

Atomic Multipole Interactions in Rare-Gas Crystals*

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It is demonstrated that one of the mechanisms seriously proposed to explain the relative stability of rare-gas solids in the cubic form, namely greater repulsion between induced electrical multipoles in the hexagonal form, is completely ineffective. The present status of the stability problem is briefly discussed.

I. INTRODUCTION

POLYMORPHISM in the crystalline rare gases has long been of theoretical interest. With the exception of He and Rn, the rare gases are observed¹ to solidify into face-centered cubic (fcc) lattices, but the computed hexagonal close-packed (hcp) cohesive energy, in the simplest approximation, is larger than that in the fcc case by about 0.01%. Many attempts to reverse this difference, by such means as the introduction of third-order two-body and second-order three-body van der Waals energies, have failed; a review through 1958 is given by Dobbs and Jones.² An approximate treatment of three-body interactions with exchange has recently been introduced by Jansen,³ who finds that the fcc lattice has somewhat greater stability than the hcp. Jansen's calculation is discussed briefly in Sec. IV.

The purpose of the present note is to discuss a proposition by Kihara⁴ that simple electrostatic multipole interactions are the primary factor in determining the rare-gas crystal structure. In particular, Kihara suggests that octupole moments induced on the atoms in the hexagonal lattice will repel each other more strongly than the hexadecapole moments in the cubic lattice, leading to the relative stability of the latter. We point out that from a purely electrostatic point of view, Kihara's multipole-multipole interaction is in fact not present in the cohesive energy of the crystal, and that a much larger interaction exists which he did not consider, namely, a monopole-multipole interaction. This inter-

action, however, is still quite small even though it would favor the fcc lattice.

In Sec. II our procedure is illustrated by consideration of the problem of dipole moments mutually induced on two atoms; in Sec. III the procedure is applied to solid argon and in Sec. IV our results are discussed.

II. PROCEDURE

Kihara has not provided a quantitative prescription for his method, but we interpret it as follows. When two neutral spherical atoms are far apart [Fig. 1(a)], there is no classical electrostatic interaction between them.⁵ When they are brought together [Fig. 1(b)] the overlapping of their charge clouds induces a change in the energy of the pair by way of at least two mechanisms. The charge distribution of each atom will "see" the nucleus of the other atom and will interact with it. Thus a Coulomb interaction exists which for most interatomic distances of interest will be attractive. This attraction will be offset by an increase in the kinetic energy of the electrons in the overlap region, which is the only way a sizeable repulsive interaction enters this model. Considerations of this type are reviewed by Born and Huang.⁶

The mutual interpenetration of the two atoms will alter the densities they have at infinite separation, which will be called $\rho_0(\mathbf{r}-\mathbf{R}_A)$ and $\rho_0(\mathbf{r}-\mathbf{R}_B)$. In the case of overlapping [Fig. 1(b)] the true charge density is not $\rho_0(\mathbf{r}-\mathbf{R}_A)+\rho_0(\mathbf{r}-\mathbf{R}_B)$, but we may write it formally as the sum of two new densities,

$$\rho_A(\mathbf{r}-\mathbf{R}_A)+\rho_B(\mathbf{r}-\mathbf{R}_B). \quad (1)$$

Each new density is no longer spherically symmetric but may be expanded in spherical harmonics:

$$\rho(\mathbf{r})=\sum_{L,M}\rho_{LM}(\mathbf{r})Y_L^M(\mathbf{r})^*. \quad (2)$$

In a well-known way, the quantities $\rho_{LM}(\mathbf{r})$ can be integrated with a weighting function r^L to define multi-

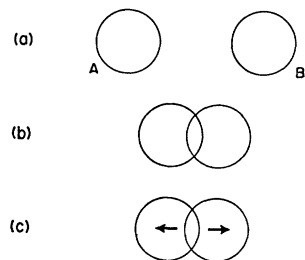


FIG. 1. Geometry of the illustrative example of two neutral charge clouds (a) at large separation, (b) beginning to overlap, and (c) inducing dipoles on each other because of overlap effects (see text).

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¹ F. Simon and C. von Simson, *Z. Physik* **25**, 160 (1924).

² E. R. Dobbs and G. O. Jones, *Rept. Progr. Phys.* **20**, 516 (1957).

³ L. Jansen, *Phys. Letters* **4**, 91 (1963); L. Jansen and S. Zimering, *ibid.* **4**, 95 (1963).

⁴ T. Kihara, *J. Phys. Soc. Japan* **15**, 1920 (1960).

⁵ We consider static interactions of *real* multipoles, and the van der Waals force does not enter.

⁶ M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, New York, 1954), pp. 4-6. A kinetic-energy correction was not considered by Kihara, but we have verified that it is small compared to at least one of the interactions in the effect (i.e., the monopole-multipole interaction).

pole moments of the distribution

$$Q_{LM} = \frac{4\pi}{2L+1} \int r^L \rho_{LM}(r) r^2 dr. \quad (3)$$

The total electrostatic energy of the new distribution will now consist of the self-energy of each atom and the interaction energy between the atoms. Our calculation involves two distinct steps: (a) determination of the magnitude of the induced multipoles and (b) the evaluation of the contribution of the interaction energies to the cohesive energy. Anticipating one of our results, we will assume that *most* of the charge in the case of rare gases continues to be spherically distributed when the atoms are at their equilibrium separation in the solid. This enables us to compute simply the electric fields in one atom caused by the overlapping of the charge of all other atoms. If large deviations from sphericity were indicated in our results, a self-consistent evaluation of the source fields would be required. This is fortunately not the case.

Returning to Fig. 1(c), we consider the effect of the lowest order multipoles induced, namely the dipoles. Each dipole is induced by the presence of the incompletely shielded nuclear charge on the other atom. The principal electrostatic interaction between the atoms is the one between the two spherical distributions. This is the monopole-monopole interaction, and its analog is ignored in our subsequent lattice calculations because we seek interactions which are different between the cases of the hcp and fcc lattices. The interaction of the dipole itself with the monopole on the other atom is, however, an important contribution whose lattice analog can be lattice-structure dependent. This dipole-monopole energy is by our definition the interaction between the $\rho_{1M}(\mathbf{r})$ components in (2) associated with one atom and the $\rho_{00}(\mathbf{r})$ component of the other. In fact, the contribution of the dipoles to the cohesive energy can be computed from the general formalism of De Wette⁷ [his Eq. (16)]; one obtains

$$E_{\text{coh}} = \frac{1}{2} \int \rho_0(\mathbf{r}-\mathbf{R}_A) V_1(\mathbf{r}-\mathbf{R}_B) d\mathbf{r} + \frac{1}{2} \int \rho_0(\mathbf{r}-\mathbf{R}_B) V_1(\mathbf{r}-\mathbf{R}_A) d\mathbf{r}, \quad (4)$$

where V_1 is that part of De Wette's $V^{(i)}$ which corresponds to the potential of a dipole distribution. In other words, only the charge-dipole interaction contributes, *not the dipole-dipole interaction*. De Wette's theorem applies to the case of arbitrary multipoles induced in nonoverlapping charge distributions having net charges, and we demonstrate this explicitly for the case of two atoms in Appendix A. The physical reason for the absence of the multipole-multipole term, which does occur in the cohesive energy of a system of rigid multi-

poles, is that an equal and opposite amount of energy is required to form the multipoles themselves.⁷ The validity of these considerations for overlapping distributions is limited only by the extent to which it is valid to define pure multipole induction, as discussed in the last paragraph of this section.

The order of magnitude of the effect which we are seeking can be appreciated by the following numerical results for two argon atoms. The dipole moment μ_1 induced on each atom, as computed by the method of the next section and at a separation of $7.1a_0$, is 8.9×10^{-22} esu cm = $3.5 \times 10^{-4} ea_0$ ($a_0 = 0.529 \times 10^{-8}$ cm). The interaction between the two dipoles would therefore be

$$2\mu_1^2/a^3 \approx 1.9 \times 10^{-8} \text{ eV}, \quad (5)$$

while the total dipole-monopole interaction is computed to be $\approx -1.3 \times 10^{-6}$ eV.

In the foregoing we have quickly passed over a rather delicate point, namely the feasibility of using multipole expansions in the case of overlapping neutral distributions. As is well known, it is possible to expand any electrostatic potential in the form

$$V(\mathbf{r}) = \sum_{LM} A_{LM} r^L Y_L^M(\mathbf{r}), \quad (6)$$

where the coefficients A_{LM} are constants, provided the sources of $V(\mathbf{r})$ are outside the region in which the expansion is taken to be valid. The LM component of $V(\mathbf{r})$ then induces on a spherical (but polarizable) system multipole moments of magnitudes

$$Q_{LM} = -\alpha_L A_{LM}, \quad (7)$$

an expression which defines the generalized multipole polarizability α_L . In our problem, the sources of V are *not* completely outside the region of interest, so we may assert only that the potential $V(\mathbf{r})$ has the more general form

$$V(\mathbf{r}) = \sum_{LM} A_{LM}(r) r^L Y_L^M(\mathbf{r}), \quad (8)$$

where the functions $A_{LM}(r)$ may be evaluated by elementary but tedious integrations. The function $A_{LM}(r)$ can have a fairly marked variation with r , and some average value \bar{A}_{LM} must be used in computing induced multipoles by Eq. (7). We define this average as the one which formally yields the value of the monopole-multipole interaction energy as computed by a straightforward extension of Kirkwood's second-order variation-perturbation theory.^{8,9} We shall not go into the details of this averaging process, but include in Appendix B a description of the results of the perturbation calculation.

III. COMPUTATIONS FOR SOLID ARGON

Following the procedure suggested in the last section, we first seek the multipoles induced on each atom in

⁸ J. G. Kirkwood, Physik Z. **33**, 57 (1932).

⁹ P. Gombás, *Theorie und Lösungsmethoden des Mehrteilchenproblems der Wellenmechanik* (Basel & Birkhauser, 1950), p. 43-44.

⁷ F. W. De Wette, Physica **25**, 1225 (1959).

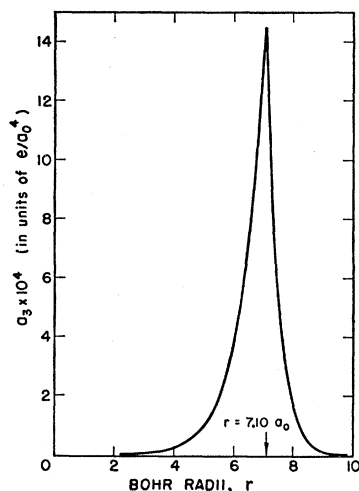


FIG. 2. The function $a_3(r)$, defined in Eq. (11). The point $r=7.1a_0$ corresponds to the position of an argon atom and r^3a_3 is the radial part of the Y_3^0 term in the expansion of the potential of its charge distribution about the origin. Also, $a_0=\hbar^2/me^2=0.529\times 10^{-8}$ cm.

the rare-gas crystal. At any given atom, then, a potential V_0 will be produced by essentially the twelve nearest neighbors, which are to be assumed still spherical for purposes of computing the potential which induces the multipoles. Thus

$$V_0(\mathbf{r}) = \sum_{\substack{\nu=1 \\ (\mathbf{R}_\nu \neq 0)}}^{12} v(\mathbf{r}-\mathbf{R}_\nu), \quad (9)$$

where v is the electrostatic potential seen by a test charge at the point \mathbf{r} in an argon atom:

$$v(\mathbf{r}) = \int \frac{\rho_0(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}'. \quad (10)$$

If we have a single atom on the z axis at $\mathbf{c}=(0,0,c)$, the potential of this atom may be expanded as in (8) but its spherical symmetry eliminates all components with $M \neq 0$ (Ref. 10):

$$v(\mathbf{r}-\mathbf{c}) = \sum_L a_L(r) r^L Y_L^0(\mathbf{r}). \quad (11)$$

Here $a_L(r)$ is the radial function $A_{LM}(r)$ for $M=0$ and for a single atom on the z axis. Introducing (11) into the sum (9) and making appropriate coordinate transformations to bring all of the spherical harmonics into a single coordinate system, we obtain for the fcc lattice

$$V_0(\mathbf{r}) = 12a_0 Y_0^0 - (7/12)a_4(r)r^4 \\ \times [Y_4^0 + (5/14)^{1/2}(Y_4^4 + Y_4^{-4})] + O(r^6), \quad (12)$$

¹⁰ The relation between a_L and Lowdin's α functions [see, e.g., P. O. Lowdin, *Advances in Physics* (Taylor and Francis, Ltd., London, 1956), Vol. 5, p. 1] is the following:

$$a_L = (2L+1)^{-1/2} r^{-L} \alpha_L(N00/ar),$$

where the radial function $f_{N00}(r)$ to be inserted in Lowdin's formalism is related to $v(r)$ by

$$v(r) = [f_{N00}(r)/r] Y_0^0(r).$$

TABLE I. Monopole-multipole interactions (E_{L0}), multipole-multipole interaction (E_{LL}), and multipole moments (Q_{LM}) in solid argon.

	hcp lattice ($L=3$)	fcc lattice ($L=4$)	Units
E_{L0}	-0.25×10^{-5}	-1.55×10^{-5}	kcal/mole
E_{LL}	0.19×10^{-8}	6.38×10^{-8}	kcal/mole
Q_{L0}	...	1.47×10^{-45}	esu cm ^L
$Q_{LL} = Q_{L,-L}$	4.57×10^{-39}	0.88×10^{-45}	esu cm ^L

while for the hcp lattice

$$V_0(\mathbf{r}) = 12a_0 Y_0^0 \\ + i(5/84)^{1/2} a_3(r) r^3 (Y_3^3 + Y_3^{-3}) + O(r^4). \quad (13)$$

By comparing the coefficients of $r^L Y_L^M(\mathbf{r})$ in Eq. (8) with those in Eqs. (12) and (13) one immediately obtains the functions $A_{LM}(r)$ for the two lattices under consideration. For example,

$$A_{44}(r) = A_{4,-4}(r) = \begin{cases} -(7/12)(5/14)^{1/2} a_4(r) & (\text{fcc}) \\ 0 & (\text{hcp}). \end{cases}$$

We have computed the necessary functions $a_3(r)$ and $a_4(r)$ from the charge densities of Ar given by Hartree-Fock wave functions,¹¹ using numerical two-center integration programs available at the University of Rochester. In Fig. 2 we show $a_3(r)$; the function $a_4(r)$ has quite a similar appearance.

The monopole-multipole energies were computed according to the method outlined in Appendix B, and the results for hcp and fcc argon are shown in Table I. Also shown are multipole moments and multipole-multipole interactions obtained from the average A_{LM} coefficients (see Sec. II) and Ar polarizabilities computed by De Wette^{7,12}:

$$\alpha_3 = 1.32 \times 10^{-56} (\text{cm})^7, \\ \alpha_4 = 2.47 \times 10^{-72} (\text{cm})^9.$$

It may be seen from Table I that the fcc lattice is favored by an energy $E_{30} - E_{40} = 1.3 \times 10^{-5}$ kcal/mole. This is less than 10% of the amount by which the van der Waals energy favors the hexagonal lattice,² $\Delta E \approx -2 \times 10^{-4}$ kcal/mole. Furthermore, even though Kihara's multipole-multipole interactions do not contribute explicitly to the cohesive energy it is worth noting that they are of the order of 10^{-7} to 10^{-9} kcal/mole and would favor the *hexagonal* lattice! It so happens that $Y_3^3 - Y_3^{-3}$ repulsive interactions are slightly weaker than $Y_4^0 - Y_4^0$ repulsive interactions. There are no $Y_3^0 - Y_3^0$ interactions in the hcp case, since there is

¹¹ D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) **A166**, 450 (1938).

¹² The polarizabilities given here are smaller than those of Ref. 7 by a factor $L/(2L-1)$. Dr. De Wette has confirmed this correction in private communication.

no Y_3^0 multipole induced. Such interactions would normally be much stronger than $Y_4^0 - Y_4^0$ interactions.

IV. DISCUSSION

We have demonstrated the ineffectiveness of simple classical induced multipoles in stabilizing rare-gas crystals in their cubic form, as proposed by Kihara⁴ in 1960. We point out that the interaction of these multipoles is (i) not the only electrostatic interaction of importance, (ii) very small compared with monopole-multipole interactions, and finally (iii) known to be identically cancelled by the "deformation energy" of the multipoles.

The problem of rare-gas cohesive energies remains a difficult one, in our opinion; although Jansen's recent results³ are encouraging, it should be pointed out that the face-centered lattice is favored only by virtue of the fact that a second-order contribution is so large that it reverses a first-order contribution to the energies. It would seem that a third-order estimate must be carried out to confirm the convergence of this process. Furthermore, a completely convincing theory will include a minimization of the fcc and hcp energies with respect to lattice constant.

One may be quite certain, however, on the basis of the results presented here, that exchange and three-body effects, such as those considered by Jansen, will outweigh electrostatic multipole effects.

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APPENDIX A

It is interesting to illustrate the absence of a dipole-dipole term in the cohesive energy of two polarizable clouds such as those in Fig. 1. For clarity, we shall assume that there is a net charge on each and that no actual overlapping occurs. Let one "He⁺ ion" be fixed at the origin. The field at the other is equal to

$$E(R) = (e/R^2) - [2\mu(R)/R^3] \quad (\text{A1})$$

and the gradient of this field [regarding $\mu(R)$ as fixed, since we only wish the gradient with respect to the field point] is

$$E'(R) = -(2e/R^3) + [6\mu(R)/R^4]. \quad (\text{A2})$$

The total force on the movable He⁺ ion is thus

$$F = eE + \mu E' = \frac{e^2}{R^2} - \frac{4e\mu(R)}{R^3} + \frac{6\mu(R)^2}{R^4}. \quad (\text{A3})$$

The total work required to bring the two ions together from ∞ to R is

$$W = \int_{\infty}^R (-F) dr = \int_{\infty}^R \left(\frac{e^2}{r^2} + \frac{4e\mu(r)}{r^3} - \frac{6\mu(r)^2}{r^4} \right) dr. \quad (\text{A4})$$

Integrating the middle term by parts,

$$4e \int_{\infty}^R \frac{\mu(r)}{r^3} dr = -\frac{2e\mu(R)}{R^2} + 2e \int_{\infty}^R \frac{\mu'(r)}{r^2} dr, \quad (\text{A5})$$

and observing that $\mu(r) = \alpha E(r)$, we have from (A1)

$$\mu(r) = \frac{\alpha e/r^2}{1 + 2\alpha r^{-3}}. \quad (\text{A6})$$

It follows that

$$\mu'(r) = -[2\mu(r)/r] + (6e/r^2)\mu(r)^2. \quad (\text{A7})$$

Substituting (A7) in (A5) and (A5) into (A4), one notes a complete cancellation of the $\mu(r)^2$ term and

$$W = (e^2/R) - [e\mu(R)/R^2]. \quad (\text{A8})$$

This is precisely the result computed from the $L=0$ and $L=1$ terms of De Wette's expression for the cohesive energy,⁷ and explicitly demonstrates the absence of a dipole-dipole term.

APPENDIX B

Let us consider a perturbation on a spherically symmetric atom,

$$U_L = -e \sum_i a_L(\mathbf{r}_i) r_i^L Y_L^0(\mathbf{r}_i),$$

where the \mathbf{r}_i are the coordinates of the electrons. We compute the contribution of s and p shells to the second-order change in the energy of this atom by Kirkwood's variation-perturbation method. Our case differs from De Wette's only in the fact that a_L is a radial function rather than a constant. We obtain, for $L \geq 3$,

$$W_L^{(2)} = I^2/2\pi e a_0 (J + K),$$

where

$$I = \int_0^{\infty} \rho(r) r^{2L} a_L(r)^2 dr,$$

$$J = L(2L+1) \int_0^{\infty} \rho(r) r^{2L-2} a_L(r)^2 dr,$$

and

$$K = \int_0^{\infty} \rho(r) r^{2L-1} a_L(r)' [r a_L(r)' + 2L a_L(r)] dr.$$

Here, $\rho(r)$ is the radial electronic charge density in the atom. For other shells and other values of L the expression for I is complicated by additional exchange-like terms which arise from the use of antisymmetrized wave functions.

The monopole-multipole energy of the lattices considered in the text can be shown to be simple multiples of $W_L^{(2)}$, viz.,

$$E_{40} = (7/12)W_4^{(2)} \quad \text{and} \quad E_{30} = (5/42)W_3^{(2)}.$$

Averaged radial coefficients of the lattice potential, \bar{A}_{LM} , can be used to determine an analytic expression

for the monopole-multipole energy per mole of substance,

$$E_{L0} = -N \sum_M [(2L+1)/8\pi] \alpha_L \bar{A}_{LM}^2.$$

Comparison with the results of the above perturbation method yields the \bar{A}_{LM} , from which the multipole-multipole interactions can be determined.

Re-examination of the Lattice Dynamics of White Tin Using a Modified Axially Symmetric Model

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Experimental measurements of both the specific heat and the Debye-Waller factor for (white) Sn suggest the presence of low-lying phonon branches. In addition, recent experiments by Rowell *et al.* displayed structure in the Sn-Sn superconductors tunneling characteristic curve associated with very low-energy Van Hove singularities in the Sn vibrational spectrum. A previous theoretical calculation of the Sn phonon spectrum using the elastic constants of Mason and Bömmel does not predict the existence of such low-lying phonon branches. A subsequent calculation based on the elastic data of Rayne and Chandrasekhar, on the other hand, clearly indicates the presence of a very low-energy acoustic branch along the [110] direction. However, in this calculation complete elastic consistency was not possible because of the constraint imposed by the *A-S* (axially symmetric) lattice dynamics model. Consequently, we have re-examined the lattice vibrational spectrum of Sn on the basis of a generalized *A-S* lattice dynamics model which allows complete elastic consistency to be obtained. The specific heat, the magnitude of the Debye-Waller factor and the low-energy structure in the tunneling experiments calculated from the dispersion curves obtained from our modified *A-S* model are in quantitative agreement with experimental observations. The anisotropy factor ϵ of the Debye-Waller factor is increased from 1.2 to 1.56 and remains in disagreement with experiment. It appears to us that with the present elastic data it is not possible to obtain a mean-square displacement larger in the z direction than that in the x direction. Furthermore, we conclude that the Mason and Bömmel elastic data are incapable of explaining the present experimental data on white tin.

I. INTRODUCTION

EXPERIMENTAL measurements of both the specific heat¹ and the Debye-Waller²⁻⁵ factor for white tin suggest the presence of low-lying phonon branches. In addition, recent experiments by Rowell *et al.*⁶ displayed structure in the Sn-Sn superconducting tunneling characteristic curve associated with very low-energy Van Hove singularities in the Sn vibrational spectrum.

A previous⁷ theoretical calculation of the Sn phonon

spectrum using the axially symmetric lattice dynamics model (*A-S* model) with the elastic data of Mason and Bömmel⁸ does not predict the existence of such low-lying phonon branches. A subsequent calculation,⁹ based on the elastic data of Rayne and Chandrasekhar,¹⁰ on the other hand, clearly indicated the presence of a very low-energy acoustic branch along the [110] direction. However, in this calculation complete elastic consistency was not possible because of the constraint imposed by the *A-S* model ($C_{44} - C_{13} - C_{66} + C_{12} = 0$). Consequently, we have re-examined the lattice vibrational spectrum of Sn on the basis of a generalized *A-S* lattice dynamics model which allows complete elastic consistency to be obtained. This generalized *A-S* model will be described in more detail in a subsequent paper on the lattice vibrational spectrum of hexagonal close packed metals. Briefly the model allows the bond-

¹ R. Hultgren, R. L. Orr, P. D. Anderson, and K. K. Kelley, *Selected Values of Thermodynamic Properties of Metals and Alloys* (John Wiley & Sons, Inc., New York, 1963).

² W. H. Wiedemann, P. Kienle, and F. Pobell, *Z. Physik* **166**, 109 (1962).

³ A. J. F. Boyle, D. St. P. Bunbury, C. Edwards, and H. E. Hall, *Proc. Phys. Soc. (London)* **A77**, 129 (1961).

⁴ R. Barloutand, J. O. Picon, and C. Tzara, *Compt. Rend.* **250**, 2705 (1960).

⁵ N. E. Alekseyevsky, Pham Zuy Hien, V. G. Shapiro, and V. S. Shunel, *Zh. Eksperim. i Teor. Fiz.* **43**, 790 (1962) [English transl.: *Soviet Phys.—JETP* **16**, 559 (1963)].

⁶ J. M. Rowell, P. W. Anderson, and D. E. Thomas, *Phys. Rev. Letters* **10**, 334 (1963).

⁷ T. Wolfram, G. W. Lehman, and R. E. DeWames, *Phys. Rev.* **129**, 2483 (1963).

⁸ W. P. Mason and H. E. Bömmel, *J. Acoust. Soc. Am.* **28**, 930 (1956).

⁹ R. E. DeWames, T. Wolfram, and G. W. Lehman, *Phys. Rev.* **131**, 529 (1963).

¹⁰ J. A. Rayne and B. S. Chandrasekhar, *Phys. Rev.* **120**, 1658 (1960).