PHYSICAL REVIEW B VOLUME 3, NUMBER 2 15 JANUARY 1971

Dipole-Dipole Hyperfine Constants and Lattice Relaxation of an Interstitial Defect in LiF†‡

Y. Hou Chu* and Robert Lee Mieher
Department of Physics, Purdue University, Lafayette, Indiana 47907

(Received 10 August 1970)

A study of the lattice relaxation about an interstitial fluorine defect in LiF has been made. Following the method of Daly and Mieher, we have calculated dipole-dipole hyperfine constants for 10 lattice shells and have compared them with experimental constants obtained by electron-nuclear double resonance. The calculations show that most of the lattice ions relaxed away from the defect.

I. INTRODUCTION

Daly and Mieher[1] have used the free F_2^- wave function of Wahl[2] to calculate the anisotropic hyperfine tensor B due to the dipole-dipole interactions between the unpaired electron of the F_2^- molecule and neighboring lattice nuclei, for several V_K-type color centers in the alkali fluorides. The V_K center or self-trapped hole is a negatively charged diatomic halide molecule (e.g., F_2^-) that is situated on two adjacent halogen sites along a $\langle 110\rangle$ direction. The theoretical values of the dipole-dipole tensor may be compared with the experimental electron-nuclear double-resonance (ENDOR) data to determine the distortion of the lattice about the defect. The general distortion of the lattice agrees qualitatively with semiphenomenological calculations of Das *et al.*[3]

We report here results of a similar study of an H-type or interstitial defect in LiF. At low temperatures the interstitial halogen in LiF is also an F_2^- molecule ion, but it is situated on a single anion site and is oriented in a $\langle 111\rangle$ direction.[4,5] This $\langle 111\rangle$ defect is a neutral defect since it is equivalent to an excess fluorine atom in the perfect lattice. The effect of the $\langle 111\rangle$ defect on the lattice is expected to be considerably different from the effect of the V_K-type defects. For instance, the repulsive energy between the defect and the lattice is expected to be larger because of the interstitial nature of the $\langle 111\rangle$ defect. Yet, the ESR[4] constants show that the wave function of the F_2^- molecule for the interstitial should not differ by much from that of the self-trapped hole.

II. CALCULATIONS AND DISCUSSION

The wave function for the unpaired spin of the F_2^- molecule ion was taken as the ground-state σ_u orbital of the free F_2^- that was calculated by Wahl using a self-consistent field technique.[2] Molecular orbitals corresponding to several values of the internuclear distance R of the molecule were calculated. The free σ_u molecular orbital is then orthogonalized to the p orbitals of the lattice ions. For the lattice ions the free Hartree-Fock electron orbits of Bagus[6] were used. Other effects such as exchange polarization of the closed shells of the molecule and ions and mutual orthogonalization of neighboring ions were not included in the calculation. Although these effects contribute significant corrections to the wave function, the qualitative picture of the distortion should not change. Additional discussion of these approximations is contained in Ref. 1.

For each lattice ion, the calculation of the dipole-dipole tensor was repeated for different relaxations. The relaxation for most nuclei was restricted by symmetry to a plane because of the $\langle 111\rangle$ symmetry of the defect. A summary of the relaxation study is listed in Table I. The angle (or direction) of relaxation α, is taken positive for the rotation from Z to Y (or X), the magnitude of relaxation r, is given as a fraction of the lattice constant $a = 3.8$ a.u. (See Fig. 1). Figure 1 illustrates the results of our study on 10 nonequivalent lattice shells (74 lattice ions total). The contours,[7] which correspond to an electron density of 0.3 electron/Å^3, are used to represent the "hard core" of the ions in LiF. The experimentally determined directions of the hyperfine principal axes[5,8] are shown for each ion.

For the V_K center in LiF, the internuclear distance of the F_2^- molecule, R, was determined by studying the relaxation of the nearest-neighbor lithium nuclei that lie in the plane that perpendicularly bisects the axis of the F_2^- molecule. These nuclei, labeled A in Ref. 1, were most sensitive to changes in R, and their direction of relaxation was restricted to an axis perpendicular to the defect by symmetry. A reliable value of R could be obtained in this way because the two major corrections to the F_2^- wave function, orthogonalization and exchange polarization, have little effect on the anisotropic hyperfine constants of the lithium ions since they have no p electrons.

For the interstitial defect the nuclei corresponding to the lithium A nuclei are the fluorine D nuclei. Only the D fluorines have a single direction of re-

TABLE I. Summary of relaxation study. Experimental hyperfine constants are compared with those calculated for the ion at the unrelaxed and relaxed positions. Magnitude of relaxation r is expressed in units of the lattice constant $a = 3.8$ a.u. and the angle of relaxation α is the angle between the direction of relaxation and the Z axis of the molecule.

Shell		a	B_x	B_y	B_z	θ (deg)	r	α (deg)
A(Li)	Expt	−1.89	−2.98	+4.96	−1.99	−17.5		
	No relax		−3.99	+6.74	−2.75	−14.1		
	Relax		−2.98	+4.97	−1.98	−17.6	0.125	40
B(F)	Expt	+27.7	−18.2	+35.0	−16.9	+29.5		
	No relax		−9.32	+17.19	−7.87	+28.3		
	Relax		−18.2	+35.0	−16.8	+28.7	0.225	−73
C(Li)	Expt	−0.43	−1.11	−1.11	+2.23	0		
	No relax		−1.34	−1.34	+2.68	0		
	Relax		−1.11	−1.11	+2.22	0	0.078	0
D(F)	Expt	−2.44	+3.56	−2.21	−1.36	−6.5		
	No relax		+4.60	−2.82	−1.78	0		
	Relax		3.63	−2.13	−1.51	0	0.146	90 (X)
E(Li)	Expt	−0.01	−0.70	+1.21	−0.50	−13.25		
	No relax		−0.70	+1.25	−0.55	−13.8		
	Relax		−0.69	+1.23	−0.54	−13.3	0.020	50
F(F)	Expt	−0.13	−1.12	+2.13	−1.01	−29.5		
	No relax		−1.31	+2.43	−1.12	−27.0		
	Relax		−1.14	+2.13	−1.00	−29.0	0.100	28
G(Li)	Expt	0.00	+0.76	−0.38	−0.37	−44.5		
	No relax		+0.78	−0.40	−0.38	−44.5		
	Relax		+0.76	−0.39	−0.38	−44.5	0.018	45
H(F)	Expt	−0.09	−0.77	−0.74	+1.50	+22.75		
	No relax		−0.91	−0.89	+1.79	+23.8		
	Relax		−0.76	−0.74	+1.50	+22.7	0.110	10
I(Li)	Expt	−0.01	−0.31	+0.58	−0.27	−12.0		
	No relax		−0.33	+0.61	−0.28	−12.1		
	Relax		−0.32	+0.59	−0.27	−12.0	0.030	90 (Y)
J(F)	Expt	+0.65	−0.65	−0.61	+1.27	−34.5		
	No relax		−0.47	−0.46	+0.93	−39.2		
	Relax	Not studied						
L(F)	Expt	+0.09	−0.62	+1.19	−0.57	+24.0		
	No relax		−0.64	+1.22	−0.58	+23.9		
	Relax		−0.62	+1.19	−0.56	+23.9	0.023	116

laxation in the plane perpendicular to the molecular axis. However, the experimentally determined rotation of the hyperfine principal axes of the D nuclei in the Y-Z plane of −6.5° and the large negative contact interaction a (see Table I) show that further corrections to the wave function are necessary besides the orthogonalization to the ion orbitals. The cylindrical symmetry of the free F_2^- wave function does not predict a rotation of the principal axes in the Y-Z plane. This rotation is probably due to transferred hyperfine effects via the shell B fluorines, which have a large mutual overlap with the σ_u and the shell D ions (see shell B discussion below). Also, the D ions are located far enough away from the defect to decrease the sensitivity of the hyperfine constants to changes in R.

For the lithium ions accurate results are expected using only the unorthogonalized F_2^- wave function. However, only the lithium A nuclei are near enough to the molecule to have a significant dependence on R. Because the A nuclei have two degrees of freedom for relaxation, it was not possible to uniquely determine R from a study of these lithium ions because calculations for several values of R could fit the experimental data. Therefore, we have chosen the value $R = 3.6$ a.u. on the basis of the g values and ESR hyperfine constants and comparison with other F_2^- centers. The internuclear distance R for the V_K center in LiF is 3.8 a.u., for the H center[9,10] in LiF it is 3.6 a.u., and for the free F_2^- molecule[2] it is 3.6 a.u. Although R could conceivably be as small as 3.4 a.u. for the ⟨111⟩ defect, this would not make any qualitative changes in our relaxation picture. For instance, if we use $R = 3.4$ a.u. then in Table I for the lithium C shell we would have $r = 0.052$ instead of 0.078. Most other shells would be less senstive to changes in R. Of course, for larger values of R the general lattice relaxation outward would be greater.

With the above choice of R it was possible to obtain agreement within experimental error for the two independent components of the hyperfine tensor and for the orientation θ of the principal axes for all shells except D (discussed above). All shells

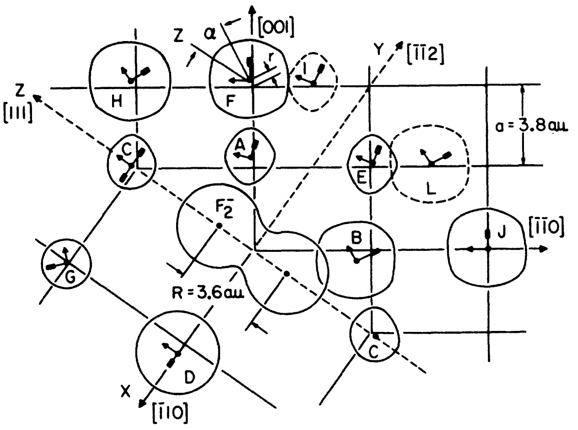

FIG. 1. Relaxation of lattice ions near the ⟨111⟩ interstitial defect in LiF. Axes at each site illustrate the experimental hyperfine principal axes. Arrows indicate the positive directions of the *z* axes and the squares indicate the positive directions of the *x* or *y* axes. The angle of relaxations *α* is illustrated for the F ion. The I and L ions are both located in planes that are rotated ±19.11° about the *Z* axis from the *Y*-*Z* plane. The J ion is shown in its unrelaxed position.

except *B* and *J* relax away from the defect.

It should also be noted that, in addition to providing a picture of lattice relaxation, these calculations were valuable in correlating distant shells with the experimental ENDOR lines.[5] The distant shells have ENDOR lines that frequently overlap or cross one another. However, since the distant shells have contact interactions *a* which are small compared to the *B* tensor values, the calculated *B* values even for the unrelaxed positions are close enough to the total hyperfine interaction to make shell identification possible.

With the *B* ions at their calculated relaxed positions and with $R = 3.6$ a.u. the distance between a *B* nucleus and the nearest fluorine nucleus of the molecule is only 3.3 a.u. This separation is smaller than *R*, which indicates an overestimate of relaxation inward. The overestimate is also indicated by the overlap of the contours in Fig. 1. This overestimate is probably due to the neglect of any bonding or charge-transfer effects between the F_2^- molecule and the *B* ions. However, these effects must contribute more than half of the anisotropic hyperfine tensor values to avoid the conclusion that the *B* ions move in toward the F_2^- molecule.

The contact interaction for the shell *B* nuclei ($a = 27.7$ MHz/sec) is large and positive which implies a large overlap with the σ_u molecule orbital. It is possible that these six fluorines are partially reaction of the shell *J* fluorines. Dipole-dipole calculations of the *J* fluorines at the unrelaxed position indicate that they relax toward the defect. However, because of the strong influence of the *B* fluorines on possible transferred hyperfine effects for the *J* shell, a detailed relaxation study of the *J* fluorines was not made.

Most of the work on lattice distortion due to interstitial defects in alkali halides has been in KCl, sponsible for the preferred ⟨111⟩ orientation of the defect.

The large overlap of the σ_u with the *B* fluorines may explain the rather large positive contact inter-NaCl, and KBr. Volume expansion measurements[11,12] show very small changes due to the halide interstitial. Since these measurements were made above the thermal bleaching temperature of the *H* center, the configuration of the interstitial is not known. Dienes, Hatcher, and Smoluchowski[13] have made energy calculations of the *H*-center configuration in KCl and KBr that was oriented along the ⟨110⟩ and ⟨111⟩ axes. They have determined for the ⟨111⟩ orientation that the lattice ions corresponding to shells *A*, *B*, and *D* relax away from the defect while the two collinear alkali ions (shell *C*) relax inward. Also, their results predict that the internuclear distance *R* does not depend on the particular orientation of the molecule in the lattice and that it is about 7% smaller than for the free molecule ion. Because of the smaller lattice constant of LiF, it is not surprising that the interstitial atom should take a different configuration or have different effects on the lattice than that of the heavier alkali halides, although the exact reasons are not understood.

III. CONCLUSION

The results of calculations of the anisotropic hyperfine constants of the ⟨111⟩ interstitial defect in LiF indicate that the surrounding lattice (with the possible exception of shells *B* and *J*) relaxes away from the defect. Although improved treatments of exchange polarization and transferred hyperfine effects are still needed for ions with *p* electrons, the qualitative picture of the relaxation should not change. Hyperfine interactions offer the most direct way to study lattice distortion about paramagnetic defects and impurities. Once the lattice distortion is known, a better understanding of the production and stability of a defect may be obtained.

ACKNOWLEDGMENT

The authors gratefully acknowledge helpful discussions with D. F. Daly during this study.

[†] Work supported by the National Science Foundation, under Grant No. NSF-GP-07779 and the Advanced Research Projects Agency.

[‡] Partially based on a thesis submitted by Y. H. C. to Purdue University, 1969 in partial fulfillment for the Ph.D. degree.

[*] Present address: Dept. of Physics and Astronomy, Kansas University, Lawrence, Kans. 66044.

[1] D. F. Daly and R. L. Mieher, Phys. Rev. Letters 19, 637 (1967); Phys. Rev. 183, 368 (1969).

[2] A. C. Wahl (private communication); see also T. L. Gilbert and A. C. Wahl, Bull. Am. Phys. Soc. 10, 1097 (1965).

[3] T. P. Das, A. N. Jette, and R. S. Knox, Phys. Rev. 134, A1079 (1965); T. P. Das, A. N. Jette, and T. L. Gilbert, *ibid.* 184, 884 (1969).

[4] Y. H. Chu and R. L. Mieher, Phys. Rev. Letters 20, 1289 (1968).

[5] Y. H. Chu and R. L. Mieher, Phys. Rev. 188, 1311 (1969).

[6] P. S. Bagus, Phys. Rev. 139, A619 (1965).

[7] H. Witte and E. Wolfel, Rev. Mod. Phys. 30, 51 (1958).

[8] The following conventions have been used in defining and illustrating the principal axes of the hyperfine tensor in Table I and in Fig. 1. The hyperfine principal axes x, y, and z are defined to be those axes making an angle θ less than 45° with the corresponding principal axes X, Y, and Z that were chosen for the F_2^- molecule. The physical meaning of a hyperfine principal axis is that when the magnetic moment of the unpaired electron is parallel to an i (x, y, or z) principal axis the hyperfine field at the nucleus is either parallel (+) or antiparallel (−) to the i axis. The arrows in Fig. 1 indicate the positive directions of the z axes and the squares indicate the positive directions of the x or y axes. Unfortunately, this convention was not systematically followed in Figs. 9–11 of Ref. 1. Therefore, the arrows in those figures illustrate the orientations of the principal axes but *not* the positive directions.

[9] M. L. Dakss, Ph.D. thesis, Columbia University, 1966 (unpublished); M. L. Dakss and R. L. Mieher, Phys. Rev. 187, 1053 (1969).

[10] W. Kanzig and T. O. Woodruff, J. Phys. Chem. Solids 9, 70 (1958).

[11] V. H. Ritz and S. Mascarenhas, Phys. Rev. 177, 1241 (1969).

[12] E. H. Farnum and B. S. H. Royce, Phys. Letters 26A, 164 (1968); Phys. Rev. 187, 1160 (1969).

[13] G. J. Dienes, R. D. Hatcher, and R. Smoluchowski, Phys. Rev. 157, 692 (1967).

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Energy Bands and Optical Properties of NaCl[†]

Nuzio O. Lipari and A. Barry Kunz
Department of Physics and Materials Research Laboratory, University of Illinois, Urbana, Illinois 61801

(Received 10 August 1970)

The energy bands of NaCl are investigated using the nonrelativistic mixed-basis (MB) method developed by one of us (ABK). Using local orbitals, the self-consistent Hartree-Fock energy bands are first obtained. Correlation effects are then taken into account and they are found to be very important in the reduction of both the energy gap, as proved in previous works, and of the valence bandwidth. Only the points Γ, X, L, and the midpoint of Δ of the first Brillouin zone were actually computed; the final energy bands have been fitted with a pseudopotential, however. The density of states for the upper valence bands and lower conduction bands, together with the imaginary part of the dielectric response function, are obtained. The results are compared with experiment and the agreement is good.

I. INTRODUCTION

In recent years, the energy bands of insulating crystals have been extensively investigated.[1] Efforts for treating the Hartree-Fock exchange correctly have been made by many.[2,3] However, in such cases no self-consistency was obtained.

Very recently, a great amount of investigation has been done toward the computation of energy bands of insulating crystals from a first-principle point of view. The authors have been successful in computing Hartree-Fock energy bands for many rare gases and alkali-halide solids.[4,5] It has been seen that true Hartree-Fock calculations give results which can be very different from the ones obtained when model potentials are used.[6] Furthermore, different model potentials often give different results, so that it seems as if the results obtained strongly depend on the kind of approximations involved in treating the exchange potential.[6]

One of us (ABK) has recently developed a local orbital theory[7] and has been able to obtain accurate wave functions for most of the alkali-halide crystals. These wave functions have been proved to be very useful in the investigation of the energy bands of these solids.

Furthermore, in the previous calculations,[4,5] it has been seen that polarization effects, clearly neglected in the Hartree-Fock approximation, are important and should be included before comparison with experiment is made. These effects can be included in two different ways. One has been proposed by Fowler,[8] and the other is based upon a many-body theory first developed by Hedin[9] and used in semiconductors by Brinkman and Goodman.[10] Both ways have been investigated in previous calculations,[4,5] and it has been seen that they are in