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## Nuclear Quadrupole Coupling in the LiH Molecule\*

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A valence-bond configuration-interaction Slater-orbital wave function for LiH was constructed with all orbital exponents optimized. The orbitals used were Li  $1s$ ,  $2s$ ,  $2p\sigma$ ,  $3d\sigma$ , and H  $1s$ ,  $2p\sigma$ ; and six configurations were included, all with undeformed inner shells ( $1s^2$ ). The core deformation and the related correction to the nuclear quadrupole coupling constant were then calculated by the method of Sternheimer and Foley, i.e., by first determining the quadrupolarization of the  $1s$  shell by the nuclear moment  $Q$  and then calculating the interaction of the external molecular charges with the nuclear  $Q$  shielded by the quadrupole moment induced in the  $1s$  shell. Denoting by  $q_0$  the value of the electric field gradient at the Li nucleus obtained from a wave function with no provision for core deformation and denoting by  $\Delta q$  the correction to  $q_0$  associated with the quadrupolarization of the core, we investigated the sensitivity of  $q_0$  and of  $\Delta q/q_0$  to changes in the wave function produced by varying the configuration mixture and altering the values of the orbital exponents. Although  $q_0$  was found to be sensitive to these changes, the fractional Sternheimer correction,  $\Delta q/q_0$ , was insensitive and in all cases stayed between the limits of  $-0.22$  and  $-0.24$ . The final values obtained for  $q_0$  and  $q$  are not highly accurate, because of the obvious limitations of the wave function, but the result that  $\Delta q/q_0 = -0.23$  is reliable enough to be useful in estimating Sternheimer corrections to the results of other workers who have used more elaborate wave functions. Combining the results of several calculations with implicit and explicit Sternheimer corrections, we estimate that  $q/2e = (-0.0170 \pm 0.0013)a_0^{-3}$  and that  $Q(\text{Li}^7) = (-4.3 \pm 0.3) \times 10^{-26} \text{ cm}^2$ .

## INTRODUCTION

AN accurate value of the electric field gradient  $q$  at the Li nucleus of the LiH molecule is needed in order to obtain the electric quadrupole moment  $Q$  of the  $\text{Li}^7$  nucleus from measurements<sup>1</sup> of the nuclear quadrupole coupling constant ( $eqQ$ ). As pointed out by Sternheimer and Foley,<sup>2</sup> it is important in calculating  $q$  to take account of the deformation of the  $1s$  shell surrounding the nucleus by the external electric charges of the molecule. In the following we denote by  $q_0$  the value of  $q$  calculated with a molecular wave function that permits no deformation of the spherically symmetric  $1s$  shell and we denote the corresponding Sternheimer correction to  $q$  for externally induced core deformation by  $\Delta q$ . The separation of  $q$  into the two parts,  $q_0$  and  $\Delta q$ , does not occur when the wave function is sufficiently flexible to allow for the distortion of the  $1s$  shell and the Sternheimer correction is then not explicit. Four of the previous calculations<sup>3-6</sup> of  $q$  in LiH have

been made with wave functions that either admixed  $3d\sigma$  to  $1s$  Slater orbitals or represented the  $1s$  orbitals in terms of elliptic coordinates; thus, the Sternheimer effect was implicitly taken into account. While the approximate agreement of the results of these calculations, which were made with different types of wave function, lends confidence to the values of  $q$  obtained, it is not certain that the core deformation is adequately taken into account in this way. The variational method deforms the core to produce a charge distribution consistent with the lowest energy but, with an incomplete set of basis functions, there is no assurance that the deformation is realistic and the value of  $q$  accurate. Indeed, as the set of basis functions is extended and the energy improved, the value of  $q$  could become worse.<sup>7</sup>

An alternate method of treating the problem, proposed by Sternheimer<sup>2</sup> and applied by Sternheimer and Foley<sup>8</sup> to the case of  $\text{Li}_2$ , employs a wave function which takes no account of core deformation and which gives the value  $q_0$  for the field gradient. It is then shown from perturbation theory<sup>8-10</sup> that the correction  $eQ\Delta q$  to the nuclear quadrupole coupling constant can be calculated simply with this wave function by first determining the

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<sup>1</sup> L. Wharton, L. P. Gold, and W. Klemperer, *J. Chem. Phys.* **37**, 2149 (1962).

<sup>2</sup> R. M. Sternheimer, *Phys. Rev.* **80**, 102 (1950); **84**, 244 (1951); R. M. Sternheimer and H. M. Foley, *ibid.* **92**, 1460 (1953).

<sup>3</sup> S. L. Kahalas and R. K. Nesbet, *J. Chem. Phys.* **39**, 529 (1963).

<sup>4</sup> J. C. Browne and F. A. Matsen, *Phys. Rev.* **135**, A1227 (1964).

<sup>5</sup> C. F. Bender and E. R. Davidson, *J. Phys. Chem.* **70**, 2675 (1966).

<sup>6</sup> C. F. Bender and E. R. Davidson, *Phys. Rev.* **183**, 23 (1969).

<sup>7</sup> Comparing the results of Refs. 3-5, we note that the calculation which gives the best energy yields the poorest dipole moment and vice versa.

<sup>8</sup> R. M. Sternheimer and H. M. Foley, *Phys. Rev.* **92**, 1460 (1953).

<sup>9</sup> T. P. Das and R. Bersohn, *Phys. Rev.* **102**, 733 (1956).

<sup>10</sup> A. Dalgarno, *Advan. Phys.* **11**, 281 (1962).

quadrupolarization of the  $1s$  shell by the nuclear moment  $Q$  and then calculating the interaction of the external molecular charges with the nuclear  $Q$  shielded by the quadrupole moment induced in the  $1s$  shell. Thus, it is immaterial whether one calculates the interaction of the nuclear  $Q$  with the core as deformed by the external charges or the interaction of the external charges with the core as deformed by the nuclear  $Q$ . The alternate method of Sternheimer is simpler because it avoids having to take account of core deformation in the wave function and furthermore, the moment induced in the  $1s$  shell by the nuclear  $Q$  is easily calculated.<sup>8</sup> In this work we follow the method of Sternheimer and calculate  $q_0$  and  $\Delta q$  with a simple six-configuration valence-bond wave function of the type previously used by Matsen and coworkers.<sup>11-13</sup> The six configurations used are:  $\text{Li}(1s^2 2s)\text{H}(1s)$ ,  $\text{Li}(1s^2 2p\sigma)\text{H}(1s)$ ,  $\text{Li}(1s^2 3d\sigma)\text{H}(1s)$ ,  $\text{Li}^+(1s^2)\text{H}^-(1s^2)$ ,  $\text{Li}^+(1s^2)\text{H}^-(1s 2p\sigma)$ , and  $\text{Li}^+(1s^2)\text{H}^-(2p\sigma^2)$ . The  $\text{Li } 1s$  shell is deliberately undeformed and, of course, important correlation effects are not taken into account but they seem likely to have no great influence on  $q_0$  and less on  $\Delta q$ . Although this wave function is inferior to the more comprehensive and flexible functions used in Refs. 3, 4, 5, and 6 and cannot be expected to deliver a very accurate result for  $q_0$ , it will be seen to provide a useful value for  $\Delta q/q_0$ . While  $q_0$  is very sensitive to changes in the wave function that hardly affect the energy, this is not true of the ratio  $\Delta q/q_0$ .

We shall first estimate  $\Delta q/q_0$  in a rough way. According to Ref. 8 the total quadrupole moment induced in the  $\text{Li } 1s$  shell by the nuclear  $Q$  is about  $0.25 Q$  and the induced quadrupole moment density  $Q_s(r)$  peaks near  $r=0.6a_0$  and is negligible beyond  $1.8a_0$ . The three contributions to  $\Delta q$  come from the proton, the valence electrons, and cross terms between the  $\text{Li } 1s$  orbitals and those of the valence electrons. The latter are expected to be small, since the shielding factor  $\gamma(r)$  is small where the  $\text{Li } 1s$  orbital is large, and were indeed found to be very small in the case of the  $\text{Li}_2$  molecule.<sup>8</sup> Since the equilibrium distance in  $\text{LiH}$  is  $3.01a_0$ , the proton will experience maximal shielding but the valence electrons can penetrate the induced moment distribution in the  $1s$  shell. If we assume a negligible penetration, the expected value of  $\Delta q/q_0$  is then about  $-0.25$ ; thus we may consider  $0.25$  to be a fairly accurate upper bound for  $|\Delta q/q_0|$ . With deep penetration and very little shielding for the valence electrons  $\Delta q/q_0$  can take on positive values but this is very unreasonable.

<sup>11</sup> R. P. Hurst, J. Miller, and F. A. Matsen, *J. Chem. Phys.* **26**, 1092 (1957).

<sup>12</sup> J. Miller, R. H. Friedman, R. P. Hurst, and F. A. Matsen, *J. Chem. Phys.* **27**, 1385 (1957). We are indebted to Dr. D. F. Zetik for rechecking some of the results given in this paper. He recalculated the energy for the 20-configuration wave function and obtained  $-7.982$  a.u. instead of the value  $-7.976$  a.u. given in the paper.

<sup>13</sup> O. Platas and F. A. Matsen, *J. Chem. Phys.* **29**, 965 (1958).

## CALCULATIONS

The particular merits of the valence-bond method for small molecules have been pointed out elsewhere.<sup>14</sup> The atomic orbitals used were Slater-type orbitals (STO's) but, in contrast to the previous calculations<sup>11-13</sup> in which the Slater values of the exponential orbital parameters ( $\zeta$ 's) were chosen and only a few other  $\zeta$ 's investigated, we have systematically adjusted the  $\zeta$ 's of all orbitals to give the lowest energy. Although the optimum value of  $\zeta$  for a given orbital in different configurations should in principle depend on the configuration, it is found in practice that a common value of  $\zeta$  can be used in all configurations with little detriment to the energy. The most important configurations are the basic  $\text{Li}(1s^2 2s)\text{H}(1s)$ , the polarized bonding configuration  $\text{Li}(1s^2 2p\sigma)\text{H}(1s)$  and the ionic configuration  $\text{Li}^+(1s^2)\text{H}^-(1s^2)$ . Using these configurations in combination, the optimal exponential parameters were found to be:  $\zeta(1s, \text{Li})=2.7$ ,  $\zeta(2s, \text{Li})=0.70$ ,  $\zeta(2p\sigma, \text{Li})=0.75$ , and  $\zeta(1s, \text{H})=1.1$ . These values were retained in subsequent calculations with admixed configurations. Although not used in the previous work,<sup>11-13</sup> we have included the  $\text{Li}(1s^2 3d\sigma)\text{H}(1s)$  configuration in order to improve the calculation of the electric field gradient  $q$ . The optimal exponential parameter is  $\zeta(3d\sigma, \text{Li})=0.80$ . Finally, in order to take account of polarization of the H-atom charge distribution, we added two previously investigated<sup>13</sup> configurations:  $\text{Li}^+(1s^2)\text{H}^-(1s 2p\sigma)$  and  $\text{Li}^+(1s^2)\text{H}^-(2p\sigma^2)$  with the optimal parameter  $\zeta(2p\sigma, \text{H})=1.2$ . Several additional configurations based on the above-mentioned orbitals (except the  $3d\sigma, \text{Li}$ ) were included in the previous work<sup>11-13</sup> but were omitted by us because they provided only very slight improvement in the energy or corresponded to the incorrect ionic structure  $\text{Li}^+\text{H}^+$ . Our  $\zeta$  values differ in almost all cases from the values used previously.<sup>11-13</sup>

A detailed account of the calculations will not be given here.<sup>15</sup> The methods used were, with few exceptions, standard ones to be found in the literature. Computer programs were written for all integrals and checked against the results of other workers. The exchange integrals were calculated by two methods, both due to Ruedenberg,<sup>16,17</sup> one analytical and the other using numerical integration. We used the zeta-function method of Barnett and Coulson<sup>18,19</sup> to evaluate the two-center hybrid integrals and Coulomb integrals, as well as all the two-center one-electron integrals appearing in

<sup>14</sup> F. A. Matsen and J. C. Browne, *J. Phys. Chem.* **66**, 2332 (1962).

<sup>15</sup> Full details are given in C. C. Lu, Ph.D. thesis, University of Tennessee, 1969 (unpublished). A preliminary abstract of this work appeared in *Bull. Am. Phys. Soc.* **13**, 1700 (1968).

<sup>16</sup> K. Ruedenberg, *J. Chem. Phys.* **19**, 1459 (1951).

<sup>17</sup> K. Ruedenberg, *Molecular Orbitals in Chemistry, Physics, and Biology: A Tribute to R. S. Mulliken* (Academic Press Inc., New York, 1964), p. 215.

<sup>18</sup> M. P. Barnett and C. A. Coulson, *Phil. Trans. Roy. Soc. London* **243**, 221 (1951).

<sup>19</sup> M. P. Barnett, *Methods Comp. Phys.* **2**, 95 (1963).

the energy calculations, the dipole-moment calculation, and the calculation of the electric field gradient. The Sternheimer correction  $\Delta q$  was obtained from the formulas of Sternheimer and Foley<sup>8</sup> which were re-derived by means of Dalgarno's interchange theorem.<sup>10,20</sup> The exchange contribution to the shielding correction, which was estimated in Ref. 8 for the Li<sub>2</sub> molecule and found to be small, is very difficult to calculate and has been omitted by us.

### RESULTS

The simple three-configuration wave function, composed of Li(1s<sup>2</sup>2s)H(1s), Li(1s<sup>2</sup>2pσ)H(1s), and Li<sup>+</sup>(1s<sup>2</sup>)H<sup>-</sup>(1s<sup>2</sup>) was found to give an energy of  $-7.984$  a.u. compared with the experimental value of  $-8.071$  a.u. This result is better than the one obtained previously<sup>12</sup> with a 20-configuration valence-bond function in which the STO ζ's were assigned the conventional Slater values ( $E = -7.982$  a.u.). However, energies much closer to the experimental value have been obtained in Refs. 4-6. Of particular interest is the sensitivity of the value of  $q_0$  to the orbital exponent ζ(2pσ, Li). Changes in ζ(2pσ, Li) which hardly affect the energy and which lead to small changes in the dipole moment were found to alter the value of  $q_0$  significantly. Thus, when ζ(2pσ, Li) = 0.70, we find that  $E = -7.984$  a.u. and  $q_0/2e = -0.0136a_0^{-3}$  but when ζ(2pσ, Li) = 0.75 the results are that  $E = -7.984$  a.u. and  $q_0/2e = -0.0151a_0^{-3}$ . The sensitive dependence of the electric field gradient on the charge distribution of the valence electrons has also been found in other calculations.<sup>8,21</sup>

The four-configuration function composed of the above three configurations plus Li(1s<sup>2</sup>3dσ)H(1s) was used to calculate  $q_0$  and  $\Delta q$ . This function gives a slightly improved energy of  $E = -7.987$  a.u. and an electric dipole moment  $\mu = -5.73D$  compared with the adjusted experimental value<sup>1</sup> of  $-5.83D$ . The inclusion of the new configuration with the 3dσ orbital gives a marked improvement in the value of the dipole moment. The calculated values of  $q_0/2e$  and  $\Delta q/2e$  are  $-0.0171a_0^{-3}$  and  $0.0039a_0^{-3}$ , respectively, which lead to a value for  $q/2e$  of  $-0.0132a_0^{-3}$ . Although  $q_0$  is less sensitive to variations in ζ(3dσ, Li) than to changes in ζ(2pσ, Li), the inclusion of the fourth configuration has an important effect on the value of  $q_0$ . Despite the sensitivity of  $q_0$  to changes in the wave function that result from adding configurations and varying the orbital exponents (ζ's), it was found in all cases that the ratio  $\Delta q/q_0$  is insensitive to these changes, e.g., for all the functions investigated  $\Delta q/q_0$  was between  $-0.22$  and  $-0.24$ . The maximum shielding factor  $\gamma(\infty)$  is 0.247; thus, the shielding of the valence electrons and the proton is close to maximal.

Our final wave function included the additional con-

figurations Li<sup>+</sup>(1s<sup>2</sup>)H<sup>-</sup>(1s2pσ), and Li<sup>+</sup>(1s<sup>2</sup>)H<sup>-</sup>(2pσ<sup>2</sup>), which provide for polarization of the H-atom orbitals. The results for this six-configuration function are:  $E = -7.992$  a.u.,  $\mu = -5.95D$ ,  $q_0/2e = -0.0175a_0^{-3}$ , and  $\Delta q/2e = 0.0040a_0^{-3}$ . The final value for  $q/2e$  is  $-0.0135a_0^{-3}$ , and this differs appreciably from the results obtained by other workers using much more elaborate wave functions; these range between  $-0.0166$  and  $-0.0182a_0^{-3}$  for functions that provide for core deformation.<sup>3-6</sup>

Since this work was completed<sup>15</sup> there has appeared a related calculation<sup>22</sup> on the LiH molecule in which the valence-bond method is generalized by replacing the valence-bond orbitals by optimal orbitals called "G1 orbitals" that are determined by an iterative procedure similar to the Hartree-Fock method. The results are more general and more accurate than those obtained by either the Hartree-Fock or conventional valence-bond methods. Since the G1 orbitals are expanded in terms of Slater orbitals as basis functions and the orbital exponents (ζ's) are optimally determined, it is possible to compare the resulting values of ζ with those of the present calculation. Except for the Li 1s orbital which was represented by two STO's with different ζ values, the same orbital set was used as in our calculation and the variationally determined orbital exponents are all in excellent agreement.

### CONCLUSIONS

The principal result is the determination of the fractional core quadrupolarization or Sternheimer correction,  $\Delta q/q_0$ , which we have found to be about  $-0.23$ , and thus close to the maximal value of  $-0.25$ . Browne and Matsen<sup>4</sup> have also evaluated the effect of core deformation on the value of  $q$  by making two calculations with related wave functions. The first wave function contained 12 terms, each of which combined an undeformed 1s<sup>2</sup> atomic-orbital core with an elliptic coordinate representation of the valence electrons. The resulting value of  $q/2e$  was  $-0.0202a_0^{-3}$ . In the second wave function, the same 12 terms were used but the core was deformed by replacing the 1s STO's by elliptic-coordinate orbitals with exponents variationally determined. The new value of  $q/2e$  was  $-0.0152a_0^{-3}$ . Thus the effective value of  $\Delta q/q_0$  obtained from this calculation is  $-0.248$ . The approximate agreement of the two values of  $\Delta q/q_0$  confirms the equivalence of the two methods of treating the Sternheimer correction. The elliptic-coordinate representation of the Li 1s orbitals is therefore adequate to take full account of the core quadrupolarization and, in fact, it appears in this case to overcorrect slightly for the Sternheimer effect. If we set  $q_0/2e = -0.0202a_0^{-3}$  and apply a correction of  $\Delta q/q_0 = -0.23$ , the result is that  $q/2e = -0.0156a_0^{-3}$ . It is interesting to note that the Palke-Goddard treat-

<sup>20</sup> A. Dalgarno and A. L. Stewart, Proc. Roy. Soc. (London) **247**, 245 (1958); **257**, 534 (1960).

<sup>21</sup> R. Bersohn, J. Chem. Phys. **32**, 85 (1960); R. C. Henderson and D. D. Ebbing, *ibid.* **47**, 69 (1967); D. M. Bishop, *ibid.* **49**, 3718 (1968).

<sup>22</sup> W. E. Palke and W. A. Goddard, J. Chem. Phys. **50**, 4524 (1969).

ment<sup>22</sup> of LiH by the method of *G1* orbitals yielded a value of  $q/2e = -0.0202a_0^{-3}$  in agreement with the Browne-Matsen result for the undeformed core. Palke and Goddard observe that the two LiH inner-shell orbitals obtained according to the *G1* method are "essentially identical" to the *G1* inner-shell orbitals for a free Li atom; thus, this method fails to take account of core deformation.

Since  $-0.0202a_0^{-3}$  appears to be a good value for  $q_0/2e$ , better than the result of  $-0.0175a_0^{-3}$  obtained from our six-configuration wave function, the value of  $q/2e = -0.0156a_0^{-3}$  obtained after applying the Sternheimer correction should be fairly reliable. This is to be compared with the results of the four direct

treatments in which the wave function explicitly provided for core deformation:  $q/2e = -0.0166$  (Kahalas and Nesbet<sup>3</sup>),  $-0.0173$  (Browne and Matsen<sup>4</sup>),  $-0.0182$  (Bender and Davidson<sup>5</sup>), and  $-0.0173a_0^{-3}$  (Bender and Davidson<sup>6</sup>). From these five values we estimate that the best current value of  $q/2e$  is  $(-0.0170 \pm 0.0013)a_0^{-3}$ . The experimental result<sup>1</sup> for the nuclear quadrupole coupling constant is  $eqQ/h = 346 \pm 1$  kc/sec from which the electric quadrupole moment  $Q$  of the Li<sup>7</sup> nucleus is found to be  $(-4.3 \pm 0.3) \times 10^{-26}$  cm<sup>2</sup>. The implications for nuclear shell theory of a quadrupole moment of this magnitude have been previously discussed.<sup>23</sup>

<sup>23</sup> R. D. Present, Phys. Rev. **139**, B300 (1965); B. M. Morris and R. D. Present, *ibid.* **140**, B1197 (1965).

## Spin-Lattice Relaxation of Tm<sup>2+</sup> in CaF<sub>2</sub>, SrF<sub>2</sub>, and BaF<sub>2</sub>

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Measurements were made of the spin-lattice relaxation time of the ground state of Tm<sup>2+</sup> in CaF<sub>2</sub>, SrF<sub>2</sub>, and BaF<sub>2</sub> over the magnetic field range of 1 to 12 kG and temperature range of 1.3 to 20°K. The one-phonon relaxation process was unambiguously identified by its characteristic fourth-power dependence on frequency and its linear temperature dependence. The Raman process with its  $T^9$  dependence begins to dominate the relaxation above 5°K. The angular dependence of the relaxation permitted the separation of the effect of the two local modes,  $E_g$  and  $T_{2g}$ , on the one-phonon process. Calculations were in good agreement with theory, and they showed that the second-order terms of the orbit-lattice interaction dominate the relaxation process. Continuous measurement of the relaxation over this magnetic field range was made possible by a technique which is independent of any microwave sources. The detection was done by monitoring the magnetic circular dichroism of the broad optical absorption bands.

### I. INTRODUCTION

SPIN-LATTICE relaxation times  $T_1$  have been extensively studied for many paramagnetic impurities<sup>1</sup> in a variety of hosts. The theory for direct interactions between the individual spins and the lattice was first presented by Kronig<sup>2</sup> and Van Vleck.<sup>3</sup> Mattuck and Strandberg<sup>4</sup> along with others have re-examined the theory for the iron group ions while Orbach<sup>5</sup> has considered the rare-earth group. Generally, the comparison between the experimental results and predictions is inconsistent. This is due to the experimental difficulties encountered in obtaining reliable data of the single-ion relaxation process and because of the theoretical complexity of the dynamic orbit-lattice interaction.

The linear variation of the relaxation rate with temperature as predicted for the one-phonon process has been observed by many authors.<sup>1</sup> The dependence of  $T_1^{-1}$  on the fourth power of magnetic field strength, predicted for direct relaxation of Kramer's ions by resonant phonons at a given temperature, has been observed in only a few cases.<sup>6</sup> In this paper, we present<sup>7</sup> extensive measurements of the spin-lattice relaxation rate of divalent thulium, a Kramer's ion, in the cubic hosts CaF<sub>2</sub>, SrF<sub>2</sub>, and BaF<sub>2</sub>. The direct one-phonon process is well demonstrated in all three hosts by both temperature- and frequency-dependent measurements. Because this is a simple system, these measurements provide a good basis for comparison with theory. It is the most complete verification to date of the  $H^4T$  term in Van Vleck's theory for the one-phonon relaxation process.

<sup>1</sup> For a collection of papers, see *Spin-Lattice Relaxation in Ionic Solids*, edited by A. A. Manenkov and R. Orbach (Harper and Row Publishers, Inc., New York, 1966).

<sup>2</sup> R. de L. Kronig, Physica **6**, 33 (1939).

<sup>3</sup> J. H. Van Vleck, J. Chem. Phys. **7**, 72 (1939); Phys. Rev. **57**, 426 (1940).

<sup>4</sup> R. D. Mattuck and M. W. P. Strandberg, Phys. Rev. **119**, 1204 (1960).

<sup>5</sup> R. Orbach, Proc. Roy. Soc. (London) **A264**, 456 (1961).

<sup>6</sup> Douglas A. Davids and Peter E. Wagner, Phys. Rev. Letters **12**, 141 (1964); N. E. Kask, Fiz. Tverd. Tela **8**, 1129 (1966) [English transl.: Soviet Phys.—Solid State **8**, 900 (1966)]; H. Panepucci and L. F. Mollenauer, Phys. Rev. **178**, 589 (1969).

<sup>7</sup> A brief account of this work was presented at the May 1968 meeting of the American Physical Society, Bull. Am. Phys. Soc. **13**, 621 (1968).