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Letters to the Editor

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Viscosity of Gaseous He^3 and He^4 between 1.3°K and 4.2°K

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WE have recently shown[1] that the symmetry effects calculated by Halpern and Gwathmey[2] which should occur with the gaskinetic collisions of *ortho-para*-H$_2$ and *ortho-para*-D$_2$ cannot be observed with even an approximately right order of magnitude. The reliability of the calculations, however, is not very high, because they are based on the hard-elastic-sphere model which is not suitable for the nonspherical potential of H$_2$ and D$_2$. Halpern[3] has therefore suggested that the influence of the statistics on the gaskinetic cross sections be reinvestigated by measuring the viscosity-difference of gaseous He^3 and He^4 at very low temperatures. In the case of He no difficulties with respect to the potential are to be expected. Since He^3 obeys Fermi statistics while He^4 obeys Bose statistics, the viscosity of gaseous He^3 should appreciably exceed the viscosity of He^4 at low temperatures. Somewhat later, de Boer and Cohen[4] have explicitly calculated the temperature-dependence of the viscosities between 0 and 5°K using a Lennard-Jones potential of the form $4\epsilon[(\sigma/r)^{12}-(\sigma/r)^6]$.

To investigate the extremely small viscosities, we have developed a measuring device based on the principle of the oscillating cylinder. The amplitudes of the oscillations are recorded by high-frequency circuits using a change in capacity connected with the oscillation. At 4.2°K the relaxation time of the oscillating system filled with He^4 amounts to 2.7 min while it exceeds 3 hr with the highest obtainable vacuum. The period of the oscillating cylinder is 1.3 sec. At a viscosity of 5 micropoise the accuracy of the measurements was better than ±1 percent.

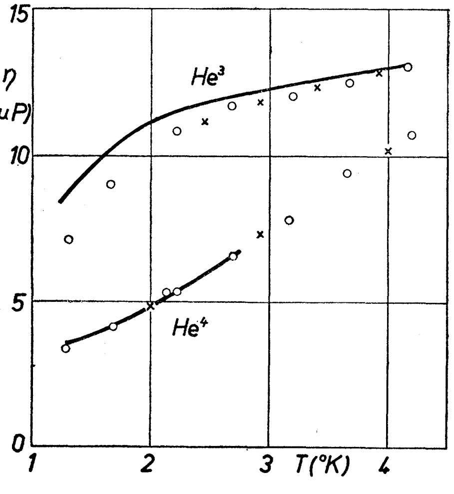

FIG. 1. The temperature dependence of the viscosity coefficient η (micropoise) of gaseous He^3 and He^4. Circles and crosses represent the experimental results obtained with decreasing and increasing temperature, respectively. Continuous lines represent theoretical curves of de Boer and Cohen.

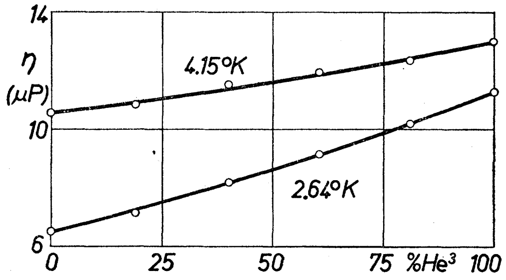

FIG. 2. Concentration dependence of the viscosity coefficient η (micropoise) of gaseous He^3-He^4 mixtures at temperatures 4.15°K and 2.64°K.

The viscosities of pure He^3 and He^4 were measured between 1.3° and 4.2°K (Fig. 1). The results for pure He^4 agree perfectly with the calculations of de Boer and Cohen. For He^3 the figure shows a small deviation between theory and experiment at low temperatures. In any case, we may presume that the results obtained confirm the predicted symmetry effect of the helium isotopes.

Furthermore, the concentration dependence of the viscosity of gaseous He^3—He^4 mixtures was determined at 4.2° and 2.6°K as shown in Fig. 2. The absolute values of η are derived from the well-known viscosity of He^4 at 77.3°K (83.68 micropoise).[5] The pure He^3 was supplied by the U. S. Atomic Energy Commission. Details will be published in the *Zeitschrift für Physik*.

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F-Center Wave Functions in Alkali Halides*

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IN recent publications[1-3] Hutchison, Kittel, and co-workers have presented important new information based on paramagnetic resonance absorption measurements capable of giving insight into the charge distributions of *F*-center electrons in KCl. From the measured[1] shift in the g factor, -0.007, Kahn and Kittel[2] have shown that the spin of the *F*-center electron is strongly coupled with orbital angular momentum; if its wave function is written as an atomic function, they have concluded, it must be of almost pure g character ($l=4$) to explain the shift in the splitting factor. Seitz has presented arguments,[3] based on the inclusion of the interaction of the electron with its surroundings, to show that a ground state described by about half s-like and half g-like behavior is a reasonable one. Secondly, Kittel *et al.* have shown the width of the resonance absorption peak, 56 oersteds in KCl, to be a result of hyperfine interactions of the electron with the nuclear magnetic moments of the neighboring ions. Knowledge of these breadths and of the magnetic moments involved in samples of KCl containing two isotopes of K has enabled them to calculate the probability density of the *F*-center electron at the surrounding nuclei.[4] From these two results Kittel and co-workers have concluded that the natural model for the

F-center wave function is that corresponding to a linear combination of atomic orbitals (LCAO) centered on the 6 positive ions closest to the negative-ion vacancy. In the present note the writer wishes to show that their experiments are also consistent with the common alternative model of the F center, based on a radial field directed at the negative-ion vacancy, when the model is properly applied.

In the molecular orbital model[5] (LCAO) preferred by Kittel and associates, the ground-state wave function is written as $\Psi=6^{-\frac{1}{2}}\Sigma_j\,\psi(\mathbf{r}-\mathbf{R}_j)$, where the $\mathbf{R}_j$ are the coordinates of the 6 nearest alkali ions, and where the small effects on the normalization because of overlapping of $\psi(\mathbf{r}-\mathbf{R}_i)$ with $\psi(\mathbf{r}-\mathbf{R}_k)$ are neglected. In KCl the ψ's must be very similar to $4s$ functions in free K atoms φ_{4s} so that the probability density at one of the K nuclei is about $\frac{1}{6}|\varphi_{4s}(0)|^2$. Hartree wave functions including exchange[6] for neutral K give for this quantity the value 0.76×10^{24} cm^{-3}, which is to be compared with the value 0.70×10^{24} cm^{-3} obtained[3] from experiment. (Some idea of the dependence of this quantity on the valence state, and hence on the environment, is found from the Hartree[6] value of 0.37×10^{24} cm^{-3} for one of the $4s$ electrons in the K$^-$ ion. An indication of the accuracy of the Hartree calculations of $\frac{1}{6}|\varphi_{4s}(0)|^2$ is given by the corresponding value 1.3×10^{24} cm^{-3} found by atomic beam experiments.[7]) Thus the LCAO model seems quite capable of explaining the observed probability densities at the K nuclei, in agreement with the conclusions of the previous workers,[3] although in this simple form it predicts nothing about the density at the nearest Cl$^-$ ions empirically found to be 0.12×10^{24} cm^{-3}.

Another type of wave function has been worked out by Tibbs,[8] Simpson,[9] and others, based on a central potential which is Coulomb-like at large distances and constant at small distances. These solutions $f(|\mathbf{r}|)$ are very similar to the ground-state function of the hydrogen atom with an equivalent Bohr radius of $3a_0$. As discussed by Tibbs[8] and Dexter,[10] the central potential is a perturbation on the regular periodic lattice potential, and the complete wave function is approximately equal to $\Psi=f(|\mathbf{r}|)g(\mathbf{r})$, where $g(\mathbf{r})$ is constant at small r and is a function with the periodicity of the lattice at larger r, where it becomes equal to the lowest energy wave function of an additional electron introduced into the conduction band $u_0(\mathbf{r})$. A function of the form $\Psi=fg$, according to the arguments of Kittel[2,3] and Seitz,[4] is capable of explaining the observed shift in the g factor. The function $g(\mathbf{r})$ is clearly required to take account of the violent oscillations of the wave function near each nucleus, where it experiences a powerful electric field. For some practical purposes $g(\mathbf{r})$ may be ignored,[10] as is the case, for example, if one is interested only in the average probability amplitude from one unit cell to the next; in the present instance of calculating the density at the center of one of these large fluctuations it is of course essential to take it into account.

Tibbs[8] has calculated $u_0(\mathbf{r})$ for the (1,0,0) direction in NaCl and has found that it behaves as a Na $3s$ function near each Na ion and as a Cl $4s$ function near each Cl ion; the charge is distributed relatively heavily near the Cl ions. Making use of Tibbs' functions, we estimate the probability density of the F-center electron at one of the 6 nearest Na nuclei to be $(2.3\times10^{21}\text{ cm}^{-3})\times(2.7\times10^2)=0.61\times10^{24}$ cm^{-3}. The quantity in the first parentheses is equal to $|f(\text{Na})|^2$ and that in the second is $|g(\text{Na})|^2$. As pointed out in reference 4, use of $|f(\text{Na})|^2$ alone leads to much too small a result.[11] We may also compute with this model the density at one of the 12 nearest Cl nuclei and find the value $(5.3\times10^{20}\text{ cm}^{-3})\times(8.5\times10^2)=0.45\times10^{24}$ cm^{-3}. The relatively large value at the Cl nuclei is a result of the larger nuclear charge in Cl, which gives a big amplitude to the $4s$-like function at the Cl nucleus. The experimental values for the probability density are not available for NaCl, but the width of the absorption peak has been measured as 162 oersteds; using the estimated probability densities above, we calculate 265 oersteds. The lack of quantitative agreement can be attributed to errors in the approximate normalization of the function $g(\mathbf{r})$. The next nearest shell of Na ions contributes only about one percent to the mean-square width, so that assumption (1) in reference 4 is sufficiently accurate for their purposes.

The function $u_0(\mathbf{r})$ has not been computed for KCl, but some qualitative conclusions can be drawn about its distribution on the basis of the similarity of the two constituents. In particular, $g(\mathbf{r})$ must be very similar near both types of ion in KCl so that the ratio $|g(\text{K})|^2/|g(\text{Cl})|^2$ is larger than the corresponding ratio in NaCl, 2.7/8.5. In order that the functions be normalized, therefore, $g(\text{Cl})$ must decrease. If the amplitudes of g are about equal at the two nuclei, as one might expect, the ratios of the probability density at the nearest K to that at the nearest Cl would be about 5.6, in good agreement with the observed ratio 5.8 obtained by Kittel and co-workers. Calculation of the actual magnitude of the probability densities at the K and Cl nuclei must await the calculation of $u_0(\mathbf{r})$ for KCl, but application of the qualitative arguments above to the estimates for NaCl indicates that the calculated magnitudes will be of the same order as observed, 0.70 and 0.12×10^{24} cm^{-3}, for K and Cl, respectively. In the writer's opinion there is no obvious advantage to either type of wave function, except that the function $f(|\mathbf{r}|)g(\mathbf{r})$ is simpler and certainly gives a more accurate description at large r than does a LCAO containing only a few terms; for the computation of tunneling probabilities, for example, the latter is essentially worthless.

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[11] Professor Kittel has been kind enough to check his calculations for $|f(\text{K})|^2$ and agrees that the value in reference 4 should be reduced by about a factor of 10 to agree with the above value. It should also be mentioned that he and his co-workers did not intend to imply a criticism of the radial field model when it is utilized in the manner described here. (Private communications from C. Kittel.)

Theoretical Calculations of *F*-Center Energy Levels*

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In an earlier letter,[1] the writer and N. Schwartz presented a criticism of certain assumptions entering previous calculations of the type discussed by Tibbs and others.[2] At the same time we summarized the results of calculations for NaCl and KCl, including corrected assumptions; the differences were noticeable but did not seriously change the previous pictures of the F center. Since the appearance of the work of Hutchison and Kittel and others,[3] some question has arisen as to the suitability of calculations of this type for explaining the observed Δg and width of the F-center spin resonance absorption lines. In the present note the writer concludes that when properly used, calculations such as those of reference 1 can give good agreement with these experiments.

Kip *et al.*[3] have shown that the observed width of the spin resonance line can be understood by assigning this width to electron-nuclear hyperfine spin coupling between the F-center electron and the nuclei of the surrounding ions in the lattice. In calculating this interaction it is necessary to know $\psi_F{}^2(r_N)$, the F-center electron density at these nuclei. In the KS and similar calculations, the assumed form of the wave function outside the vacancy is $\psi_F=fu_0$. Here $f(r)$ is a slowly varying function which measures the average charge density in a unit cell, and $u_0(r)$ is the