Letters to the Editor

Ferroelectricity in Ammonium Sulfate

B. T. MATTHIAS AND J. P. REMEIKA

Bell Telephone Laboratories, Murray Hill, New Jersey
(Received May 10, 1956)

THE dielectric anomalies of $(NH_4)_2SO_4$ have been known and thoroughly investigated over a long period of time.[1,2] Our discovery of ferroelectricity in $(NH_2)_3Al(SO_4)_2 \cdot 6H_2O$ and its isomorphs[3] and the subsequent discovery by Pepinsky et al.[4] of the ferroelectricity in some alums suggested a new approach to the problem. It seems that the $N-H-O$ bond may perhaps be more important for the occurrence of ferroelectricity than had previously been anticipated.

$(NH_4)_2SO_4$ has no water of crystallization and was therefore an ultimate test to this hypothesis. We have found that $(NH_4)_2SO_4$ becomes ferroelectric parallel to the a-axis below its transition point at $-49.5°C$. The spontaneous polarization at $-58°C$ is 2.54×10^{-7} coulomb/cm². The coercive field at this temperature is about 2000 v/cm and decreases with increasing temperature. The hysteresis loops are very rectangular and show no bias.

[1] R. Guillien, Compt. rend. **208**, 980 (1939).
[2] L. Couture et al., Compt. rend. **243**, 1804 (1956).
[3] Holden, Matthias, Merz, and Remeika, Phys. Rev. **98**, 546 (1955).
[4] Pepinsky, Jona, and Shirane (to be published). We wish to thank Professor Pepinsky for the personal communication of his results.

Phase Separation in $He^3 - He^4$ Solutions*

G. K. WALTERS† AND W. M. FAIRBANK

Department of Physics, Duke University, Durham, North Carolina
(Received May 10, 1956)

USING nuclear magnetic resonance techniques,[1,2] we have detected a separation of $He^3 - He^4$ solutions into two distinct liquid phases at temperatures below 0.8°K. A separation had been predicted on theoretical grounds independently by Prigogine et al.[3] and by Chester.[4]

For detecting the phase separation and making quantitative measurements on the He^3 concentrations of the two phases, a sample container having three vertically arranged sections, connected by small holes, was constructed. When this container is placed in a magnetic field having a gradient from top to bottom, the solutions in each of the three sections come to resonance at a constant frequency for different values of the steady magnetic field. Thus, the resonance line as observed on an oscilloscope is split into three separate peaks, each corresponding to the resonance of the He^3 nuclei in a known section of the container. Changes in the relative amplitudes of these three peaks as a function of temperature give a measure of the concentration of He^3 atoms in each section of the sample container, hence a measure of the He^3 concentrations of the two phases.

Using this method on 40% and 60% solutions of He^3 in He^4, we have arrived at an approximate phase diagram, shown in Fig. 1, for $He^3 - He^4$ solutions. In calculating this diagram from the experimental data, it was necessary to approximate the liquid mixture densities by assuming the law for perfect solutions using the known values of the molar volumes at 1.2°K of pure He^4 and pure He^3. It was necessary also to make an assumption regarding the susceptibility per atom of He^3 in solutions of varying He^3 concentration. For both the 40% and 60% samples at temperatures above the phase separation temperature, very little deviation was observed from the Curie inverse temperature law for the susceptibility. Thus it was assumed that the susceptibility per He^3 atom at any temperature lies for all He^3 concentrations between that value predicted
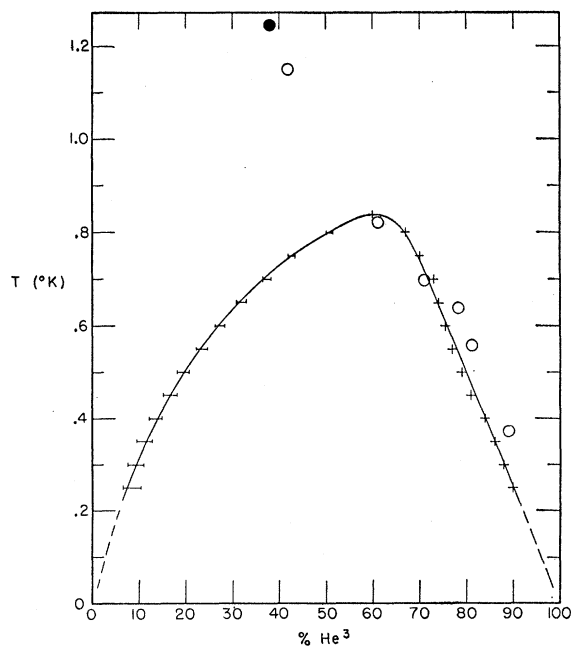

FIG. 1. Phase diagram for $He^3 - He^4$ solutions. The open circles represent T_λ measurements of Daunt and Heer. The closed circle represents a T_λ measurement made by us.

by the Curie law and the experimentally determined value for pure He³.[1,2] Points to the left of the maximum in Fig. 1, indicated by bars, were calculated under this assumption, the extremities of each bar corresponding to the limits imposed above on the susceptibility per atom. Points to the right of the maximum, indicated by crosses and corresponding to higher He³ concentrations, were calculated under the assumption that the susceptibility per He³ atom is the same as for pure He³. Our measurements indicate that this assumption is approximately correct for high He³ concentrations.

The open circles in Fig. 1 represent the T_λ measurements of Daunt and Heer[5] and the solid circle represents a T_λ determination made by us from thermal relaxation time measurements. Daunt's points fall close to the phase curve, easily within our experimental error. These points were measured by observing the warmup rate of a container of solution connected thermally to the helium bath through a fine capillary. The λ point was identified as that point at which the rate of warmup of the solution decreased suddenly due to the disappearance of the creeping film. However, since at any point below the phase curve in Fig. 1 there is a phase of low He³ concentration which is below its λ point, we think it quite likely that Daunt has in fact measured one side of this phase curve, the low He³ concentration phase disappearing as the curve is crossed during the warmup.

We hope to obtain shortly a more accurate phase diagram, and perhaps an answer to the question raised in the preceding paragraph, by working with solutions of other concentrations. A complete report on these findings will be reported later.

[1] Fairbank, Ard, Dehmelt, Gordy, and Williams, Phys. Rev. 92, 208 (1953).
[2] Fairbank, Ard, and Walters, Phys. Rev. 95, 566 (1954).
[3] Prigogine, Bingen, and Bellemans, Physica 20, 633 (1954).
[4] G. V. Chester, Proceedings of the Paris Conference on the Physics of Low Temperatures, 1955 (Centre National de la Recherche Scientifique and UNESCO, Paris, 1956), p. 385.
[5] J. G. Daunt and C. V. Heer, Phys. Rev. 79, 46 (1950).

Nuclear Resonance Experiments on Pure He³ Under Pressure*

G. K. Walters† and W. M. Fairbank

Department of Physics, Duke University, Durham, North Carolina

PRELIMINARY measurements using nuclear magnetic resonance techniques[1,2] have been made on the density of He³ at 1.2°K as a function of pressure, and on the nuclear susceptibility of He³ as a function of pressure between 0.2°K and 1.2°K.

TABLE I. Density of He³ as a function of pressure at 1.2°K.

Pressure (atmospheres)	Volume susceptibility (arbitrary units)	Density[a] (grams per cc)
0	1.00	0.0815
0.62	1.02	0.0831
0.97	1.04	0.0847
3.75	1.12	0.0913
6.89	1.20	0.0978
10.8	1.24	0.101
21.7	1.34	0.109
32.8	1.40	0.114

[a] Density values are relative to the value at zero pressure as measured by Kerr.[3]

Densities were determined from measurements as a function of pressure of the strength of the nuclear resonance absorption signal from a He³ sample of constant volume. Pressures were transmitted to the sample through the compressed vapor above it. Since at 1.2°K, where these measurements were made, the susceptibility of liquid He³ at its saturated vapor pressure is known to deviate from the Curie value by no more than 5%,[1,2] while measurements reported below indicate that if anything, the deviation becomes smaller as the pressure is increased. The error introduced by assuming the density to be directly proportional to the strength of the observed absorption signal should be no more than 5% at the highest pressures, and proportionately less at lower pressures.

An independent check on the density data, accurate to about 5%, was made by measuring the quantity of He³ required at each pressure point to fill the constant-volume sample container. Agreement between results of the two methods was quite good.

Results of the density measurements are tabulated in Table I. The error in the values given there should be less than ±2%, excluding the possible error discussed above due to changes in the susceptibility per atom as the pressure is increased. Since only relative values of the density could be measured by the method used, the data are normalized to the known value of the density of He³ at 1.2°K under its saturated vapor pressure.[3] The coefficient of isothermal compressibility at 1.2°K is determined graphically from these data to be about 3% per atmosphere for He³ under its saturated vapor pressure, a value approximately three times the corresponding value for He⁴. Using this value for the compressibility, the velocity of sound at 1.2°K in liquid He³ at its saturated vapor pressure is calculated, from the classical formula, to be 195 meters per second, about $\frac{4}{5}$ the velocity in He⁴.

For each pressure point, the sample was cooled to 0.2°K and changes in the volume of the compressed vapor above the sample were observed as the system warmed up to 1.2°K. In this way it was determined that the change in density of liquid He³ at any pressure is less than 1% for all temperatures between 0.2°K and 1.2°K. Hence, the data tabulated in Table I hold,