbar is slightly higher than indicated on the $\sigma-\epsilon$ curves, Figs. 4–12, and is given by $(\frac{2}{3})\Delta V/V_0$. The quantity $\Delta V/V_0$ is listed in Table II. This correction increases slightly all the $\delta\sigma/\sigma$ listed in the first column of Table II. For example, $\delta\sigma/\sigma$ for hard LiF corrects to 0.8×10^{-2}, for hard NaCl to 4×10^{-2}, for hard KCl to 9.6×10^{-2}, and for hard CsBr to 17×10^{-2}. This creates better agreement between $\delta K_s/K_s$ and $\delta\sigma/\sigma$ for hard LiF and NaCl and places $\delta\sigma/\sigma$ for hard KCl slightly higher above $\delta K_e/K_e$. For CsBr, $\delta\sigma/\sigma$ now falls midway between $\delta K_s/K_s$ and $\delta K_e/K_e$, so that one can no longer suppose which species is rate limiting. For the soft crystals of each type $\delta\sigma/\sigma$ is much larger so the correction is of minor significance. The activation volume V^* (see text) increases only slightly.

The values of $\delta\sigma/\sigma$ observed in soft samples of all the crystals tested except LiF are much too big to be accounted for by an elastic effect, indicating that different mechanisms control plastic flow in the hard and soft crystals. To investigate this, it is useful to consider the activation volume for plastic flow. One can write the relation between mean dislocation velocity $\bar{v}$ and the activation free energy G^* when $\bar{v}$ is determined by a single activated process, as

$$\bar{v} = A\,\exp(-G^*/kT). \qquad (6)$$

The relation can still be used to describe experimental results when more than a single process is active but the derived quantities no longer have simple interpretations in terms of atomic models. The derivative of $\ln\bar{v}$ with pressure, assuming A is insensitive to pressure, is

$$(d\ln\bar{v}/dP)_{T,\sigma} = (d/dP)(-G^*/kT) = -V^*/kT, \qquad (7)$$

where V^* is the activation volume (to be distinguished from the quantity having dimensions of volume and given the same name which is obtained from differential strain rate experiments). Equation (7) can be rewritten as

$$V^*/kT = (\partial\ln\bar{v}/\partial\ln\sigma)_{T,P}(\partial\ln\sigma/\partial P)_{T,\bar{v}}, \qquad (8a)$$

or, from the strain-rate equation, $\dot{\epsilon} = \Lambda b\bar{v}$, where Λ is the mobile dislocation density and b is the Burgers vector, Eq. (8a) can be written as [provided that $(\partial\ln\Lambda/\partial\ln\sigma)_{T,P} = 0$]

$$V^*/kT = (\partial\ln\dot{\epsilon}/\partial\ln\sigma)_{T,P}(\partial\ln\sigma/\partial P)_{T,\bar{v}}. \qquad (8b)$$

We have determined the second partial derivative in Eq. (8); the first may be obtained directly from strain-rate experiments [Eq. (8b)] or indirectly if one assumes a dislocation velocity–stress model, Eq. (8a). For example, if we choose the model of Gilman and Johnston,[11] $\bar{v} = v_0 e^{-D/\sigma}$, where σ is the shear stress, D, the characteristic drag stress and v_0, the shear wave velocity, then $(\partial\ln\bar{v}/\partial\ln\sigma)_{T,P} = D/\sigma$. Equation (8a) can be written then as

$$V^* = (D/\sigma)(kT/\delta P)\ln(\sigma_2/\sigma_1). \qquad (9)$$

If a power-law expression is chosen, i.e., $\bar{v} = B\sigma^m$, then $(\partial\ln\bar{v}/\partial\ln\sigma)_{T,P} = m$. Both D and m may be evaluated by dislocation etch-pitting experiments; Nadgornyi and Gutmanas[19] show that such experiments usually yield m in the range 14 to 21 for the alkali halides. The etch-pitting experiments of Johnston and Gilman[16] for LiF give $D/\sigma = 18.5$ (for σ corresponding to the flow stress). The strain-rate experiments of Phillips[20] give $(\partial\ln\dot{\epsilon}/\partial\ln\sigma)_{T,P} \simeq 16$ for both LiF and NaCl, and those of Johnston and Stein[21] yield a value of ~20 at low strain ($\sim2\%$) in LiF. Alternatively one can determine $(\partial\ln\bar{v}/\partial\ln\sigma)_{T,P}$ by fitting the strain-rate equation to our 1-atm stress–strain curves. According to the work of Gilman and Johnston[11] and Gilman[22,23] this equation can be written to a good

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approximation as

$$\dot{\epsilon}=\phi(\Lambda_0+M\epsilon)bv_0\exp[-(D+W\epsilon)/\sigma], \qquad (10)$$

where ϵ is the shear strain. Here Λ is replaced by $(\Lambda_0+M\epsilon)$, where Λ_0 equals the initial dislocation density and $M\epsilon$ represents the linear increase in dislocation density with strain. (Haasen and Hesse[24] have indicated that a linear dependence does not always hold for the alkali halides, but for moderate strains it should be a fair approximation). The average dislocation velocity, $\bar{v}$, is expressed as $v_0\exp[-(D+W\epsilon)/\sigma]$, where v_0 is the limiting dislocation velocity (acoustic velocity of (110) $[\bar{1}10]$ shear waves in the NaCl structure and of (110) $[001]$ shear waves in the CsCl structure) and $(D+W\epsilon)$ is the drag stress of the crystal; $W\epsilon$ represents the change in drag stress with work hardening. Since the strain rate $\dot{\epsilon}$, the Burgers vector b, and the appropriate shear-wave velocity v_0, are known for the materials tested, only values for Λ_0 and M need be determined to fit the σ–ϵ curves. It would be tedious to determine Λ_0 and M for every crystal so we have adopted here values of Λ_0 in the range 10^5 to $10^6/cm^2$ (adjusted to achieve the best fit) and $M=10^9/cm^2$. Gilman[25] indicates that $M=10^9/cm^2$ is of the correct order of magnitude for LiF and KCl and we assume that it is not greatly different for the other alkali halides. Values of Λ_0 much less than 10^5 to $10^6/cm^2$ lead to very sharp yield drops on initial loading which we do not observe in our crystals. (It is noted that mechanical polishing of the specimens undoubtedly increases Λ_0 by generating fresh dislocations prior to compression. Some tendencies toward yield-drop formation on initial loading are noted, however, in the heavily irradiated crystals.) Fortunately, Λ_0 and M enter in a preexponential term so they need only be known approximately. While Eq. (10) itself is only an approximation (in particular, the logarithmic form of the dislocation-velocity–stress relation apparently gives a poor representation of data for soft crystals), it is found to give a reasonably good fit to the σ–ϵ curves with the selected values of Λ_0 and M. For the 16 curves fitted for various soft and hard crystals of the alkali halides, $(\partial \ln\bar{v}/\partial \ln\sigma)_{T,P}=(D+W\epsilon)_1/\sigma_1$ (for $\epsilon\sim1\%$) falls between 17 and 21, with an average value near 18.5. [As $v_0\simeq10^5$ cm/sec for all the alkali halides, this indicates, in effect, that the dislocation velocity at the flow stress is $\sim10^{-3}$ cm/sec ($\dot{\epsilon}\sim10^{-4}$ sec^{-1}).] As this value of $(D+W\epsilon)/\sigma$ is in reasonable agreement with the measured values of m and $(\partial \ln\dot{\epsilon}/\partial \ln\sigma)_{T,P}$ given above, we shall use it in Eq. (8) with the appropriate $\delta\sigma/\sigma$, to compute V^*.

Figure 13 shows that $\delta\sigma/\sigma$ for soft KCl drops very rapidly in a narrow range of stress. Ideally, if different mechanisms are completely dominant in the hard and soft crystals one would expect to find a constant value of $\delta\sigma/\sigma$ separated by a sharp transition. As no constant

value is observed for the soft crystals, it appears that no single rate-limiting mechanism controls plastic flow in the soft material. For the purpose of computing an effective V^* we choose the maximum $\delta\sigma/\sigma$ shown by KCl in Fig. 13 and the maximum $\delta\sigma/\sigma$ shown by the other materials. The values of $\delta\sigma/\sigma$ so chosen and the values of V^* thus computed are listed in Table II. It is apparent that V^* for soft crystals of NaCl, KCl, KBr, KI, and RbI and CsBr is equal to 0.5 to 0.85 of the anion volume V_a which is also shown in the table. (The anion volume is estimated by computing the molecular volume, i.e., the volume of $M^+ X^-$, and then assigning portions of this volume to the anion and cation in the ratio of their ionic radii[26] cubed.) This comparison of V^* and V_a suggests that for the soft material the $\sigma_{P.D.}$ term makes an important contribution to the flow stress. A plausible mechanism is vacancy formation by the climb of an edge jog, one ion wide, on a screw dislocation. During climb cation and anion vacancies must be created in succession, but, presumably, the creation of the larger defect is the more difficult step. If this mechanism were rate limiting V^* equal to about $2V_a$ should obtain.[27] That vacancies are generated by plastic deformation is shown by the observed decrease in density of cold-worked KCl.[28] Another possible mechanism is the thermally activated diffusion of impurity pinning points in the stress field of moving dislocations. There are perhaps three possible reasons why, in the present experiments, plastic deformation in the soft crystals is not completely controlled by a "point defect" mechanism. For one, the alkali halides tested, while quite pure,[29] may not be pure enough to eliminate completely the importance of the elastic interaction of impurity atoms and dislocations. In the case of LiF, where $\delta\sigma/\sigma$ is not stress-dependent and the ratio of edge dislocation velocity to screw dislocation velocity is about 50, the jogs or pinning points on screw dislocations may be so firmly anchored that they won't move. Third, in these experiments some work hardening of a crystal occurs prior to determination of $\delta\sigma/\sigma$ (due to $\sim1.0\%$ shear strain), which may give rise to sizable, elastic dislocation–dislocation interactions and/or elastic defect–dislocation interactions, if defects are created by plastic flow. This, in effect, states that the qualitative nature of the mechanism limiting plastic flow in a soft crystal is changed by sufficient work hardening. For example, in Fig. 13 for KCl $\delta\sigma/\sigma$ drops very rapidly with work hardening (increasing σ_s) in the soft crystals but for the hard crystals, where plastic deformation is pre-

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