Susceptibility Measurements of Impurity-Helium Condensates Containing Magnetic Impurities

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Abstract. The magnetic susceptibilities of impurity-helium condensates (IHCs), containing nanocrystals of molecular oxygen and atomic nitrogen free radicals embedded in molecular $\text{N}_2$ have been measured via a SQUID magnetometer in the temperature range between 1.1 and 2.1 K. The susceptibilities of the samples containing nitrogen atoms followed Curie-Weiss behavior with very small Weiss temperatures ranging from 0 to -0.4 K. The behavior of samples composed of $\text{O}_2$ nanocrystals deviated sharply from results for bulk solid. The susceptibilities of the samples were $10^2$ larger than for bulk solid $\text{O}_2$ and showed Curie-Weiss behavior with a Weiss temperature in the range from -4.5 K to -5 K. This result is qualitatively consistent with results obtained in other laboratories for $\text{O}_2$ confined in restricted geometries.

1. Introduction
Impurity-Helium Condensates (IHCs), also known as Impurity-Helium Solids, are formed when a beam consisting of mixed gases of helium and an impurity (in our case either molecular oxygen, or molecular nitrogen containing free radical atomic nitrogen) penetrates through the surface of superfluid $^4\text{He}$ contained in a sample beaker [1, 2, 3]. The impurity molecules adhere to one another to form clusters of order 5-10 nm diameter [4, 5, 6], each coated by a thin layer of solid helium. The clusters then aggregate into a gel-like condensate in the sample beaker. The N atoms are produced when the beam is passed through a radiofrequency discharge in route to the sample collection beaker. The strongly paramagnetic molecular oxygen contained in the samples has been studied by SQUID magnetometer techniques in this work. Similarly, the magnetization of small populations ($\sim 10^{18} - 10^{19}$ cm$^{-3}$) of atomic N contained in the molecular nitrogen samples was also studied by this method. Previously, magnetic studies on bulk solid $\text{O}_2$ were performed by Kamerlingh-Onnes and Perrier in 1910 [7]. More recent work has been reviewed by DeFotis [8] and Freiman and Jodl [9]. The magnetization of N atoms embedded in solid $\text{N}_2$ was measured in AC bridge studies by Fontana in 1959 [10]. Extensive electron spin resonance studies [11] recently performed on IHCs composed of N atomic free radicals contained in $\text{N}_2$ clusters will be compared with SQUID data obtained in this work.

2. Apparatus & Procedure
The detailed experimental arrangement in these studies is described elsewhere [12]. The SQUID magnetometer and the sample preparation system were inside a glass helium Dewar. The samples...
were first collected in the funnel at the top of the beaker shown in fig. 1a. A Teflon plunger was then employed to push the sample into the cylindrical tube at the bottom of the beaker, after which the sample was further compressed. Final sample heights were between 0.5 and 1.4 cm. The gas flow into the low temperature region was carefully metered, but previous experiments showed that the collection efficiency into the cell was only 14% [13]. The sample mass actually collected was obtained by taking this into account. The sample density was obtained by dividing this quantity by the sample volume.

Following sample collection, the quartz sample beaker is lowered into the region of the Dewar containing the SQUID pick up coils. The coil system consisted of a pair of counter wound coils (shown in fig. 1a) separated by a distance of 24 mm. The magnetization measurements were performed by the method of extraction, in which the sample beaker is raised and lowered through the coil system. A typical SQUID voltage trace is obtained as the sample is moved through the pickup coils as shown in fig. 1b. The calibration of the SQUID apparatus was performed with a small Pb sphere of known mass. The results were also corrected for the different lengths of the samples as discussed in Ref. [14]. A more extensive discussion of our experiments has recently been published [12].

3. Results

3.1. N-N2-He samples

Plots of the inverse susceptibility vs temperature for three of the N-N2-He samples are displayed in fig. 2. The two sets of data are for the same sample with different compressions. The lines correspond to a Curie-Weiss temperature dependence \( \chi = C/(T - \theta) \), where the small temperature intercepts indicate that the magnetic interactions between the N atomic radicals are very weak with values ranging from +0.04 K and to -0.38 K. The value of \( n \), the number of N free radicals was obtained by employing the Curie-Weiss formula

\[
\chi = m/H = \frac{n g^2 \mu_B^2 S(S + 1)}{3k_B(T + \theta)}
\]

where \( \chi \) is the susceptibility, \( m \) is the measured magnetic moment of the sample, \( H \) is the applied field, \( k_B \) is the Boltzmann constant, \( T \) is temperature, and \( \theta \), the Weiss temperature, corresponds to the intercepts of the lines with x axis in fig. 2. A further small correction can be made for the hyperfine levels of nitrogen, but this was found to be negligible [12].
Figure 2. The temperature dependence of the inverse susceptibility of the N-N$_2$-He samples obtained by condensing gas mixture of N$_2$:He=1:100. Symbols: □- first sample with 1.4 cm height, △- second sample compressed to 0.6 cm height, ○- third sample with 1.0 cm height, ◦- third sample compressed to 0.5 height. The lines in the figure represent Curie-Weiss dependences as discussed in the text.

Typical average N radical concentrations were found to be $(1.55 \pm 0.65) \times 10^{18}$ cm$^{-3}$, which is considerably smaller than the largest concentrations, $2 \times 10^{19}$ cm$^{-3}$ found in the previous ESR measurements [11]. This discrepancy might be explained by possible recombination during the compression of the sample from the funnel into the lower portion of the cell. Further compression increased concentrations to values of $5 \times 10^{18}$ cm$^{-3}$.

3.2. O$_2$-He samples
Since oxygen molecules are strongly paramagnetic, it was not necessary to subject the incoming beam to a radiofrequency discharge to provide a magnetic sample. Furthermore, since every O$_2$ molecule is a paramagnetic center, an extremely high density of paramagnets was obtained. The magnetic susceptibilities were again obtained by taking into account the 14% collection efficiency discussed for the nitrogen experiments [13]. The inverse magnetic susceptibilities vs. $T$ for the same O$_2$ sample with different compressions are plotted in fig. 3. The most notable features of these results are the extremely large values of $\theta$, in the range -4.5 K to -5 K, and the very large susceptibilities $\sim 7 \times 10^{-3}$ cm$^3$/g. The large magnitude of $\theta$ reflects the strong antiferromagnetic tendencies of the O$_2$ molecules in the clusters forming the IHC samples in these experiments. The large susceptibilities observed in these experiments contrast sharply with earlier measurements on bulk solid O$_2$ in the $\alpha$ phase [15]. The susceptibility of the bulk solid O$_2$ between 1 and 4 K is only $5 \times 10^{-5}$ cm$^3$/g, two orders of magnitude less than that observed in the IHC samples. Since the oxygen molecules are confined in small $\sim 10$ nm diameter sized clusters, their magnetic and Van der Waals interactions will be affected. Therefore it is of interest to make comparisons between our data and the magnetic properties of solid oxygen confined in porous media. Studies of O$_2$ confined in porous Vycor glass [16] (pore size $\sim 6.5$ nm) and more recently in gelsil [17] (pore size $\sim 4.5$ nm) at least qualitatively confirm the IHC results obtained in this work. The confinement seems to have the effect of suppressing the antiferromagnetic transition seen in bulk solid O$_2$, leading to much larger susceptibilities in the confined samples.
Figure 3. The temperature dependence of the inverse susceptibility for the O$_2$-He condensates formed by condensing gas mixture of O$_2$:He=1:200. Symbols: • - sample with height 1 cm and ⊙- the same sample compressed to 0.5 cm height. The lines in the figure represent Curie-Weiss dependences as discussed in the text.

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