Superconductivity of Lanthanum and Some Lanthanum Alloys*

G. S. ANDERSON, S. LEGVOLD, AND F. H. SPEDDING
Institute for Atomic Research and Department of Physics, Iowa State College, Ames, Iowa
(Received September 23, 1957)

Superconductivity has been observed for two structures of lanthanum. A close-packed hexagonal structure was found to have a transition temperature near 5.0°K and the face-centered cubic structure had a transition temperature of 5.95°K. The initial slope of the H_c-T curve for the face-centered cubic structure was 550 oe/deg. The transition temperature decreased with decreasing lanthanum content for the La-Y and La-Lu alloys studied.

I. INTRODUCTION

THERE has been considerable disagreement concerning the superconductivity of lanthanum.[1–6] Ziegler, Young, and Floyd[7] made a study of the crystal structure and the superconductivity of lanthanum and concluded that two structures of lanthanum are superconducting with different transition temperatures. They suggested that the face-centered cubic structure has a transition temperature of 5.4°K, whereas the hexagonal close-packed structure should have a transition temperature somewhat above 3.9°K.

It has been suggested that the transition temperature should be a function of the atomic volume, the atomic mass, and the number of valence electrons per atom.[8,9] For the alloys of lanthanum with yttrium and lutetium studied in this work, the number of valence electrons per atom is constant. This should make it possible to study the effects of the atomic volume and the atomic mass on the transition temperature.

II. EXPERIMENTAL TECHNIQUE

1. Temperature Control and Measurement

The apparatus used in the range 1.2°K to 6°K is illustrated in Fig. 1. The experimental chamber was made of thick-walled copper tubing and was essentially isothermal. It was thermally connected to the bath by means of a stainless steel tube. The heater wound on this tube was used to raise the temperature of the copper chamber above the temperature of the bath. Helium exchange gas, at a pressure of approximately 50 microns, maintained the sample and the copper sample holder at the temperature of the chamber walls. Temperatures from 4.2°K to 1.2°K were obtained by pumping on the liquid helium. The vapor pressure of the bath was measured and temperatures were based on the 1955 (Naval Research Laboratory) international scale.[10]

Temperatures from 4.2°K to 6°K were obtained by use of the heater. A heater power of approximately 6.5 mw maintained the sample at a temperature two degrees above the bath temperature. Temperatures above 4.2°K were measured by means of a gas thermometer of the type described by Woodcock.[11] It is believed that temperatures near 6°K were determined with a precision of 0.05 deg. The apparatus was tested by measuring the H_c-T curves for tin and lead; the results were in agreement with the data of Daunt and Mendelssohn.[12]

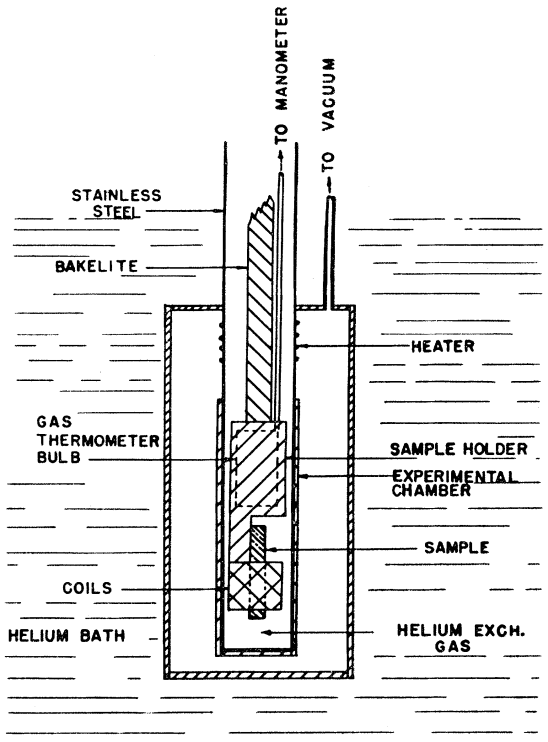

FIG. 1. Apparatus for temperature control.

* Contribution No. 543 from the Institute for Atomic Research and Department of Physics, Iowa State College, Ames, Iowa. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

[1] McLennan, Allen, and Wilhelm, Phil. Mag. **10**, 500 (1930).
[2] K. Mendelssohn and J. G. Daunt, Nature **139**, 473 (1937).
[3] D. Shoenberg, Proc. Cambridge Phil. Soc. **33**, 577 (1937).
[4] W. T. Ziegler, J. Chem. Phys. **16**, 838 (1948).
[5] Parkinson, Simon, and Spedding, Proc. Roy. Soc. (London) **A207**, 137 (1951).
[6] James, Legvold, and Spedding, Phys. Rev. **88**, 1092 (1952).
[7] Ziegler, Young, and Floyd, J. Am. Chem. Soc. **75**, 1215 (1953).
[8] B. T. Matthias, Phys. Rev. **92**, 874 (1953).
[9] B. T. Matthias, Phys. Rev. **97**, 74 (1955).
[10] Clement, Logan, and Gaffney, Phys. Rev. **100**, 743 (1955).
[11] A. H. Woodcock, Can. J. Research **16A**, 133 (1938).
[12] J. G. Daunt and K. Mendelssohn, Proc. Roy. Soc. (London) **A160**, 127 (1937).

2. Detection of Transition

The method employed for measuring the zero-field transitions was similar to that used by Webber, Reynolds, and McGuire.[13] This is an ac method in which the sample is part of the core of a mutual inductance with 250 turns in the primary and 450 turns in the secondary. The samples were cylinders $\frac{3}{16}$ in. in diameter and 2 in. long. The 100 cps primary current produced a maximum field at the center of the primary of 0.1 oe. The secondary voltage, which was bucked out when the sample was in the normal state, was amplified and read on an oscilloscope.

For some of the samples the transition was observed by means of the electrical resistivity as well as by the ac method. In each case superconductivity, as determined by the ac method, is first evidenced as the electrical resistivity reaches zero.

The critical field values were determined when possible by a dc method similar to that used by Keeley and Mendelssohn.[14] The coil, which was used as the secondary coil for the ac work, was used as a pickup coil and was connected to a ballistic galvanometer. A solenoid, capable of producing fields up to 1000 oe, was used to produce a longitudinal magnetic field. The magnetic field was varied abruptly in steps and the corresponding galvanometer deflections were recorded. The accumulated galvanometer deflections were plotted as a function of the field.

3. Samples Studied

The chemical similarity of yttrium and elements of the lanthanide series has made the separation of these elements a difficult problem. Using an ion-exchange method, Spedding and Powell[15] have obtained pure rare earths. The development of techniques for preparing the pure metals has been accomplished by Spedding and Daane.[16] The alloys were prepared by melting together the proper amounts of each component in tantalum crucibles. The samples were then turned down to the proper size.

The crystal structure of small needles cut from the bulk metal was determined by powder diffraction techniques. These needles were given the same heat treatment as the samples, and were assumed to have the same structure as the samples. It was also assumed that there was no structure transformation below room temperature. This seems to be a reasonable assumption for pure lanthanum.[5–7] It seems plausible to make the same assumption for the alloys examined.

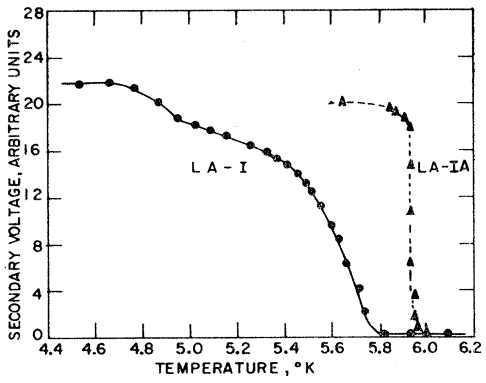

FIG. 2. Secondary voltage *vs* temperature for La-I and La-IA.

III. RESULTS

1. Lanthanum

A pure lanthanum sample (La-I) was polycrystalline and exhibited both the face-centered cubic structure and a close-packed hexagonal structure with a stacking sequence *ABAC* . . . instead of the usual *ABAB* . . . The secondary voltage as a function of temperature for this sample is shown in Fig. 2. We note that there are two broad transitions: one near 5.0°K and another near 5.8°K.

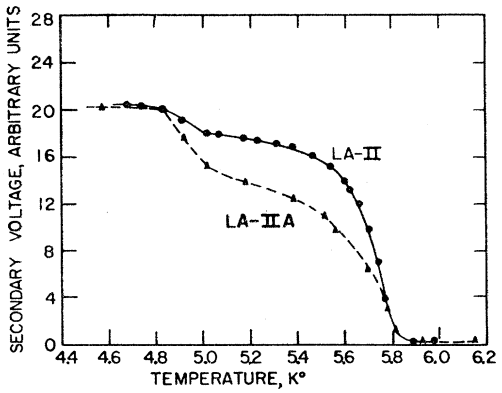

FIG. 3. Secondary voltage *vs* temperature for La-II and La-IIA.

Barson, Legvold, and Spedding[17] noted a phase transition in lanthanum near 300°C. Above this temperature the stable crystal structure is face-centered cubic.[7] To obtain the face-centered cubic structure for this work the sample was annealed at 400°C for 4½ days and quenched. The sample is now designated as La-IA. The secondary voltage as a function of temperature for La-IA is also shown in Fig. 2. The one transition observed was sharp and occurred at 5.95°K. X-ray studies showed that this sample had the face-centered cubic structure.

A second sample of pure lanthanum (La-II) had the same structures as La-I. The secondary voltage as a function of temperature for this sample is shown in Fig. 3. This curve is similar to the corresponding curve for La-I. This sample was then annealed at 200°C for

[13] Webber, Reynolds, and McGuire, Phys. Rev. **76**, 293 (1949).
[14] T. C. Keeley and K. Mendelssohn, Proc. Roy. Soc. (London) **A154**, 378 (1936).
[15] F. H. Spedding and J. E. Powell, J. Metals **6**, 1131 (1954).
[16] F. H. Spedding and A. H. Daane, J. Metals **6**, 504 (1954).
[17] Barson, Legvold, and Spedding, Phys. Rev. **105**, 418 (1957).

five days. It is now designated as La-IIA. The secondary voltage as a function of temperature for the sample in this state is also shown in Fig. 3. The annealing caused an enhancement of the transition near 5.0°K, but both structures remained. Attempts to get the pure hexagonal form were not successful. It may be concluded that face-centered cubic lanthanum has a transition temperature of 5.95°K, and that the close-packed hexagonal lanthanum, with the c axis double its normal value, has a transition temperature near 5.0°K.

2. Lanthanum-Yttrium

A sample containing 60% lanthanum and 40% yttrium by atoms had the lanthanum hexagonal structure and a transition temperature of 1.7°K. A sample containing 75% lanthanum and 25% yttrium had this same structure. The secondary voltage as a function of temperature for this sample is shown in Fig. 4. This curve is representative of the curves for the alloys studied in this work and is the only one reproduced

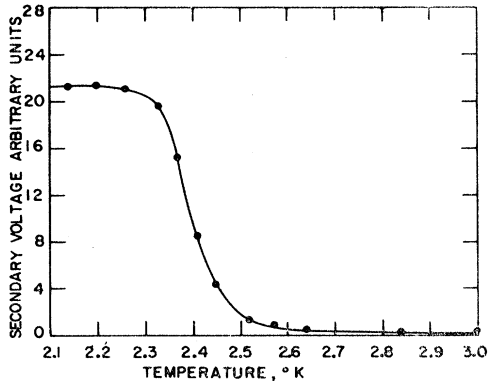

FIG. 4. Secondary voltage *vs* temperature for the alloy containing 75% lanthanum and 25% yttrium.

here. Its transition temperature, as determined in this manner, is 2.5°K. A sample containing 85% lanthanum and 15% yttrium was also hexagonal and had a transition temperature of 3.2°K. A sample containing 95% lanthanum and 5% yttrium exhibited both the hexagonal structure and the face-centered cubic structure. The secondary voltage as a function of temperature for this sample as cast, showed only one transition and this was at 5.4°K. The sample was annealed at 360°C for 16 days in an attempt to obtain the hexagonal form. It then appeared to have more of the hexagonal structure. The secondary voltage as a function of temperature for the sample after this heat treatment again showed only one transition, but it was now at 4.4°K. This transition was assumed to be associated with the hexagonal structure.

Figure 5 is a summary of the data for the lanthanum-yttrium alloys. The transition points fall on two separate curves. The curve lying on the lower temperature side is for the hexagonal structure and the other curve is for the cubic structure. For these alloys the transition temperature decreases with decreasing lanthanum content. It is not possible to predict from these data whether or not yttrium should be a superconductor, since yttrium has the ordinary hexagonal close-packed structure and there may be another curve for this structure. We note, however, that Goodman[18] found yttrium to be nonsuperconducting down to 0.10°K.

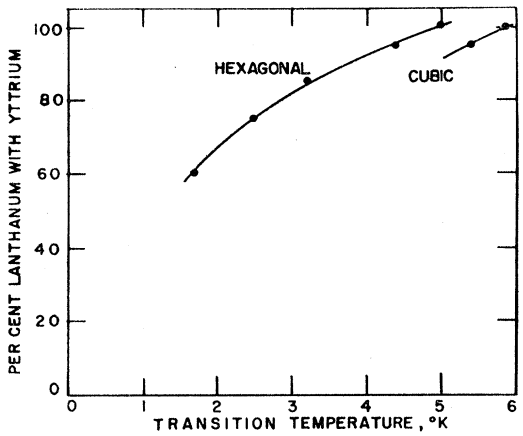

FIG. 5. Transition temperatures *vs* composition for the lanthanum-yttrium alloys.

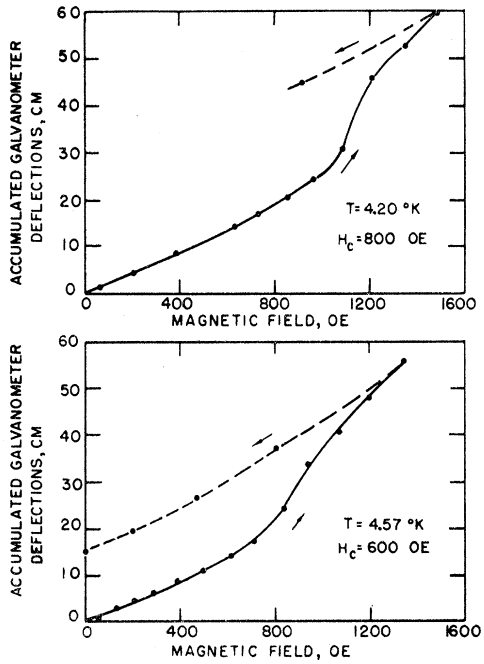

FIG. 6. Isotherms (4.20°K and 4.57°K) of accumulated galvanometer deflections *vs* the applied longitudinal magnetic field for the La-IA sample.

[18] B. B. Goodman, Nature **167**, 111 (1951).

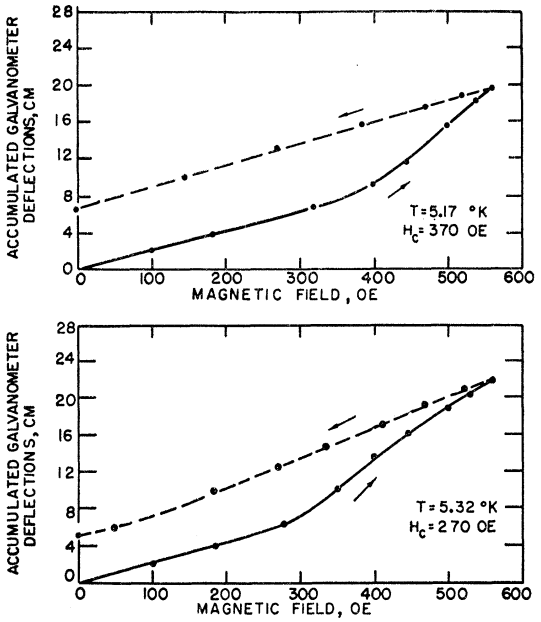

FIG. 7. Isotherms (5.17°K and 5.32°K) of accumulated galvanometer deflections *vs* the applied longitudinal magnetic field for the La-IA sample.

3. Lanthanum-Lutetium

A sample containing 80% lanthanum and 20% lutetium by atoms had the lanthanum hexagonal structure. The secondary voltage as a function of temperature for this sample indicated a transition temperature of 3.4°K. A sample containing 55% lanthanum and 45% lutetium also had the lanthanum hexagonal structure and had a transition temperature of 2.2°K. For these alloys the transition temperature decreases with decreasing lanthanum content.

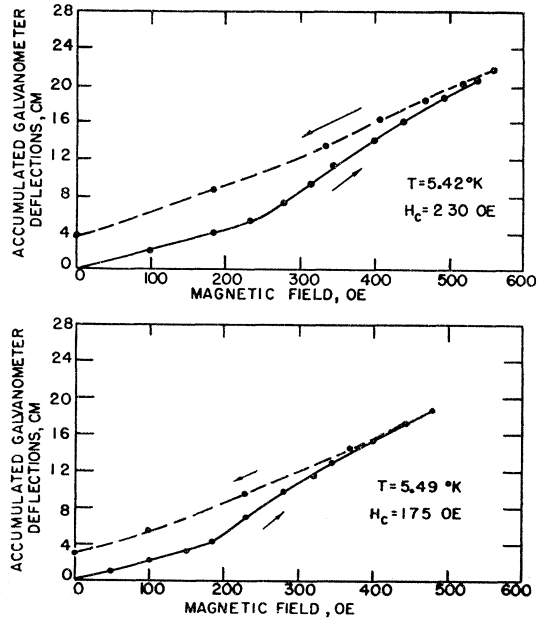

FIG. 8. Isotherms (5.42°K and 5.49°K) of accumulated galvanometer deflections *vs* the applied longitudinal magnetic field for the La-IA sample.

4. Critical Field Curve for f.c.c. Lanthanum

The sharpness of the transition of La-IA suggested that it might be possible to do critical field measurements on this sample. The accumulated galvanometer deflections as a function of the applied magnetic field for various isotherms are shown in Figs. 6–8. Penetration of the magnetic field commences at a rather well-defined value, but it is necessary to apply very strong fields before the sample is entirely in the normal state. The present authors, along with others,[19–21] believe that the penetration fields are much nearer equilibrium fields than are the completion fields. A plot of the penetration fields *vs* T^2 is shown in Fig. 9. The transition temperature, as determined by extrapolation of the H_c-T^2 curve (Fig. 9) to zero field, is 5.84°K. This is not in good agreement with the 5.95°K found by the ac method. From a plot of H_c *vs* T the initial slope, $-dH_c/dT|_{T=T_c}$, was found to be 550 oe/deg. A value of 1600 oe was found for H_0. The difference in heat capacities of the normal and superconducting states, calculated by use of Rutger's formula, is approximately 0.075 cal/mole deg. The only published specific heat data for lanthanum is the work of Parkinson, Simon, and Spedding[5] who reported ΔC=0.0139 cal/mole deg with a transition temperature of 4.37°K.

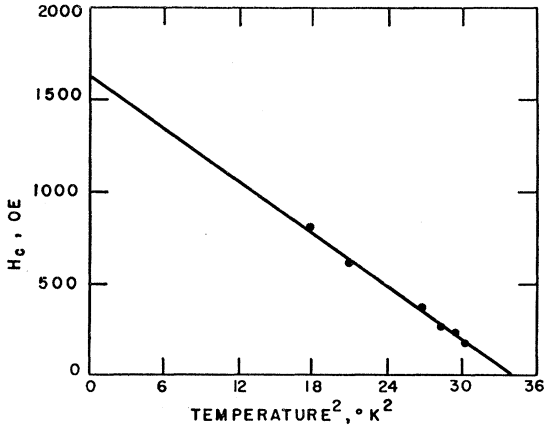

FIG. 9. Penetration fields *vs* the square of the temperature for the La-IA sample.

IV. DISCUSSION

Crystal structure is very important in superconductivity. For pure lanthanum and one of the lanthanum-yttrium alloys the cubic form has a super-

[19] L. C. Jackson and H. Preston-Thomas, Phil. Mag. **41**, 1284 (1950).
[20] W. F. Love, Phys. Rev. **92**, 238 (1953).
[21] A. Wexler and S. Corak, Phys. Rev. **85**, 85 (1952).

conducting transition temperature nearly one degree higher than that for the hexagonal form. For these samples the mean volume per ion seems to be very nearly the same for either structure. There seems to be a general rule that the superconducting transition temperatures are higher for cubic structures than for hexagonal structures.[22] There is presently no good explanation for the role of structure in superconductivity.

There is a definite decrease in transition temperature with decreasing lanthanum content for the lanthanum-yttrium and lanthanum-lutetium alloys. For the alloys studied here no valence effects would be expected. The mass dependence of the isotope effect certainly is not the principal factor involved because, while lutetium is heavier than lanthanum, yttrium is lighter. Matthias[8] has suggested that the transition temperature should vary with the mean volume per ion to some power between 4 and 10. The mean volume per ion to approximately the eighth power would fit the lanthanum-lutetium system. The lanthanum-yttrium system, however, would require a power of approximately 24. It does not seem probable that we could fit all of the data to some universal expression of this type involving only the volume and mass. It is quite clear that crystal structure effects prevent any predictions on the possible superconductivity of pure yttrium and lutetium since these have the $ABAB\ldots$ stacking.

[22] B. T. Matthias and J. K. Hulm, Phys. Rev. **87**, 799 (1952).

ACKNOWLEDGMENTS

We wish to thank J. Powell for preparing the rare-earth salts and J. Hanak, R. Valletta, and A. H. Daane for preparing the metals and alloys from the salts.

PHYSICAL REVIEW VOLUME 109, NUMBER 2 JANUARY 15, 1958

Paramagnetic and Optical Spectra of Divalent Nickel in Cubic Crystalline Fields*

W. Low
Enrico Fermi Institute for Nuclear Studies, The University of Chicago, Chicago, Illinois, and Department of Physics, The Hebrew University, Jerusalem, Israel

(Received July 9, 1957)

The paramagnetic resonance spectrum of divalent nickel in cubic MgO was investigated. The spectrum is isotropic with one line at $g=2.227\pm0.002$. Eight optical absorption lines at 8600, 13 400, 14 800, 21 550, 24 500, 25 950, 28 300, and 34 500 cm^{-1} were detected. These absorption lines are interpreted as transitions between the singlet ground state and all possible Stark levels of the F, P, D, and G levels. Agreement is obtained to within 300 cm^{-1} by using crystalline field theory, with parameters $Dq=860$ cm^{-1}, $E_P=13\,000$ cm^{-1}, $E_D=10\,900$ cm^{-1}, $E_G=19\,600$ cm^{-1}, and λ (the spin-orbit coupling constant) $=-245$ cm^{-1}. The significance of the reduced values of the energy levels and the spin-orbit coupling constant is discussed.

I. INTRODUCTION

DIVALENT nickel has eight $3d$ electrons and in the free gaseous ion has a ground state $^3F_4$. The sevenfold orbital degeneracy is removed in part by a cubic field, and this results in Stark splittings as in trivalent chromium. For a crystalline field of octahedral symmetry this results in a low-lying orbital singlet and two higher orbital triplet states. The orbital singlet is threefold degenerate in the spin quantum number. This degeneracy is not removed under the combined action of a cubic field and spin-orbit interaction.

The paramagnetic resonance spectra of Ni^{2+} have been studied intensively in a number of crystals, particularly in fluosilicate[1,2] and in Tutton salts.[3] The crystalline electric field symmetry is trigonal and tetragonal, respectively. In a trigonal or tetragonal field the spin triplet is split into a singlet and doublet with splittings of the order of 0.1–0.5 cm^{-1}. In the Tutton salts Griffith and Owen[3] report that the triplet is split into three singlets because of additional rhombic symmetry components and that the splittings are as large as 4 cm^{-1}.

There has also been some research on the optical absorption spectra of Ni^{2+} ions in solutions[4–6] and some preliminary work on single crystals.[7] These authors report usually three transitions which can be identified as the optical transitions between the Stark levels and a transition between the ground state and the excited ^3P state. In addition several weak transitions were observed[7] in the region from 17 500–20 500 cm^{-1}. The identification of these weak lines was not conclusive.

We wish to report here data on the paramagnetic resonance spectrum as well as the optical spectra of

* Supported in part by the U. S. Atomic Energy Commission.
[1] Holden, Kittel, and Yager, Phys. Rev. **75**, 1443 (1949).
[2] R. P. Penrose and K. W. H. Stevens, Proc. Phys. Soc. (London) **63**, 29 (1949).
[3] J. H. E. Griffith and J. Owen, Proc. Roy. Soc. (London) **A213**, 459 (1952).
[4] Th. Dreisch and W. Trommer, Z. physik Chem. **B37**, 40 (1937).
[5] D. S. McClure, Office of Naval Research Technical Report No. 3, ONR N-6-Ori-211-III, 1955 (unpublished).
[6] C. K. Jorgensen, Acta Chem. Scand. **9**, 1362 (1955).
[7] G. Gielessen, Ann. Physik **22**, 537 (1935).