

## Nuclear Quadrupole Interactions in Alkali-Halide Solid Solutions\*

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Nuclear quadrupole interactions in dilute alkali halide solid solutions are studied in detail using the results of the calculations in the preceding paper of the relaxation and electronic polarization of ions around the solute ion. It is shown that the available experimental data on first- and second-order effects on nuclear magnetic resonance spectra in the solid solutions NaCl-Br, NaBr-Cl, and KBr-Na can be explained quite well using calculated values of antishielding factors for the  $\text{Na}^+$  and  $\text{Br}^-$  ions. The electronic polarization of the ions is found to be an important contributor to the field gradients at the nuclei, the results being rather sensitive to the choice of polarizabilities for the ions. Better agreement with experiment is obtained when Sternheimer's calculated values of the polarizabilities are used rather than Tessman, Kahn, and Shockley's empirical values. For a nucleus which is quite distant from the solute ion, the ions nearest to the nucleus are seen to be more effective contributors to the field gradient at the nucleus than the ions near the impurity.

### I. INTRODUCTION

IN an earlier (the preceding) paper,<sup>1</sup> referred to hereafter as I, we obtained the displacements of the ions and the induced dipole moments on the ions around the solute ion in an alkali-halide lattice and made theoretical estimates of the heats of solution and expansions in volume of dilute alkali-halide solid solutions. These distortions and induced dipole moments destroy the cubic symmetry at lattice sites in the neighborhood of the solute ion. This loss of cubic symmetry produces finite field gradients at the nuclei in the solid solution. Experimental results<sup>2,3</sup> have been obtained for the nuclear quadrupole interactions at certain lattice sites in some solid solutions. It is the purpose of this paper to calculate the field gradients at these sites and from them to estimate the nuclear quadrupole coupling constants<sup>4,5</sup> and first-order frequency splittings and second-order frequency shifts in nuclear magnetic resonance and compare them with experiment. Our original motivation in doing this was to investigate whether the good agreement with experiment for field gradients at positive-ion nuclei and poor agreement for negative ion nuclei, found using point charge and point multipole models for the ions in free alkali-

halide molecules,<sup>6</sup> also applied to the alkali-halide crystals. Because of the larger distance between the ions in the crystal as compared to the molecule, one would expect lesser contributions from overlap effects and therefore better agreement with experiment for the negative-ion nuclei in the crystal. In Sec. II, algebraic expressions are deduced for the field-gradient tensor components at the lattice sites (0,0,1), (1,0,1), (1,0,2), and (1,1,3) [the position of the solute ion defining the origin (0,0,0)] that arise from the displaced ions and induced dipole moments in the crystal. The field-gradient tensor components are tabulated at these sites both with the crystal axes as basis, as well as in the principal axis system. In Sec. III, first-order frequency splitting producing satellite lines in nuclear magnetic resonance (NMR) and the second-order shifts of the central NMR line are tabulated for the various sites considered. Wherever available, the experimental data are compared with the calculated results. In Sec. IV, the probable reasons for the nature of the agreement between theory and experiment in various cases are discussed, and future experiments are suggested which would enable a better test of the theory for these solid solutions. The general conclusions that can be derived from our work are summarized in the last section entitled Concluding Remarks.

### II. CALCULATION OF FIELD GRADIENTS AT LATTICE SITES

The field gradient at a nucleus in the perfect lattice is zero because of cubic symmetry. In the impure crystal, the cubic symmetry is lost because of the displacements and electronic polarizations of the ions *ABC* of Fig. 1 of I in the neighborhood of the solute ion. The field gradient at a nucleus is given by:

\* T. P. Das and M. Karplus, *J. Chem. Phys.* **30**, 848 (1959); G. Burns, *ibid.* **31**, 1253 (1959).

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<sup>1</sup> B. G. Dick and T. P. Das, preceding paper [*Phys. Rev.* **127**, 1053 (1962)], referred to as "I."

<sup>2</sup> H. Kawamura, E. Otsuka, and K. Ishiwatari, *J. Phys. Soc. Japan* **11**, 1064 (1956).

<sup>3</sup> E. Otsuka and H. Kawamura, *J. Phys. Soc. (Japan)* **12**, 1071 (1957).

<sup>4</sup> M. H. Cohen and F. Reif in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 5.

<sup>5</sup> A. K. Saha and T. P. Das, *Nuclear Induction* (Saha Institute of Nuclear Physics, Calcutta, India, 1957), Chap. 6. Also see R. V. Pound, *Phys. Rev.* **79**, 685 (1950); R. Bersohn, *J. Chem. Phys.* **20**, 1505 (1952); G. Volkoff, *Can. J. Phys.* **31**, 820 (1953); T. P. Das and E. L. Hahn in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Suppl. 1.

TABLE I. Field-gradient tensor components for points (0,0,1) and (1,0,1).

Approx \ Comp	Point (0,0,1) <sup>a</sup>			Point (1,0,1) <sup>b</sup>				
	$E_{zz}$	$E_{zz}$	$E_{zz}$	$q$	$\eta$	$\lambda_1(\lambda_i^x, \lambda_i^y, \lambda_i^z)$	$\lambda_2$	$\lambda_3$
NaCl-Br								
(VDW) <sub>TKS</sub> <sup>0</sup>	-0.775	0.204	0.500	0.337	0.843	10-1	010	101
(VDW) <sub>TKS</sub> <sup>M</sup>	-0.812	0.230	0.502	0.339	0.824	10-1	010	101
(VDW) <sub>TKS</sub> <sup>I</sup>	-0.980	0.231	0.521	0.352	0.830	10-1	010	101
(VDW) <sub>Stern.</sub> <sup>0</sup>	-1.337	0.377	0.569	0.392	0.752	10-1	010	101
(VDW) <sub>Stern.</sub> <sup>M</sup>	-1.460	0.426	0.584	0.405	0.728	10-1	010	101
(VDW) <sub>Stern.</sub> <sup>I</sup>	-1.433	0.445	0.606	0.420	0.726	10-1	010	101
(BM) <sub>TKS</sub>	-0.680	...	...	...	...	...	...	...
(BM) <sub>Stern.</sub>	-1.153	...	...	...	...	...	...	...
NaBr-Cl								
(VDW) <sub>TKS</sub> <sup>0</sup>	0.862	-0.228	-0.539	-0.305	0.837	10-1	010	101
(VDW) <sub>TKS</sub> <sup>M</sup>	0.944	-0.253	-0.551	-0.313	0.825	10-1	010	101
(VDW) <sub>TKS</sub> <sup>I</sup>	0.788	-0.244	-0.519	-0.296	0.820	10-1	010	101
(VDW) <sub>Stern.</sub> <sup>0</sup>	1.778	-0.502	-0.737	-0.428	0.745	10-1	010	101
(VDW) <sub>Stern.</sub> <sup>M</sup>	2.100	-0.593	-0.805	-0.470	0.726	10-1	010	101
(VDW) <sub>Stern.</sub> <sup>I</sup>	1.852	-0.553	-0.755	-0.440	0.727	10-1	010	101
(BM) <sub>TKS</sub>	0.503	...	...	...	...	...	...	...
(BM) <sub>Stern.</sub>	1.408	...	...	...	...	...	...	...
KBr-Na								
(VDW) <sub>TKS</sub> <sup>0</sup>	-0.465	0.034	0.940	0.380	0.985	10-1	010	101
(VDW) <sub>TKS</sub> <sup>M</sup>	-0.583	0.066	0.892	0.362	0.970	10-1	010	101
(VDW) <sub>TKS</sub> <sup>I</sup>	-0.586	0.066	0.893	0.363	0.971	10-1	010	101
(VDW) <sub>Stern.</sub> <sup>0</sup>	-0.184	-0.123	0.818	-0.335	0.941	101	010	10-1
(VDW) <sub>Stern.</sub> <sup>M</sup>	-0.307	-0.071	0.788	-0.321	0.964	101	010	10-1
(VDW) <sub>Stern.</sub> <sup>I</sup>	-0.311	-0.071	0.079	-0.321	0.964	101	010	10-1
(BM) <sub>TKS</sub>	-0.435	0.081	0.076	...	...	...	...	...
NaBr-K								
(VDW) <sub>TKS</sub> <sup>0</sup>	0.565	-0.085	-0.862	-0.473	0.961	10-1	010	101
(VDW) <sub>TKS</sub> <sup>M</sup>	0.654	-0.115	-0.867	-0.477	0.947	10-1	010	101
(VDW) <sub>TKS</sub> <sup>I</sup>	...	-0.115	-0.863	-0.476	0.947	10-1	010	101
(VDW) <sub>Stern.</sub> <sup>0</sup>	0.242	0.032	-0.739	0.403	0.983	101	010	10-1
(VDW) <sub>Stern.</sub> <sup>M</sup>	0.303	-0.003	-0.753	-0.410	0.999	10-1	010	10-1
(VDW) <sub>Stern.</sub> <sup>I</sup>	...	-0.001	-0.749	-0.407	1.000	10-1	010	101
(BM) <sub>TKS</sub>	0.358	-0.050	-0.738	...	...	...	...	...

<sup>a</sup> For point (0,0,1),  $E_{zz}$  is in units of  $10^{-1}(3e/a^3)$ .

<sup>b</sup> For point (1,0,1),  $E_{zz}$ ,  $E_{zz}$ , and  $q$  are, respectively, in units of  $10^{-2}(3e/a^3)$ ,  $10^{-1}(3e/a^3)$ , and  $10^{14}$  esu  $\text{cm}^{-3}$ .

$q$  = field gradient due to the displaced and polarized ions  $ABC$  + field gradient due to the rest of the ions in the lattice = the field gradient due to the displaced and polarized ions  $ABC$  - field gradients due to the ions  $ABC$  before displacement (1)

If we require the result to only first order in the displacement and dipole parameters  $\xi$ ,  $\eta$ ,  $\delta$ ,  $\mu_A$ ,  $\mu_B$ , and  $\mu_C$ , we can replace Eq. (1) by

$q$  = field gradient due to the "net" dipole moments at  $A$ ,  $B$ , and  $C$ . (2)

The "net" dipole moment  $Mea$  at a point represents the sum of the displacement and electronic dipoles so that for the cases of NaCl-Br and NaBr-Cl:

$$M_A = (\xi + \mu_A), \quad M_B = -(\eta - \mu_B), \quad M_C = -(\delta - \mu_C),$$

and for KBr-Na and NaBr-K: (3)

$$M_A = -(\xi - \mu_A), \quad M_B = (\eta + \mu_B), \quad M_C = \delta + \mu_C).$$

To make use of Eq. (2), a general expression is required for the components of the field-gradient tensor due to a

dipole. For a point dipole of magnitude  $\mu$  with orientation described by the direction cosines  $(l_1, l_2, l_3)$  in a Cartesian coordinate system, the components of the field-gradient tensor at a point with coordinates  $(x_1, x_2, x_3)$  relative to the point dipole as origin are given by

$$E_{ii} = -\frac{\partial^2 V}{\partial x_i^2} = \frac{3\mu}{r^5} \left[ (3l_i x_i + l_j x_j + l_k x_k) - \frac{5x_i^2}{r^2} (l_i x_i + l_j x_j + l_k x_k) \right], \quad (4)$$

$$E_{ij} = -\frac{\partial^2 V}{\partial x_i \partial x_j} = \frac{3\mu}{r^5} \left[ (l_i x_j + l_j x_i) - \frac{5x_i x_j}{r^2} (l_i x_i + l_j x_j + l_k x_k) \right],$$

where

$$r = (x_1^2 + x_2^2 + x_3^2)^{1/2}.$$

Using Eqs. (4), the components of the field-gradient tensors at the points (0,0,1), (1,0,1), (1,0,2), and (1,1,3)

TABLE II. Field-gradient tensor components for points (1,0,2) and (1,1,3).

	$E_{xx}$	$E_{yy}$	Point (1,0,2) <sup>a</sup>			$\lambda_1$	$\lambda_2$	$\lambda_3$
			$E_{zz}$	$q$	$\eta$			
NaCl-Br								
(VDW) <sub>TKS</sub> <sup>0</sup>	-0.160	-0.254	-0.713	0.129	0.745	0.981 0 0.195	0 1 0	0.195 0 -0.981
(VDW) <sub>TKS</sub> <sup>M</sup>	-0.163	-0.263	-0.592	0.128	0.735	0.987 0 0.162	0 1 0	0.162 0 -0.981
(VDW) <sub>TKS</sub> <sup>I</sup>	-0.194	-0.394	-0.687	0.158	0.677	0.988 0 0.155	0 1 0	0.155 0 -0.988
(VDW) <sub>Stern.</sub> <sup>0</sup>	-0.241	-0.549	-0.170	0.191	0.629	0.999 0 0.032	0 1 0	0.032 0 -0.999
(VDW) <sub>Stern.</sub> <sup>M</sup>	-0.257	-0.604	0.008	0.205	0.619	1.000 0 0.001	0 1 0	0.001 0 -1.000
(VDW) <sub>Stern.</sub> <sup>I</sup>	-0.292	-0.747	-0.006	0.237	0.592	1.000 0 0.001	0 1 0	0.001 0 -1.000
NaBr-Cl								
(VDW) <sub>TKS</sub> <sup>0</sup>	0.176	0.290	0.733	-0.119	0.735	0.983 0 0.183	0 1 0	-0.183 0 0.983
(VDW) <sub>TKS</sub> <sup>M</sup>	0.188	0.332	0.665	-0.126	0.713	0.988 0 0.157	0 1 0	-0.157 0 0.988
(VDW) <sub>TKS</sub> <sup>I</sup>	0.158	0.223	0.571	-0.103	0.766	0.987 0 0.162	0 1 0	-0.162 0 0.987
(VDW) <sub>Stern.</sub> <sup>0</sup>	0.318	0.738	0.157	-0.213	0.624	1.000 0 0.022	0 1 0	0.022 0 1.000
(VDW) <sub>Stern.</sub> <sup>M</sup>	0.368	0.900	-0.020	-0.249	0.607	1.000 0 -0.022	0 1 0	0.002 0 1.000
(VDW) <sub>Stern.</sub> <sup>I</sup>	0.325	0.749	-0.030	-0.218	0.626	1.000 0 -0.004	0 1 0	0.004 0 1.000
KBr-Na								
(VDW) <sub>TKS</sub> <sup>0</sup>	-0.177	0.057	-2.920	-0.138	0.817	0.494 0 -0.870	0 1 0	0.870 0 -0.494
(VDW) <sub>TKS</sub> <sup>M</sup>	-0.188	-0.036	-2.630	0.132	0.978	0.890 0 0.455	0 1 0	0.455 0 -0.890
(VDW) <sub>TKS</sub> <sup>I</sup>	-0.189	-0.038	-2.640	0.132	0.977	0.891 0 0.455	0 1 0	0.455 0 -0.891
(VDW) <sub>Stern.</sub> <sup>0</sup>	-0.138	0.105	-3.280	-0.145	0.941	0.559 0 -0.829	0 1 0	0.829 0 0.559
(VDW) <sub>Stern.</sub> <sup>M</sup>	-0.149	0.032	-2.950	-0.134	0.980	0.526 0 -0.850	0 1 0	0.850 0 0.526
(VDW) <sub>Stern.</sub> <sup>I</sup>	-0.150	0.030	-2.950	-0.134	0.982	0.525 0 -0.851	0 1 0	0.851 0 0.526
NaBr-K								
(VDW) <sub>TKS</sub> <sup>0</sup>	0.179	0.018	2.430	-0.123	0.988	0.893 0 0.450	0 1 0	-0.450 0 0.893
(VDW) <sub>TKS</sub> <sup>M</sup>	0.191	0.065	2.310	-0.123	0.957	0.906 0 0.423	0 1 0	-0.423 0 0.906
(VDW) <sub>TKS</sub> <sup>I</sup>	0.188	0.054	2.300	-0.122	0.964	0.905 0 0.426	0 1 0	-0.426 0 0.905
(VDW) <sub>Stern.</sub> <sup>0</sup>	0.126	-0.099	2.570	0.117	0.932	-0.535 0 0.845	0 1 0	0.845 0 0.535
(VDW) <sub>Stern.</sub> <sup>M</sup>	0.140	-0.054	2.460	0.115	0.962	-0.507 0 0.862	0 1 0	0.862 0 0.507
(VDW) <sub>Stern.</sub> <sup>I</sup>	0.137	-0.064	2.460	0.114	0.954	-0.511 0 0.859	0 1 0	0.859 0 0.511

TABLE II (continued)

	$E_{xx}$	$E_{zz}$	Point (1,1,3) <sup>b,c</sup>		$\eta$	$\lambda_1$	$\lambda_2$	$\lambda_3$
			$E_{xy}$	$q$				
NaCl-Br								
(VDW) <sub>TKS</sub> <sup>0</sup>	-0.542	-0.695	-0.145	0.100	0.299	0.642 0.638 0.426	0.705 -0.709 -0.001	0.301 0.301 -0.905
(VDW) <sub>TKS</sub> <sup>M</sup>	-0.619	-0.744	-0.160	-0.163	0.219	-0.191 -0.191 0.963	-0.707 0.707 0.000	0.681 0.681 0.270
(VDW) <sub>TKS</sub> <sup>I</sup>	-0.772	-0.903	-0.200	-0.202	0.213	-0.187 -0.187 0.965	-0.707 0.707 0.000	0.682 0.682 0.264
(VDW) <sub>Stern.</sub> <sup>0</sup>	-1.310	-1.310	-0.315	0.217	0.219	0.658 0.656 0.369	0.706 -0.708 -0.001	0.261 0.261 -0.930
(VDW) <sub>Stern.</sub> <sup>M</sup>	-1.500	-1.450	-0.355	0.245	0.210	0.660 0.658 0.361	0.706 -0.708 -0.001	0.256 0.256 -0.932
(VDW) <sub>Stern.</sub> <sup>I</sup>	-1.710	-1.650	-0.408	0.280	0.209	0.660 0.659 0.361	0.706 -0.708 -0.001	0.255 0.255 -0.933
NaBr-Cl								
(VDW) <sub>TKS</sub> <sup>0</sup>	0.624	0.779	0.165	-0.096	0.290	0.643 0.640 0.420	-0.706 0.708 0.001	0.297 0.297 -0.908
(VDW) <sub>TKS</sub> <sup>M</sup>	0.733	0.868	0.189	0.161	0.218	-0.189 0.189 0.964	-0.707 0.707 0.000	0.681 0.681 0.267
(VDW) <sub>TKS</sub> <sup>I</sup>	0.595	0.720	0.153	0.131	0.223	-0.192 0.192 0.962	-0.707 0.707 0.000	0.680 0.680 0.272
(VDW) <sub>Stern.</sub> <sup>0</sup>	1.768	1.747	0.424	-0.245	0.216	0.659 0.657 0.366	-0.706 0.708 0.000	0.259 0.259 -0.930
(VDW) <sub>Stern.</sub> <sup>M</sup>	2.162	2.086	0.514	-0.297	0.209	0.660 0.659 0.361	-0.706 0.708 0.000	0.255 0.255 -0.933
(VDW) <sub>Stern.</sub> <sup>I</sup>	1.902	1.839	0.451	-0.262	0.209	0.660 0.659 0.361	-0.706 0.708 0.000	0.255 0.255 -0.932
KBr-Na								
(VDW) <sub>TKS</sub> <sup>0</sup>	0.550	-0.159	0.063	-0.046	0.000	0 -0.995 0.095	-0.996 0.009 0.093	0.094 0.095 0.991
(VDW) <sub>TKS</sub> <sup>M</sup>	0.323	-0.307	0.016	-0.032	0.584	0.669 0.669 -0.322	-0.707 0.707 0.000	-0.228 -0.228 -0.947
(VDW) <sub>TKS</sub> <sup>I</sup>	0.321	-0.309	0.015	-0.032	0.575	0.668 0.668 -0.326	-0.707 0.707 0.000	-0.230 -0.230 0.945
(VDW) <sub>Stern.</sub> <sup>0</sup>	0.944	0.153	0.147	-0.077	0.000	0.000 -0.999 -0.054	-0.999 0.003 -0.054	-0.054 -0.054 0.997
(VDW) <sub>Stern.</sub> <sup>M</sup>	0.703	-0.003	0.097	-0.057	0.000	0.000 -1.000 0.002	-1.000 0.000 0.002	0.002 0.002 1.000
(VDW) <sub>Stern.</sub> <sup>I</sup>	0.700	-0.006	0.096	-0.057	0.000	0.000 -1.000 0.003	-1.000 0.000 0.003	0.003 0.003 1.000
NaBr-K								
(VDW) <sub>TKS</sub> <sup>0</sup>	-0.278	0.308	0.010	0.029	0.517	-0.653 -0.648 0.392	-0.714 0.699 -0.035	-0.252 -0.303 -0.919
(VDW) <sub>TKS</sub> <sup>M</sup>	-0.144	0.409	0.019	0.031	0.123	-0.544 -0.541 0.641	-0.711 0.703 -0.011	-0.445 -0.462 -0.767
(VDW) <sub>TKS</sub> <sup>I</sup>	-0.157	0.395	0.015	0.030	0.155	-0.558 -0.555 0.617	-0.712 0.701 -0.014	-0.425 -0.447 -0.787
(VDW) <sub>Stern.</sub> <sup>0</sup>	-0.652	-0.026	-0.095	-0.065	0.626	-0.009 -0.009 1.000	-0.707 -0.707 0.000	0.707 0.707 0.013
(VDW) <sub>Stern.</sub> <sup>M</sup>	-0.514	0.082	-0.065	-0.047	0.766	-0.037 -0.999 -0.029	0.707 0.000 0.707	0.706 -0.053 0.707
(VDW) <sub>Stern.</sub> <sup>I</sup>	-0.531	0.065	-0.069	-0.050	0.736	-0.029 -0.029 -1.000	0.707 -0.707 0.000	0.707 0.707 -0.040

<sup>a</sup> For the point (1,0,2),  $E_{xx}$ ,  $E_{yy}$ ,  $E_{zz}$ , and  $q$  are, respectively, in units of  $10^{-1}(3e/a^3)$ ,  $10^{-2}(3e/a^3)$ ,  $10^{-2}(3e/a^3)$ , and  $10^{12}$  esu  $\text{cm}^{-3}$ .  
<sup>b</sup> For the point (1,1,3),  $E_{xx}$ ,  $E_{zz}$ ,  $E_{xy}$ , and  $q$  are, respectively, in units of  $10^{-3}(3e/a^3)$ ,  $10^{-3}(3e/a^3)$ ,  $10^{-3}(3e/a^3)$ , and  $10^{12}$  esu  $\text{cm}^{-3}$ .  
<sup>c</sup> For the points (1,0,2) and (1,1,3) the quantities  $\lambda_1^2$ ,  $\lambda_2^2$ ,  $\lambda_3^2$  are written in order vertically down.

are given by the Eqs. (5), (6), (7), and (8). The choice of axes is as shown in Fig. 1 of I. The numerical coefficients appearing in Eqs. (5) through (8) are characteristic of the NaCl structure but do not depend on lattice dimensions.

(0,0,1) Site

$$E_{zz} = -2E_{xx} = -2E_{yy} = (3e/a^3)(-1.1857M_A + 2.3332M_B - 2.0247M_C), \quad (5)$$

$$E_{xx} = E_{yy} = E_{xy} = 0.$$

(1,0,1) Site

$$E_{zz} = E_{xx} = -\frac{1}{2}E_{yy} = (3e/a^3)(0.12131M_A + 0.21710M_B + 0.17870M_C), \quad (6)$$

$$E_{xx} = (3e/a^3)(2.32116M_A + 0.74014M_B - 0.47040M_C),$$

$$E_{xy} = E_{yz} = 0.$$

(1,1,3) Site

$$E_{xx} = E_{yy} = -E_{zz}/2 = (3e/a^3)(-0.004360M_A - 0.001157M_B - 0.054153M_C),$$

$$E_{yz} = E_{zx} = (3e/a^3)(-0.009793M_A + 0.014876M_B - 0.03022M_C), \quad (7)$$

$$E_{xy} = (3e/a^3)(-0.010598M_A + 0.027025M_B - 0.10222M_C).$$

(1,0,2) Site

$$E_{xx} = (3e/a^3)(-0.27921M_A + 0.64923M_B - 0.04319M_C),$$

$$E_{yy} = (3e/a^3)(0.1071M_A + 0.41375M_B - 0.038972M_C), \quad (8)$$

$$E_{zz} = (3e/a^3)(0.1721M_A - 1.0630M_B + 0.08216M_C),$$

$$E_{xx} = (3e/a^3)(-0.13722M_A + 0.94554M_B + 1.02948M_C),$$

$$E_{xy} = E_{yz} = 0.$$

Using the values of  $\xi$ ,  $\eta$ ,  $\delta$ ,  $\mu_A$ ,  $\mu_B$ , and  $\mu_C$  for the various cases in Table IV of I, we have obtained the components of the field-gradient tensor at the four lattice points which are listed in Tables I and II. Also tabulated are the quantities  $q$ ,  $\eta$ , and the direction cosines of the principal axes in each case. The principal axis<sup>4,5</sup> system XYZ is characteristic by the vanishing of off-diagonal components:

$$E_{x'y'} = E_{x'z'} = E_{y'z'} = 0$$

and

$$E_{z'z'} = q \quad \text{and} \quad (|E_{x'x'}| - |E_{y'y'}|) / |E_{z'z'}| = \eta, \quad (9)$$

$\eta$  being termed the asymmetry parameter. In Table I, the field-gradient components  $E_{zz}$  for point (0,0,1) and  $E_{zz}$ ,  $E_{xx}$ ,  $q$ ,  $\eta$ , and the direction cosines of the principal axes for the point (1,0,1) are tabulated. In Table II are tabulated the components  $E_{xx}$ ,  $E_{yy}$ , and

TABLE III. Values of constants required to calculate splittings and shifts of NMR lines.

Nucleus	$Q^a$	$(1-\gamma)^b$	$H$ (Oe)	$\nu_L^c$ (Mc/sec)	$A(1-\gamma_\infty)$	$A^2/[3\nu_L(1-\gamma_\infty)^2]$
Na <sup>23</sup>	0.1	5.53	3600	4.054	$0.4008 \times 10^{-7}$	$0.3302 \times 10^{-22}$
K <sup>39</sup>	0.11	13.8	10,000	1.987	$0.526 \times 10^{-7}$	$0.4645 \times 10^{-21}$
Cl <sup>35</sup>	-0.07894	50.3	10,000	4.172	$1.438 \times 10^{-7}$	$0.1652 \times 10^{-20}$
Br	0.28	100	3600	3.840	$1.017 \times 10^{-6}$	$0.8978 \times 10^{-19}$

<sup>a</sup> The tabulated values are in barns ( $10^{-24}$  cm<sup>2</sup>). See T. P. Das and E. L. Hahn supplement to *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958).

<sup>b</sup> T. P. Das and R. Bersohn, Phys. Rev. **102**, 733 (1956), E. G. Wikner and T. P. Das, *ibid.* **109**, 360 (1958). See also G. Burns, J. Chem. Phys. **31**, 1253 (1959).

<sup>c</sup> The NMR frequencies  $\nu_L$  are calculated using the magnetic moments tabulated in Table I of the paper by G. E. Pake in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1956), Vol. 2.

$E_{xx}$  for the point (1,0,2) and the components  $E_{xx}$ ,  $E_{zz}$ , and  $E_{xy}$  for the point (1,1,3) as well as the principal component  $E_{z'z'}$ , the asymmetry parameter  $\eta$ , and the direction cosines of the principal axes in both cases. The principal field-gradient components are all expressed in units of  $10^{-14}$  esu cm<sup>-3</sup> while the other components are in units of  $3e/a^3$ . For each of the four solid solutions considered in this paper, the field-gradient components are tabulated for the first six approximations of I. In addition, for the point (0,0,1), the field gradients are tabulated for the approximations (BM)<sub>TKS</sub> and (BM)<sub>Stern.</sub> in the cases of NaCl-Br and NaBr-Cl and for only (BM)<sub>TKS</sub> for KBr-Na and NaBr-K. The notations  $\lambda_i^x$ ,  $\lambda_i^y$ , and  $\lambda_i^z$  are used for the direction cosines of the principal axes 1(X'), 2(Y'), and 3(Z').

The calculated components of the field-gradient tensor are seen to be less sensitive in general to the choice of van der Waals force constants than either the heat of solution or the expansion in volume of the lattice.<sup>1</sup> The reason for this probably is that a large part of the contribution to the components of the field-gradient tensor arises out of the induced electronic dipole moments. The calculated field-gradient tensor components are however rather sensitive to the choice of polarizabilities. This dependence is more marked for the field-gradient components in the solid solutions NaCl-Br and NaBr-Cl which involve negative ions as solute. In these cases, the components of the field-gradient tensor are found to be larger when Sternheimer<sup>7</sup> polarizabilities are used. This is to be expected because, as seen from Table III of I, the Sternheimer polarizabilities of the negative ions are larger than those given by Tessman, Kahn, and Shockley.<sup>8</sup>

The dependence of the components of the field-gradient tensor on the choice of polarizabilities is less marked in the cases of KBr-Na and NaBr-K solutions, where the solute ions are positive ions. In these cases, the set of twelve  $B$  ions are the less polarizable positive ions as contrasted to the cases of NaCl-Br and NaBr-Cl

<sup>7</sup> R. M. Sternheimer, Phys. Rev. **96**, 951 (1954).

<sup>8</sup> J. R. Tessman, A. H. Kahn, and W. Shockley, Phys. Rev. **92**, 890 (1953).

solutions, where the set of  $B$  ions are negative ions. For the point (1,1,3), however, the calculated field-gradient components for the KBr-Na and NaBr-K solutions show a tendency to be larger when Sternheimer polarizabilities are used than for TKS polarizabilities, indicating that for distant points, a major part of the field gradient arises from the dipole moments on the  $A$  and  $C$  ions. For the points (1,0,1) and (2,1,0) in these two solid solutions, the field-gradient components calculated using Sternheimer and TKS polarizabilities are almost equal showing that for these points, a major part of the field gradient arises out of the  $B$  ions.

The orientations of the principal axes of the field-gradient tensor do show some dependence on the choice of the van der Waals force constants and polarizabilities although there appears to be no significant general trend. It does appear however that there is a somewhat more sensitive dependence on the choice of polarizabilities in the cases of NaBr-K and KBr-Na than in the other two cases. This tendency is the reverse of that found for the magnitudes of the principal components. This is not surprising as the orientations of the principal axes depend on the relative magnitudes of the components of the field-gradient tensor in the crystal axis system and not on their absolute magnitudes.

### III. CALCULATION OF QUADRUPOLE COUPLING CONSTANTS, AND FIRST-ORDER SPLITTINGS AND SECOND-ORDER SHIFTS OF NUCLEAR MAGNETIC RESONANCE LINES

In this section we derive the expected first-order splittings in frequency of the nuclear magnetic resonance of the  $\text{Na}^{23}$ ,  $\text{K}^{39}$ ,  $\text{Cl}^{35}$ , and  $\text{Br}^{81}$  nuclei at various points in the lattice using the components of the field-gradient tensors in Tables I and II. For this purpose, we require expressions<sup>4,5</sup> relating the first-order frequency splittings and second-order frequency shifts of NMR lines to the calculated field-gradient components.

The first-order displacement in frequency from the center of the line arising out of the transition  $m \leftrightarrow m-1$  is given by

$$\nu_m^{(1)} = -A(1-\gamma_\infty)E_{zz}(m-1/2),$$

where

$$A = 3eQ/2I(2I-1)h. \quad (10)$$

$(1-\gamma_\infty)$  is the antishielding<sup>9</sup> factor arising from the deformation of the electron orbitals of the ions in which the nucleus is embedded, the deformation being caused by the field gradient itself. In Eq. (10)  $E_{zz}$  is the diagonal component of the field-gradient tensor in the direction of the applied magnetic field and  $I$  is the spin of the nucleus and  $Q$  its quadrupole moment. For  $m=1/2$  and  $I=3/2$ , as is the case for all the four nuclei with which we shall be concerned, there will be two satellite lines arising out of the transitions  $\pm 3/2 \leftrightarrow \pm 1/2$  on either

side of the central line  $+1/2 \leftrightarrow -1/2$  which is undisplaced in first order. The frequency separation between each satellite line and the central line is then given by

$$\nu^{(1)} = A(1-\gamma_\infty)E_{zz}, \quad (11)$$

where

$$A = eQ/2h.$$

When the magnetic field is applied in the direction of the principal axis  $Z'$ , the frequency separation between the satellites is  $(eQq/h)(1-\gamma_\infty)$ . This quantity is called the quadrupole coupling constant and would give twice the frequency  $\nu_Q$  of the NQR (nuclear quadrupole resonance<sup>6</sup>) line if the asymmetry parameter were zero. When a finite asymmetry parameter is present, the NQR frequency is given by

$$\nu_Q = (eQq/h)(1-\gamma_\infty)(1+\frac{1}{3}\eta^2)^{1/2}. \quad (12)$$

When the nuclear quadrupole interaction is strong, there is a second-order shift of the central line  $+1/2 \leftrightarrow -1/2$ . The second-order frequency shift of the NMR line  $m \leftrightarrow m-1$  is given by the general expression<sup>4,5</sup>:

$$\begin{aligned} \nu_m^{(2)} = & \frac{A^2(1-\gamma_\infty)^2}{12\nu_L} \left\{ \frac{2}{3}(E_{zz}^2 + E_{zy}^2)[24m(m-1) \right. \\ & \left. - 4I(I+1) + 9] - \frac{1}{12}[(E_{xx} - E_{yy})^2 + 4E_{xy}^2] \right. \\ & \left. \times [12m(m-1) - 4I(I+1) + 6] \right\}, \quad (13) \end{aligned}$$

where  $\nu_L = \gamma H/2\pi$  is the NMR frequency in the applied magnetic field  $H$  and  $\gamma$  the magnetogyric ratio of the nucleus. For  $I=3/2$ , the frequency shift of the central line  $+1/2 \leftrightarrow -1/2$ , from Eq. (13), will be given by

$$\begin{aligned} \nu^{(2)} = & A^2/3\nu_L(1-\gamma_\infty)^2 \left\{ -2(E_{zz}^2 + E_{zy}^2) \right. \\ & \left. + \frac{1}{4}[(V_{xx} - V_{yy})^2 + 4V_{xy}^2] \right\}. \quad (14) \end{aligned}$$

The values of  $Q$ ,  $(1-\gamma_\infty)$ , magnetic field  $H$ ,  $\nu_L$ ,  $A$ , and  $A^2/3\nu_L$  for  $\text{Na}^{23}$ ,  $\text{K}^{39}$ ,  $\text{Cl}^{35}$ , and  $\text{Br}^{81}$  nuclei in the various ions considered in this work are tabulated in Table III. These quantities are necessary to calculate  $\nu^{(1)}$  and  $\nu^{(2)}$  as given by Eqs. (11) and (14) using the field-gradient tensor components in Tables I and II. For  $\text{K}^{39}$  and  $\text{Cl}^{35}$ , the magnetogyric ratios are small and so the NMR frequencies are low which makes the experimental measurements at low fields difficult for these nuclei. Also, if  $\nu_L$  is small, the second-order perturbation theory used in the derivation of Eq. (13) is not justifiable. For this reason, a magnetic field of 10 kOe is used in the calculations of  $\text{K}^{39}$  and  $\text{Cl}^{35}$  nuclei. For the other two nuclei,  $H=3.6$  kOe is employed.

In Tables IV and V, the predicted first-order frequency splittings and second-order frequency shifts for the positive ion nuclei  $\text{Na}^{23}$  and  $\text{K}^{39}$ , at various lattice points are tabulated for the four solid solutions considered in this paper. These frequency splittings and shifts are calculated using Eqs. (11) and (14), the

<sup>9</sup> N. J. Bloembergen and T. J. Rowland, Acta Met. 1, 731 (1953).



TABLE VI. First-order splittings and second-order shifts of NMR lines for negative-ion nuclei.

Nucleus solid solution and point	KBr <sup>81</sup> -Na(0,0,1)			NaBr <sup>81</sup> -K(0,0,1)			NaCl <sup>35</sup> -Br(1,0,1)			NaBr <sup>81</sup> -Cl(1,0,1)										
	First-order splitting (Mc/sec)	Second-order shift (Mc/sec)	Approx Z	First-order splitting (Mc/sec)	Second-order shift (Mc/sec)	Approx Z	First-order splitting (kc/sec)	Second-order shift (kc/sec)	Approx Z	First-order splitting (Mc/sec)	Second-order shift (Mc/sec)	Approx Z								
(VDW) <sub>TKS</sub> <sup>0</sup>	0.995	1.907	0.152	0	1.563	3.126	0.479	0	12.28	24.57	0.484	-14.42	7.21	33.24	68.63	0.137	3.106	0.457	0.229	0.147
(VDW) <sub>TKS</sub> <sup>M</sup>	1.197	2.392	0.240	0	1.809	3.618	0.641	0	13.83	27.66	0.487	-14.49	7.25	32.28	75.97	0.152	3.188	0.478	0.239	0.151
(VDW) <sub>TKS</sub> <sup>I</sup>	1.202	2.404	0.242	0	...	...	...	...	13.91	27.81	0.506	-15.64	7.82	30.80	73.33	0.147	3.007	0.424	0.212	0.132
(VDW) <sub>Stern</sub> <sup>0</sup>	0.378	0.755	0.024	0	0.670	1.338	0.089	0	22.62	45.24	0.564	-18.65	9.33	27.88	0.151	0.302	4.352	0.854	0.427	0.229
(VDW) <sub>Stern</sub> <sup>M</sup>	0.630	1.259	0.066	0	0.838	1.675	0.138	0	25.57	51.14	0.583	-19.51	9.77	35.96	0.178	0.356	4.782	1.019	0.510	0.262
(VDW) <sub>Stern</sub> <sup>I</sup>	0.638	1.275	0.068	0	...	...	...	...	26.75	53.50	0.604	-21.10	10.23	38.40	0.166	0.332	4.480	0.896	0.449	0.234
(BM) <sub>TKS</sub>	0.892	1.784	0.133	0	0.990	1.980	0.192	0	...	...	...	...	...	...	...	...	...	...	...	...

TABLE VII. First-order splittings and second-order shifts of NMR lines for negative-ion nuclei.

Nucleus solid solution and point	KBr <sup>81</sup> -Na(1,0,2)			NaBr <sup>81</sup> -K(1,0,2)										
	First-order splitting (Mc/sec)	Second-order shift (Mc/sec)	Approx Z	First-order splitting (Mc/sec)	Second-order shift (Mc/sec)	Approx Z								
(VDW) <sub>TKS</sub> <sup>0</sup>	0.704	0.727	0.023	1.407	-0.240	0.170	1.001	0.991	0.010	1.246	-0.293	-0.244	-0.293	-33.00
(VDW) <sub>TKS</sub> <sup>M</sup>	0.787	0.772	0.015	1.300	-0.189	0.155	1.092	1.056	0.036	1.253	-0.257	-0.243	-0.262	-31.31
(VDW) <sub>TKS</sub> <sup>I</sup>	0.791	0.775	0.015	1.342	-0.189	0.155	1.069	1.039	0.030	1.238	-0.256	-0.238	-0.260	-30.98
(VDW) <sub>Stern</sub> <sup>0</sup>	0.524	0.567	0.043	1.475	-0.311	0.184	0.644	0.699	0.055	1.188	-0.346	-0.216	-0.339	-26.68
(VDW) <sub>Stern</sub> <sup>M</sup>	0.598	0.611	0.013	1.360	-0.248	0.160	0.744	0.773	0.029	1.167	-0.312	-0.212	-0.309	-27.48
(VDW) <sub>Stern</sub> <sup>I</sup>	0.602	0.615	0.013	1.362	-0.248	0.160	0.720	0.756	0.036	1.160	-0.311	-0.208	-0.308	-26.68



TABLE VIII. First-order splittings and second-order shifts of NMR lines for negative-ion nuclei.

Nucleus solid solution and point	KBr <sup>81</sup> -Na(1,1,3)						NaBr <sup>81</sup> -K(1,1,3)					
	First-order splitting <sup>a</sup>			Second-order shift			First-order splitting			Second-order shift		
	Z (kc/sec)	X (kc/sec)	Z' (kc/sec)	Z (kc/sec)	X (kc/sec)	Z' (kc/sec)	Z (kc/sec)	X (kc/sec)	Z' (kc/sec)	Z (kc/sec)	X (kc/sec)	Z' (kc/sec)
(VDW) <sub>TKS</sub> <sup>0</sup>	45.11	22.56	45.56	-0.022	0.044	0.000	30.76	15.38	29.76	0.016	-0.098	-0.005
(VDW) <sub>TKS</sub> <sup>M</sup>	26.52	13.26	32.57	0.013	-0.051	0.008	15.94	7.97	31.07	-0.051	-0.168	0.000
(VDW) <sub>TKS</sub> <sup>I</sup>	26.38	13.19	32.56	0.013	-0.053	0.008	17.37	8.69	30.18	-0.039	-0.166	0.000
(VDW) <sub>Stern</sub> <sup>0</sup>	77.50	38.75	78.16	-0.605	0.302	0.000	72.18	36.09	65.87	-0.228	0.241	-0.037
(VDW) <sub>Stern</sub> <sup>M</sup>	57.65	28.83	57.65	-0.260	0.138	0.000	56.93	28.47	48.12	0.069	0.106	-0.030
(VDW) <sub>Stern</sub> <sup>I</sup>	57.43	28.72	57.44	-0.250	0.136	0.000	58.70	29.35	50.35	0.088	0.123	-0.030

<sup>a</sup> Splittings and shifts with the magnetic field in the X direction are the same as those with the magnetic field in the Y direction.

TABLE IX. Summary of experimental data on first-order splittings and second-order shifts of NMR lines in solid solutions.

Solid solution	Nucleus	Point	Direction of magnetic field	Data	Ref.
NaCl-Br	Na <sup>23</sup>	(0,1,0)	Z	2nd order shift = 2.82 kc/sec	a
NaBr-Cl	Na <sup>23</sup>	(0,1,0)	Z	2nd order shift = 3.94 kc/sec	a
NaCl-Br	Na <sup>23</sup>	(1,0,2)	Z	1st order splitting ≥ 10 kc/sec	a
KBr-Na	Br <sup>79</sup>	(2,0,3)	Z	2nd order splitting ≥ 1.07 kc/sec	b
KBr-Na	Br <sup>81</sup>	(1,1,3)	Z	2nd order splitting ≥ 1.20 kc/sec	b

<sup>a</sup> Reference 2.  
<sup>b</sup> Reference 3.

field-gradient components in Tables I and II and the constants tabulated in Table III. Tables VI, VII, and VIII list the corresponding splitting and shift frequencies for the negative-ion nuclei Cl<sup>35</sup> and Br<sup>79</sup>. In Table IX, the available experimental data on nuclear quadrupole effects in NMR studies of solid solutions are listed. The experimental data in the third, fourth, and fifth rows of Table IX are obtained by the critical sphere analysis first employed by Bloembergen and Rowland.<sup>9</sup> For example, the data for Na<sup>23</sup> nuclei in NaCl-Br at the (1,0,2) position indicates that the first-order frequency splittings for all the nuclei at (1,0,2) positions and nearer are less than 10 kc/sec. There are twenty-four points equivalent to (1,0,2), and when the magnetic field is applied in the Z direction, the nuclei at some of these points will have splittings equal to that which would be produced at the nucleus at (1,0,2) when the magnetic field is in the X or Y directions. In order that none of these twenty-four nuclei can contribute to the intensity of the central line, the necessary condition is that the linewidth of 10 kc/sec be less than the least value of the first-order frequency splitting at any of these twenty-four points. From Table V, this would require that the first-order splittings for Na<sup>23</sup> nuclei at the point (1,0,2) when the magnetic field is applied in the Y direction should be greater than 10 kc/sec. A similar interpretation is to be applied to the results for Br<sup>79</sup> and Br<sup>81</sup> nuclei in Table IX.

The following conclusions may be drawn by comparing the theoretical results in Tables IV-VIII with the experimental results in Table IX.

The second-order frequency shifts at the point (0,0,1) for an applied magnetic field in the X direction for both NaCl-Br and NaBr-Cl [or what is equivalent, the second-order frequency shift at the point (0,1,0) for applied field in Z direction] agrees best with experiment when Mayer's values of the van der Waals constants are used together with Sternheimer polarizabilities. This is indeed gratifying because as discussed in I, Mayer's values of the VDW force constants are the most justifiable among the three choices made. In

general, the predicted frequency shifts agree better with experiment when Sternheimer polarizabilities are used. This remark also applies to the calculated results in all other cases where experimental data are available. The ratio of the calculated second-order frequency shift for  $\text{Na}^{23}$  nuclei in  $\text{NaCl-Br}$  and  $\text{NaBr-Cl}$  is about 0.69 for the  $(\text{VDW})_{\text{stern.}^{\text{M}}}$  case in excellent agreement with the experimental value of about 0.71. The nearly exact agreement is fortuitous, but it is significant that the calculated ratio is less than unity in all approximations when Sternheimer polarizabilities are used as opposed to the calculated ratio greater than unity obtained when TKS polarizabilities are used. Unfortunately, there are no data on the second-order shifts for  $\text{Br}^{81}$  nuclei in  $\text{KBr-Na}$  or  $\text{NaBr-K}$  to compare with theory. The theoretical results indicate that the second-order shifts for  $\text{Br}^{81}$  nuclei in these cases are about a factor of 100 larger than those found for  $\text{Na}^{23}$  nuclei in  $\text{NaCl-Br}$  and  $\text{NaBr-Cl}$ . This happens because the antishielding factor  $(1-\gamma_{\infty})$  for  $\text{Br}^{-}$  ions is about 20 times as large as for  $\text{Na}^{+}$  ions and the quadrupole moment of  $\text{Br}^{81}$  is about three times as large as the quadrupole moment of  $\text{Na}^{23}$ . This large second-order shift for  $\text{Br}^{81}$  nuclei explains why the presence of a few dislocations or impurities broadens the  $\text{Br}^{81}$  resonance so effectively<sup>3</sup> while the effect on  $\text{Na}^{23}$  resonance of dislocations or impurities is less marked.

The first-order splitting for  $\text{Na}^{23}$  nuclei at the (1,0,2) position in  $\text{NaCl-Br}$  with magnetic field in the  $Y$  direction compares favorably with the lower limit of 10 kc/sec by experiment. The agreement is again seen to be better with Sternheimer polarizabilities, the best value being obtained when the isoelectronic assumption is made for the van der Waals force constants. The value of the calculated shift for this case is 9.68 kc/sec. But, as mentioned in I, this isoelectronic assumption for the force constants is not too justifiable. So we should really compare the experimental value of the splitting with the theoretical value for the case  $(\text{VDW})_{\text{stern.}^{\text{M}}}$  which is 7.8 kc/sec, that is, about 78% of the experimental value. This situation can be compared to the situation for the second-order shift at the (0,0,1) position where the theoretical value is about 59% of the experimental result. No results are available for the (1,0,2) position in  $\text{Na}^{23}\text{Br-Cl}$ , but the calculated results indicate that the first-order critical sphere would again include the (1,0,2)-type points in the lattice. For the (1,0,2) position in the cases of  $\text{NaBr-K}$  and  $\text{KBr-Na}$ , both the first-order splittings and second-order shifts for  $\text{Br}^{81}$  nuclei when the magnetic field is in the  $Y$  direction, are much larger than the width 1.20 kc/sec of the NMR line and hence these points would be inside both the first- and second-order critical spheres as is indeed found to be the case experimentally.

The second-order shifts at the point (1,1,3) for  $\text{Br}^{81}$  nuclei (when the field is in the  $X$  or  $Y$  directions) in  $\text{KBr-Na}$  are in reasonable qualitative agreement with experiment, but the quantitative agreement is not too

good. Again, the agreement with experiment is better when Sternheimer polarizabilities are used. The agreement with experiment is seen to be best for the  $(\text{VDW})_{\text{stern.}^{\text{O}}}$  case (this notation indicates the No VDW case of I.) where the calculated shift is about a factor of 3.8 smaller than experiment. But, as discussed in I, the neglect of van der Waals force is not justifiable when Huggins-Mayer force constants are used, so the experimental result has to be compared with the theoretical value for the  $(\text{VDW})_{\text{stern.}^{\text{M}}}$  case. This value is found to be a factor of about 8.5 times smaller than experiment. In Sec. IV, we shall discuss possible causes for an underestimation in our theoretical value. If, however, we assumed that the error was due solely to an error in  $(1-\gamma_{\infty})$  we would require a value of nearly 300 for  $(1-\gamma_{\infty})$  as compared to the theoretical value of 100 obtained<sup>10</sup> from the electronic wave functions for the free ion. This value is to be compared with the much smaller values of about 39 obtained by a simple continuum compression theory and the value of 10 required<sup>6</sup> to interpret the  $\text{Br}^{81}$  quadrupole coupling constant found from molecular beam measurements on  $\text{KBr}$  molecule using a purely ionic model.

The second-order critical sphere for  $\text{Br}^{79}$  resonance is expected<sup>3</sup> to enclose points of the type (1,1,3) so that the smallest predicted shifts at these points should be larger than the width 1.07 kc/sec of the  $\text{Br}^{79}$  NMR line. Multiplying the tabulated values in Table VIII by a factor  $(0.33/0.28)^2$  to take account of the larger quadrupole moment  $(0.33 \times 10^{-24} \text{ cm}^2)$  of the  $\text{Br}^{79}$  ion, we find that the predicted shifts are again only about a seventh of the width. From Table IX, the proper points to compare with the experimental width are, however, the points (2,0,3). The calculated first-order frequency splittings for  $\text{Na}^{23}$  nuclei in  $\text{NaCl-Br}$  at the points (1,1,3) are seen to be much smaller than the width 10 kc/sec of the NMR line, as is to be expected since these points are outside of the first-order critical sphere.

#### IV. DISCUSSION OF THEORETICAL RESULTS

The best values of the calculated  $\text{Na}^{23}$  second-order frequency shifts for  $\text{NaCl-Br}$  and  $\text{NaBr-Cl}$  at the point (1,0,0) are about 60% of the experimental values. If one attributed this disagreement entirely to an error in  $(1-\gamma_{\infty})$ , a value of about 7.1 would be required as compared to the value 5.53 calculated<sup>10</sup> from Hartree-Fock wave functions for the ion. However, there are two reasons besides this to explain why the calculated field gradient may be underestimated. We have considered the contribution to the field gradient only from the displacements and electronic dipoles on the ions of the sets  $A$ ,  $B$ , and  $C$ . In Table X the relative contributions to the field gradient (without antishielding)

<sup>10</sup> R. M. Sternheimer, H. M. Foley, and D. Tycko, *Phys. Rev.* **93**, 734 (1954); R. M. Sternheimer and H. M. Foley, *ibid.* **102**, 731 (1956); T. P. Das and R. Bersohn, *ibid.* **102**, 733 (1956); E. G. Wikner and T. P. Das, *ibid.* **109**, 360 (1958).

at the point (0,0,1) from the sets of ions  $A$ ,  $B$ , and  $C$  are compared for the  $(VDW)_{\text{Stern. M}}$  case. It can be seen that the contributions from the sets of ions  $B$  and  $C$  are comparable and larger than from the set  $A$ . This is understandable because the electronic dipole moments on the negative ions  $B$  and  $C$  are much larger than those on the positive ions  $A$  and the electronic dipole moments contribute substantially to the field gradient. It is therefore not unreasonable to expect that other ions in the lattice can contribute about one-half of the field gradient arising from either the  $B$  and  $C$  ions, which would bring the calculated results in agreement with experiment. Of the ions that have been neglected, the set of ions at points  $(\pm 2, \pm 1, \pm 1)$  and  $(\pm 1, \pm 1, \pm 1)$  are expected to make the most important contributions. In the case of NaCl-Br and NaBr-Cl, the former set  $(\pm 2, \pm 1, \pm 1)$  of ions are negative ions and they would be expected to make a significant contribution through their larger electronic dipoles. In the case of KBr-Na and NaBr-K, however, the ions  $(\pm 1, \pm 1, \pm 1)$  are negative ions and they would make an important contribution to the field gradient.

Another source of error in our calculation of the field gradients is the neglect of the contribution from overlaps between the electron orbitals of the ion containing the nucleus and other neighboring ions which relax. There are two ways<sup>6</sup> in which a change in the overlap can contribute to the field gradient, by a distortion of the orbitals from spherical symmetry arising out of the overlap itself, as well as an alteration in the covalent binding between neighboring ions. However, from the analysis of field-gradient data in alkali-halide molecules, the overlap distortion and covalent effects are seen to contribute much less significantly to the field gradients at the positive-ion nuclei than what they do for negative-ion nuclei. It is not unjustified, therefore, to assume that a greater fraction of the small disagreement (20%) in the predicted and experimentally observed field gradients at positive-ion nuclei in (0,0,1) positions arises from the first cause discussed in the previous paragraph. There seems to be further indirect evidence in support of this from the field-gradient data at  $\text{Na}^{23}$  nucleus at the point (1,0,2). The predicted field gradient in this case is 22% less than the observed field gradient, as compared to the similar 20% discrepancy found at the point (0,0,1). Since overlap effects would be larger near the impurity ion than at points farther away, one would expect a better agreement of our result with experiment at the point (1,0,2) if overlap were the only source of error. The observation that the errors at (0,0,1) and (1,0,2) are comparable leads us to conclude that it is the neglect of the contribution from the displacements and dipole moments of other ions besides  $A$ ,  $B$ , and  $C$  which is mostly responsible for the observed errors in the calculated field gradients.

The disagreement between the calculated and experimental field gradients at the negative-ion nuclei at the point (1,1,3) is more serious than in the cases of the

positive-ion nuclei already considered. The theoretical field gradient is found to be about a factor of three smaller than the observed value. The same two sources of error discussed before are again operative here. The nearest-neighbor ions of the point (1,1,3) are (0,1,3), (2,1,3), (1,0,3), (1,2,3), (1,1,2), and (1,1,4). None of these ions have been allowed to displace in our calculations. Although their displacements are expected to be small relative to those of the ions  $A$ ,  $B$ , and  $C$ , these nearest-neighbor ions are much closer to the point (1,1,3) and their displacements would be relatively more effective in influencing the field gradient. We have calculated the field gradient at (1,1,3) due to these ions assuming a continuous elastic displacement due to the multipole stress arising from the relaxation of ions  $A$ ,  $B$ , and  $C$ . The details of the calculation are given in the Appendix. It is found that the contributions from these nearest-neighbor ions to the field-gradient components are of the same order of magnitude and usually larger than the direct contribution from the sets of ions  $A$ ,  $B$ , and  $C$ . Thus, for the  $(VDW)_{\text{Stern. M}}$  approximation in the case of KBr-Na, we have the components of the field-gradient tensor at (1,1,3) given by

$$\begin{aligned} E_{xx} &= -(3e/a^3)(0.00163), \\ E_{yy} &= -(3e/a^3)(0.00124), \\ E_{zz} &= -(3e/a^3)(0.000335). \end{aligned} \quad (15)$$

Comparing with the components in Table II, we find that the contributions from the nearest-neighbor ions is larger than the contribution from ions  $A$ ,  $B$ , and  $C$  for the components  $E_{xx}$  and  $E_{zz}$  and smaller for the component  $E_{yy}$ . Also the signs of the contributions are different for  $E_{xx}$  and  $E_{yy}$  and the same for  $E_{zz}$ . We thus have the total contributions from near ions as well as  $A$ ,  $B$ , and  $C$  ions to the field-gradient components given by

$$\begin{aligned} E_{xx} &= -(3e/a^3)(0.000927), \\ E_{yy} &= -(3e/a^3)(0.001243), \\ E_{zz} &= -(3e/a^3)(-0.000636). \end{aligned} \quad (16)$$

Using these components, one gets the second-order frequency shift for  $\text{Br}^{81}$  nuclei at the point (1,1,3) as 0.85 kc/sec when the magnetic field is in the  $Z$  direction. This value is to be compared with the experimental value of 1.2 kc/sec. The theoretical value is now about two-thirds the experimental value as contrasted to the factor of 8.5 that was obtained when only the contributions of the ions  $A$ ,  $B$ , and  $C$  were considered. The field gradients and NMR frequency shifts of nuclei at distant points are thus seen to depend quite sensitively on the relaxation of the ions which are nearest neighbors to the nucleus considered. In the present case, since the nearest-neighbor ions, especially (1,1,2), (0,1,3), and (1,0,3), are not very far from the impurity ion, the application of the continuum model is not expected to be very accurate. This is probably the reason that our

calculated value of the second-order shift including the effect of the nearest neighbors still differs somewhat from the experimental value. Another possible cause for disagreement with experiment is that the contributions from the electronic dipole moments on the nearest neighbor to the field gradient at the point (1,1,3) has not been considered. In I, it was demonstrated that the electronic dipole polarization of distant ions due to the electric hexadecapole moment around the impurity is negligible. However, when these distant ions are displaced, they may polarize each other. The induced electronic dipole moments, due to their proximity, may affect the field gradient at (1,1,3) appreciably and perhaps increase the calculated field gradient to agree better with experiment. The overlap effect is known<sup>6</sup> to be very important in affecting the field gradients at negative-ion nuclei in alkali-halide molecules. However, it is found to act in opposition to the field gradient from the multipoles in the ionic model. This tendency is in the opposite direction to the discrepancy that we have with experiment at the point (1,1,3). This observation, as well as the fact that the displacements of the near-neighbor ions of (1,1,3) are so small, makes us expect that the effects of overlap are not of primary importance in influencing the field gradients at nuclei at the point (1,1,3).

#### V. CONCLUSION

Our calculations show in general then that one can get fairly satisfactory values of the field gradients at nuclei in dilute alkali halide solutions with the Born-Mayer ionic model for these crystals. The results are quite sensitive to the choice of repulsive force constants, van der Waals force constants and most sensitive to the choice of electronic polarizabilities. In general, the Sternheimer polarizabilities give better agreement with experiment in all cases considered. The main source of disagreement between theoretical and experimental field gradients appears to be the neglect of the displacements of ions other than the twenty-four ions belonging to the sets *A*, *B*, and *C* near the impurity ion that have been considered. For further improvement in the theoretical results, the displacements of more ions will have to be taken into account. Indirect evidence has been cited to show that contributions to field gradients from overlap effects are relatively unimportant for positive-ion nuclei and distant negative-ion nuclei. One would, however, expect overlap effects to be significant at negative-ion nuclei adjacent to the impurity. It would, therefore, be helpful to have experimental data on the field gradients at Br<sup>81</sup> nuclei at the point (0,0,1) in KBr-Na and NaBr-K solid solutions.

We would like to say something about the anti-shielding factors that we have used in our interpretation. The value of 5.53 seems to be quite adequate for  $(1-\gamma_\infty)$  for the Na<sup>+</sup> ion. For the Br<sup>-</sup> ion the value 100 employed for  $(1-\gamma_\infty)$  was calculated<sup>10</sup> using interpo-

lated wave functions as no wave functions are available with or without exchange. However, the calculations in this paper do show that 100 is a reasonable value and there seems to be some evidence that it may be even larger.<sup>11</sup> This conclusion is in keeping with the recent failure of Burns and Wikner<sup>12</sup> to obtain substantial decreases in  $(1-\gamma_\infty)$  for halogen negative ions from the values for free ions inside crystals by reasonable contractions of the electronic orbitals. Their attempt was conditioned by the erroneous conclusion that experimental data seemed to indicate that the probable values for  $(1-\gamma_\infty)$  for Cl<sup>-</sup>, Br<sup>-</sup>, and I<sup>-</sup> ions were 10, 35, and 50 as opposed to calculated values<sup>10</sup> of about 50, 100, and 170, respectively. However, the value 35 for the Br<sup>-</sup> ion was obtained by Otsuka and Kawamura<sup>3</sup> from the use of a simple compression theory in the calculation of the field gradient. As shown in I, such a theory leads to erroneous estimates of the displacements of the lattice points and also neglects the important contribution from the displacements and electronic polarizations of the ions adjacent to the nucleus whose nuclear quadrupole interaction is being considered. The value 50 quoted for the I<sup>-</sup> ion by Otsuka<sup>13</sup> was a lower limit based on an approximate calculation of the field gradients at I<sup>127</sup> nuclei in KI crystal due to dislocations. Otsuka's choice of the value 50 depended heavily on the earlier erroneous value<sup>3</sup> of 35 that was arrived at for the Br<sup>-</sup> ion. Our present experience with the field gradients in solid solutions leads us to expect that in general in imperfect crystals, the calculated values of  $(1-\gamma_\infty)$  for both free positive and negative ions<sup>10</sup> are reasonable to use and can explain observed splittings and shifts in frequency of NMR lines if the field gradients due to the charges and dipoles on the ions of the crystal are calculated carefully. There is only one important exception, namely when the negative ion nuclei immediately adjacent to the impurity are considered. In these cases, covalent and electron overlap effects are expected to make significant contributions to the field gradient; however, as mentioned in Sec. IV, more experimentation is necessary to test this exception. We would also suggest that for those pure crystals in which the nuclei are already at sites of less than cubic symmetry, it is reasonable to

<sup>11</sup> In an earlier brief report on these calculations at the American Physical Society—American Chemical Society Conference on Nonmetallic Crystals at Northwestern University, Evanston, Illinois, 1961 (proceedings to be published by W. A. Benjamin and Company, New York), the agreement with experiment for the NaBr-Cl was presented as worse than it really is. This happened because the "empirical" values of  $(1-\gamma_\infty)$  tabulated there for this case were obtained by comparing theoretical unshielded values of the field gradient with the experimental value  $2.0 \times 10^{23}$  cm<sup>-3</sup> quoted by Kawamura *et al.* Actually from the value of the shift in Table V, the experimental value is about  $1.7 \times 10^{23}$  cm<sup>-3</sup> using Eq. (3) of reference 2. Consequently the empirical values of  $(1-\gamma_\infty)$  for the NaBr-Cl case in Table VII of our earlier report have all to be multiplied by a factor 0.85, bringing the best empirical value of  $(1-\gamma_\infty)$  for this case in agreement with the best value for the NaCl-Br case.

<sup>12</sup> G. Burns and E. G. Wiker, Phys. Rev. **121**, 155 (1961).

<sup>13</sup> E. Otsuka, J. Phys. Soc. Japan **13**, 1155 (1958).

use the free-ion values<sup>10</sup> of the antishielding factors in the calculation of the ionic contributions to the field gradients. The difference between the calculated ionic contribution to the field gradient and the observed gradient can then be ascribed to covalent and overlap effects between neighboring ions. An interpretation of this type is more justifiable than ignoring the covalent and overlap contributions altogether and trying to explain the observed field gradient by an unreasonable alteration of the antishielding factor from the free ion value.

In several connections in this work it has been seen that employment of Sternheimer's polarizabilities gives better agreement with experiment than the use of the TKS polarizabilities. For the large negative-ion polarizabilities the Sternheimer values are greater than the TKS values, while the reverse is true of the small positive-ion polarizabilities. Thus improved agreement with experiment seems to follow when polarization effects are given a bigger role. It is interesting to note in this connection that more elaborate models constructed to correct discrepancies in the dielectric theory have as a feature the opposite effect: a reduction of the role played by polarization. It therefore seems doubtful that using more detailed models of the polarization mechanism would improve the agreement of the calculated and experimental results. Although there is the suggestion in this work that the Sternheimer polarizabilities are to be preferred for point-defect calculations, it should be stated that the use of these polarizabilities in the dielectric theory leads to serious discrepancies there. If we use the Lorentz-Lorentz equation,

$$(\epsilon_{\infty} - 1)/(\epsilon_{\infty} + 2) = (4\pi N/3)(\alpha_+ + \alpha_-),$$

and the Sternheimer polarizabilities to deduce  $\epsilon_{\infty}$ , the calculated values of  $\epsilon_{\infty}$  are in very poor agreement with the observed values. If the difference between the Sternheimer free-ion polarizabilities and the TKS crystal polarizabilities be ascribed to exchange effects according to the model of Dick and Overhauser,<sup>14</sup>

$$\alpha_{\text{TKS}}^{\pm} = \alpha_{\text{Stern}}^{\pm} \mp (n_{\pm} e D + D^2)/k_{\pm},$$

it is found that it is impossible to find real values of  $D$  which satisfy this equation for reasonable values of  $n$  and  $k$ . Thus, in spite of their relative success when used in mixed crystal calculations, the Sternheimer polarizabilities do not appear to be good choices for use in the dielectric theory in its present state. It is imperative, therefore, in view of these observations, to reexamine carefully the nature and assumptions of the theory of dielectric constants in its present form.

It is hoped that our calculations will stimulate further experimental work aimed at obtaining field gradients at the lattice points considered in this work as well as at additional points in these and other solid

<sup>14</sup> B. G. Dick and A. W. Overhauser, Phys. Rev. **112**, 90 (1958).

solutions. Field gradients at negative-ion nuclei are particularly interesting from a theoretical standpoint. It must be possible with very well annealed crystals to obtain pure quadrupole resonance for Br<sup>79</sup> and Br<sup>81</sup> nuclei at the point (0,0,1) and (1,0,2) in KBr-Na and NaBr-K as the expected frequencies are in the range 1.2 to 2.0 Mc/sec about the same range as N<sup>14</sup> nuclear quadrupole resonances.<sup>5</sup> The total number of ions in these special positions with respect to solute ions is rather small, namely,  $6cN$  for the (0,0,1) points and  $24cN$  for (1,0,2), where  $c$  is the impurity concentration and  $N$  the total number of nuclei. The expected signals would therefore be rather weak. The "lost signal technique" developed by Anderson and Redfield<sup>15</sup> holds some promise for measuring these field gradients. In addition, NMR at very high fields (about 40 kOe), which are becoming increasingly available, may be helpful in observing some satellite lines that would be unobservable at the lower signal-to-noise ratios that obtain at lower fields.<sup>16</sup>

## APPENDIX

### Contribution to the Field-Gradient Components at (1,1,3) from the Nearest Neighbors

The six nearest neighbors of a nucleus inside an ion at the lattice point  $(L_1, L_2, L_3)$  are  $(L_1 \pm 1, L_2, L_3)$ ,  $(L_1, L_2 \pm 1, L_3)$ , and  $(L_1, L_2, L_3 \pm 1)$ . The displacement at each of these points, using a continuum model beyond the ions of the set  $B$  and  $C$ , is given by Eq. (26) of I, namely,

$$\mathbf{U} = K' \mathbf{r}/r^3, \quad (\text{A1})$$

where

$$K' = (a^2/\pi c_{11})(A/\rho^2)e^{-a/\rho}(\delta + \sqrt{3}\eta),$$

$A$  and  $\rho$  being the repulsive force constants (Born-Mayer without VDW forces) between positive and negative ions in the crystal,  $c_{11}$  the relevant elastic constant for the crystal, and  $a$  the lattice constant. Using the values of these constants for KBr together

TABLE X. Relative contributions to field gradient at site (0,0,1) from sets of ions  $A$ ,  $B$ , and  $C$ .

Solid solution <sup>a</sup>	Contributions from $A$ ions	Contributions from $B$ ions	Contributions from $C$ ions	Total predicted field gradient	Required field gradient to fit experiment
NaCl-Br	-0.044	-0.051	-0.051	-0.146	-0.185
NaBr-Cl	0.062	0.074	0.073	0.210	0.252

<sup>a</sup> All field gradients are quoted in units of  $(3e/a^3)$  without the antishielding factor  $(1 - \gamma_{\infty})$  for the  $(\text{VDW})_{\text{Stern}}$  approximation.

<sup>15</sup> A. Anderson, Phys. Rev. **115**, 863 (1959).

<sup>16</sup> Dr. W. G. Clark has pointed out to us (private communication) that the spin-echo technique developed by Solomon for random quadrupole interaction in solids [see I. Solomon, Phys. Rev. **110**, 61 (1958)] and also W. G. Clark, Office of Naval Research Technical Report No. 5, Contract N-onr-401(15) (unpublished)] would be quite useful for plotting the field gradients at various lattice points in solid solutions.

TABLE XI. Dipole moments and their direction cosines nearest to the point (1,1,3).

Point	$\mu$	$l_1$	$l_2$	$l_3$
(0,1,3)	$eK'/10a^2$	0	$1/(10)^{\frac{1}{2}}$	$3/(10)^{\frac{1}{2}}$
(2,1,3)	$eK'/14a^2$	$2/(14)^{\frac{1}{2}}$	$1/(14)^{\frac{1}{2}}$	$3/(14)^{\frac{1}{2}}$
(1,0,3)	$eK'/10a^2$	$1/(10)^{\frac{1}{2}}$	0	$3/(10)^{\frac{1}{2}}$
(1,2,3)	$eK'/14a^2$	$1/(14)^{\frac{1}{2}}$	$2/(14)^{\frac{1}{2}}$	$3/(14)^{\frac{1}{2}}$
(1,1,2)	$eK'/6a^2$	$1/(6)^{\frac{1}{2}}$	$1/(6)^{\frac{1}{2}}$	$2/(6)^{\frac{1}{2}}$
(1,1,4)	$eK'/18a^2$	$1/(18)^{\frac{1}{2}}$	$1/(18)^{\frac{1}{2}}$	$4/(18)^{\frac{1}{2}}$

with the values of  $\delta$  and  $\eta$  for the case of KBr-Na in the approximation (BM)<sub>Stern.</sub>, we get

$$K' = a^3(0.513) \times (-0.02615) = -a^3(0.01341). \quad (\text{A2})$$

The dipole moment at any point because of the displacement will be given by

$$\mathbf{u} = (eK'/r^2)(\mathbf{r}/r) = \mu\mathbf{r}/r, \quad (\text{A3})$$

for a positive ion. For a negative ion, there will be a negative sign on the right-hand side of (A3).

To get the field gradient at  $(L_1, L_2, L_3)$  due to an ion at  $(L_1', L_2', L_3')$  due to the dipole moments given by (A3), we make use of Eqs. (4) of the text. We shall require for this purpose the direction cosines of  $\mathbf{u}$  and the components of the radius vector joining the point

$(L_1, L_2, L_3)$  to the point dipole at  $(L_1', L_2', L_3')$ . These are given by

$$\begin{aligned} l_1' &= L_1' / (L_1'^2 + L_2'^2 + L_3'^2)^{1/2}, & x_1 &= (L_1 - L_1')a, \\ l_2' &= L_2' / (L_1'^2 + L_2'^2 + L_3'^2)^{1/2}, & x_2 &= (L_2 - L_2')a, \\ l_3' &= L_3' / (L_1'^2 + L_2'^2 + L_3'^2)^{1/2}, & x_3 &= (L_3 - L_3')a. \end{aligned} \quad (\text{A4})$$

The dipole moments at (0,1,3), (2,1,3), (1,0,3), (1,2,3), (1,1,2), and (1,1,4) and their direction cosines are given in Table XI.

From Eq. (4) of the text it then follows that

$$\begin{aligned} E_{xx} = E_{yy} &= -\frac{1}{2}E_{zz} = -\frac{3eK'}{a^3} \left[ \frac{1}{7(14)^{\frac{1}{2}}} + \frac{1}{3(6)^{\frac{1}{2}}} - \frac{2}{9(18)^{\frac{1}{2}}} \right], \\ E_{zz} &= -\frac{3eK'}{a^3} \left[ \frac{1}{6(6)^{\frac{1}{2}}} - \frac{1}{18(18)^{\frac{1}{2}}} + \frac{3}{10(10)^{\frac{1}{2}}} - \frac{3}{14(14)^{\frac{1}{2}}} \right], \\ E_{xy} &= -\frac{3eK'}{a^3} \left[ \frac{2}{10(10)^{\frac{1}{2}}} - \frac{2}{14(14)^{\frac{1}{2}}} \right]. \end{aligned} \quad (\text{A5})$$

Using the values of  $K'/a^3$  in (A2), one then gets

$$\begin{aligned} E_{xx} &= -(3e/a^3)(0.00163), \\ E_{xy} &= -(3e/a^3)(0.000335), \\ E_{zz} = E_{yy} &= -(3e/a^3)(0.00124). \end{aligned} \quad (\text{A6})$$