Possible role of adsorbed O$_2$ on the ^{3}He–cerium-magnesium-nitrate thermal boundary resistance*

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(Received 11 August 1975)

The effect of adsorbed O$_2$ on the thermal boundary resistance between ^{3}He and either cerium magnesium nitrate or metals with magnetic impurities is discussed. The assumption that the ^{3}He interacts magnetically with magnetic moments right on the surface is justified, and certain features of the experimental data are reinterpreted.

The thermal boundary resistance between liquid ^{3}He and either magnetic salts or metals with magnetic impurities is of considerable importance in low-temperature physics. The normal Kapitza resistance R_K (heat carried by phonons) varies as T^{-3}, whereas the magnetic resistance R_M apparently varies as T or T^{-2}, depending on whether the temperature is above or below the ordering temperature of the magnetic atoms. Thus at very low temperatures the observed thermal resistance across the interface can be much less than expected due to phonon conduction alone. This fact is central to the technical problem of refrigerating ^{3}He to submillidegree temperatures.

The magnetic atoms at or near the surface of the solid play a crucial role in coupling to the dipole moment of the ^{3}He atoms. In this paper, we discuss the effect adsorbed paramagnetic O$_2$ molecules might have on the resistance, and re-examine an approximation made in the theories of this resistance and some of the experimental data.

Experimental data on R_M have been obtained by Abel *et al.*,[1] Black *et al.*,[2] and Bishop *et al.*[3] on the magnetic boundary resistance between ^{3}He and cerium magnesium nitrate (CMN); by Bishop and Mota[4] on Na$_3$[Ce(C$_7$H$_3$NO$_4$)$_3$]·15H$_2$O (CDP); by Avenel *et al.*[5] on Pd and Au containing magnetic impurities; and by Bishop *et al.*[6] on Pt. A theoretical explanation of the linear dependence of R_M on T as seen in CMN and CDP was first given by Leggett and Vuorio.[7] Their result was rederived by Guyer[8] in a way that relates R_M to the longitudinal relaxation time of the magnetic ions. Mills and Béal-Monod[9] showed that any magnetic coupling between ^{3}He and the conduction-electron spins in a metal is several orders of magnitude too small to account for the resistances reported in Ref. 5, and they concluded the coupling was with magnetic impurities. In addition, they examined[10] the effect of the ordering temperature of the magnetic ions in the solid on the magnetic resistance and derived the T^{-2} dependence reported in Ref. 6 for R_M in Pt below the transition temperature of the magnetic impurities at all but the lowest concentrations of ^{4}He in ^{3}He.

The very good agreement between the experimentally observed temperature dependence of R_M in CMN and Pt and that predicted by theory makes a strong case for the correctness of the basic assumption of magnetic coupling between the magnetic moments of ^{3}He and the solid. In addition, the agreement[8,11] between experiment and theory on the dependence of R_M on an applied magnetic field and on R_M between solid ^{3}He and CMN lends further weight.

There is, however, the distinct possibility that the magnetic coupling is not between He and magnetic atoms right at or near the surface, but rather partly or completely between ^{3}He and adsorbed paramagnetic O$_2$ molecules, which are right on the surface. There is direct experimental evidence[12,13] that O$_2$ is absorbed on Y(C$_2$H$_5$SO$_4$)$_3$ ·9H$_2$O (YES) and that it is paramagnetic. There is indirect evidence[13] for adsorption on La$_2$Mg$_3$(NO$_3$)$_{12}$ ·24H$_2$O (LMN). The experiments described in Refs. 12 and 13 are concerned with the spin-bath relaxation of nuclear Zeeman energy at the surface of small crystallites at He temperatures. The presence of paramagnetic O$_2$ on YES was verified by the observation of an increased relaxation time when the crystallites were ground and sifted in a nearly O$_2$-free environment rather than in air. The LMN crystallites exhibited relaxation times that had the same crystallite size dependence as did the YES and which can only be explained by assuming that they too had paramagnetic O$_2$ adsorbed on the surface. The only difference between CMN and LMN is the substitution of Ce for La; thus the CMN and LMN should behave identically with respect to adsorbed O$_2$. Data on the adsorption of O$_2$ at NTP on silica gel,[14] and powdered NaCl,[15] indicate that the coverage might be the order of $\frac{1}{100}$ of a complete monolayer. This corresponds to an average O$_2$-O$_2$ spacing of about 37 Å.

If we assume, then, that paramagnetic O$_2$ is adsorbed on CMN (as well as other materials in contact with ^{3}He), we can make several observa-

tions. The first concerns the justification for the contact-interaction approximation made in several of the theoretical papers, and the second concerns the interpretation of the effects of adding ^{4}He to ^{3}He. The authors of Refs. 7 and 9 assume that the Ce atoms are located right on the surface. Since the dipole interaction falls off as r^{-6}, this has the effect of singling out only those interactions between ^{3}He atoms right next to a Ce ion as important in contributing to the energy transfer. When this contact-interaction approximation is made, surprisingly good agreement with experiment is obtained. It is highly unlikely, however, that the Ce ions are located right on the surface. There are 123 other atoms for every two Ce atoms and it is probable that each Ce ion near the surface is still surrounded by at least some of the water molecules. In contrast, adsorbed O_2 would be right on the surface, and the contact-interaction approximation is valid with respect to the O_2-^{3}He coupling. The coupling of the O_2 to the Ce ions is certainly much stronger than the coupling between ^{3}He and either O_2 or Ce, since the magnetic moment of O_2 is some 10^3 times larger than the ^{3}He moment and its frequency of motion is much closer to that of Ce than that of the ^{3}He atoms. Thus the O_2-Ce contact will not be a limiting factor.

Support for the assumption that the ^{3}He atoms interact predominantly with magnetic moments right on the surface of CMN is also found in the experimentally observed[2] increase of R_M when small amounts of ^{4}He are added to the ^{3}He. It is known[16] that a ^{4}He surface film is formed in a ^{3}He-^{4}He solution. This ^{4}He film will completely coat the CMN particles when the amount of ^{4}He in the ^{3}He is large enough. When roughly monolayer coverage is provided, R_M increases many times. In the past this has been explained qualitatively with the statement that the separation of the ^{3}He and Ce ions is increased. If the Ce ions were right on the surface this would be plausible. If, on the other hand, the Ce ions are located beneath the surface with a separation from the ^{3}He of several He-atom diameters, then an increase of another He-atom diameter in the spacing will not have an abrupt effect. With the Ce below the surface and no adsorbed O_2, there is no explanation for the experimentally observed, very abrupt increase in R_M when roughly one monolayer of ^{4}He forms on the CMN particles.[2] It is found that the surface resistance increases to the normal phonon

Kapitza value. There is no contradiction if the interaction is between adsorbed O_2 on the surface and ^{3}He. Thus the abrupt change in resistance when a roughly-one-monolayer ^{4}He film covers the CMN supports the contact-interaction assumption, and the presence of O_2 right on the surface makes this assumption plausible.

A qualitatively different behavior, however, is seen in the data of Bishop et al.[6] on R_M between Pt and ^{3}He. For ^{4}He concentrations in the ^{3}He above about 500 ppm, R_M gradually increases, reaching a value about eight times the minimum R_M when the ^{4}He concentration is 7000 ppm. This gradual increase is in contrast to the very abrupt change of R_M with Ce and ^{3}He when ^{4}He is added. The temperature dependence of R_M for Pt-^{3}He remains the same as ^{4}He is added, $R_M \propto T^{-2}$, rather than going over to a T^{-3} dependence characteristic of the phonon Kapitza resistance. This behavior is expected if the magnetic impurities in Pt are well below the surface, for then an increase of several He-atom diameters in the ^{3}He-magnetic-impurity separation owing to the ^{4}He film would have only gradual effect.

The data for the lowest concentration of ^{4}He in ^{3}He, 30 ppm, however, show R_M definitely deviating from the T^{-2} dependence below about 4 mK; the value of R_M appears to be leveling off as T is reduced. If there were a small amount of O_2 adsorbed on the Pt wires and if 30 ppm ^{4}He corresponds to about one-monolayer coverage, then the leveling off of R_M as T is reduced is due to the onset of a magnetic coupling between ^{3}He and O_2. At lower concentrations of ^{4}He we would then expect to see $R \propto T$, as with CMN.

It would be interesting to have experimental data on the effect of adsorbed O_2 on the thermal resistance between ^{3}He and various substances. However, there are experimental problems that will make it difficult to remove adsorbed gases without destroying the crystal. An attempt to grind up a crystal of yttrium ethyl sulfate in an O_2-free atmosphere did reduce the amount of adsorbed O_2 but did not eliminate it.[13] Small particles of metals and more stable crystals can probably be heated in a high vacuum to remove the O_2, H_2O, and other adsorbed gases, and then kept clean until covered with ^{3}He. In any case, an exact quantitative interpretation of an experiment on the magnetic thermal resistance must take into account the effects of any adsorbed O_2, as well as water vapor and other gases.

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