

TABLE IX. Ratio of the change of the chemical shift at the transition to the initial slope of the chemical shift vs pressure for the rubidium halides. See Sec. VC.

Nucleus	Salt	K-Y ^a	K-Y ^b	K-Y ^c	$\Delta\sigma_T/\Delta\sigma_0$ K-Y ^d	Sum ^{e,e}	Exptl. ^f
Rb ⁸⁷	RbCl	-0.69	+0.36	-0.12	-0.38	-0.06	-1.8±0.8
Rb ⁸⁷	RbBr	-0.94	-0.34	-0.61	-0.76	-0.57	-2.6±0.7
Rb ⁸⁷	RbI	-1.17	-0.88	-1.01	-1.09	-0.99	-4.4±0.9
Br ⁸¹	RbBr	-0.94	+0.22	+1.13	+2.62	+0.80	+1.4±0.5
I ¹²⁷	RbI	-1.17	+0.45	+1.70	+3.61	+1.19	+4.0±2.0

^a Nearest-neighbor interactions only.^b Next-nearest-neighbor interactions included, with $\delta=\delta_{\text{Cub}}$.^c Next-nearest-neighbor interactions included, with $\delta=\delta_{\text{Cub}}+0.2$.^d Next-nearest-neighbor interactions included, with $\delta=\delta_{\text{Cub}}+0.4$.^e Suitable sum of K-Y and Y-M, see text.^f Includes second-order quadrupole shift correction.

effects to overlap effects follows from the considerations given above. This is especially true in view of the discrepancies between the theoretical dependence of σ on pressure and crystal structure which are described below. However, it should also be pointed out that the functional dependence of $\sigma(P)$ has very little effect on $(\Delta\sigma_0)_M/(\Delta\sigma_0)_H$, since its only effect is that of the next-nearest-neighbor contributions to $\Delta\sigma_0/\sigma_0$, and since $(\Delta\sigma_0)_M/(\Delta\sigma_0)_H$ depends mainly on the values of $\langle 1/r^3 \rangle$. Conversely, as will be seen below, the addition of the charge-transfer effects onto the overlap effects makes very little difference in the functional dependence of $\sigma(P)$. These results are very suggestive, and the theoretical aspects should be considered more thoroughly.

C. Behavior of σ at the Transition

The behavior of σ for the rubidium halides at the transition between the NaCl and the CsCl phases is one of the most interesting features of the experimental results, and allows a sensitive test of the assumed functional dependence of σ . The experimental results for $\Delta\sigma_T$, corrected for the second-order quadrupole shifts discussed above, are given in Table III. The striking feature of these results is the difference in sign between $\Delta\sigma_T$ for the rubidium and for the halide chemical shifts. If only nearest-neighbor interactions are considered, neither the theory of K-Y nor the theory of Y-M contains a mechanism capable of explaining this change in sign. This is because in both theories $(\Delta\sigma_T/\Delta\sigma_0)_M = (\Delta\sigma_T/\Delta\sigma_0)_H$ for metal and halide in the same salt. This is shown in Table IX, where the values of $\Delta\sigma_T/\Delta\sigma_0$ given by the K-Y theory when only nearest-neighbor interactions are considered are compared with the experimental results.

By including the effects of next-nearest-neighbor interactions into the K-Y theory, the results shown in column 2 of Table IX are obtained. The sign of $\Delta\sigma_T/\Delta\sigma_0$ for the halides is now correct, however $\Delta\sigma_T/\Delta\sigma_0$ for Rb⁸⁷ in RbCl now has the wrong sign. In this calculation,

the values of δ given by Cubicciotti have been used. However, as Cubicciotti³⁰ points out, his calculations, wherein he determines $r_+ + r_-$ and δ to give the best possible agreement between the calculated and experimental values of r_0 , are quite insensitive to δ . A change in δ by $+0.2\text{\AA}$ (with $r_+ + r_-$ unchanged) changes the calculated values of r_0 by no more than $0.01\text{\AA}$ (except for CsI, where $\Delta r_0 = 0.02\text{\AA}$). This change in r_0 is comparable to the scatter in the values of $(r_0)_{\text{calc}} - (r_0)_{\text{exptl}}$ obtained by Cubicciotti. The results obtained by using the values $\delta = \delta_{\text{Cub}} + 0.2$ and $\delta = \delta_{\text{Cub}} + 0.4$ to calculate $\Delta\sigma_T/\Delta\sigma_0$ are shown in columns 3 and 4 of Table IX. The signs of $\Delta\sigma_T/\Delta\sigma_0$ are now all correct, and by a proper choice of δ , a reasonable quantitative fit with the experimental values for the halides is possible. No adjustment of δ will improve the fit to the rubidium results. If the sum of σ_{Y-M} and σ_{K-Y} is formed as it was above, the values of $\Delta\sigma_T/\Delta\sigma_0$ do not change significantly, as is shown in column 5 of Table IX.

There are several reasons for the fact that the inclusion of next-nearest-neighbor interactions into the theory accounts for the difference in behavior of metal and halide chemical shifts. These are: (1) that the next-nearest-neighbor distance, unlike the nearest-neighbor distance which increases, decreases during the transition from NaCl to CsCl phase; and (2) the halide ion is bigger than the metal ion. Thus, because of the large size of the halide ion, the contribution of the halide-halide interactions in the CsCl phase (where $k = 1.155$) may become comparable to the contribution of the nearest-neighbor interactions. Since, in addition the next-nearest-neighbor distance decreases much more than the nearest-neighbor distance increases (-23% as compared to $+4\%$), the next-nearest-neighbor interactions dominate the behavior of the halide chemical shifts at the transition. Conversely, the smaller size of the metal ion makes the contribution

³⁰ D. Cubicciotti (private communication).