Temperature-Dependent Electrical Resistivity of Potassium below 2 K

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Recent measurements of the temperature-dependent electrical resistivity ρ_T of potassium down to 1.1 K have indicated the presence of a possible new term AT^n, with $2>n>1$ and $A\propto\rho_0$, the residual resistivity. We have measured ρ_T down to $\simeq 0.5$ K in order to confirm the existence of this term and to examine it more closely. We indeed find $A\propto\rho_0$ and $n\simeq 1.5$. We speculate that it arises from the electron-electron interaction modified by a size effect and possibly dislocation scattering.

Recent developments in high-precision techniques[1] have made possible the measurement of the temperature-dependent resistivity, ρ_T, of pure metals below 1 K. Our bridge is capable of resolving 0.1 ppm of a ~500-$\mu\Omega$ four-terminal resistor with a power dissipation in the resistor of less than 500 nW. The precision is obtained by using a commercial dc current comparator[2] developed by MacMartin and Kusters[3] and the sensitivity is obtained by using a SQUID (superconducting quantum interference device) null detector. Earlier measurements[4,5] were limited in precision to ~100 ppm and could not explore ρ_T in potassium below ~2 K. Van Kempen *et al.*[6,7] have used a bridge similar to ours and have measured down to 1.1 K using a pumped ^{4}He bath, whereas we have investigated ρ_T from 4 down to 0.5 K using a ^{3}He cryostat.[8]

Our samples were made from high-purity potassium purchased from the Mine Safety Appliance Company. A wire 0.79 mm in diameter and typically 1.8 m in length was extruded in the ^{4}He atmosphere of a "dry box." Then it was loosely wrapped into a helical groove which had been previously machined in a 3-cm-diam Teflon cylinder. Potassium wires, which served as potential leads, were welded to the specimen. The length between probes was carefully measured to evaluate the shape factor. The ends of the current and potential leads were melted onto tinned copper wires which had previously been immersed in mercury for 3 h. The copper wires were sealed through holes in a brass plate with epoxy resin and the specimen was enclosed in a brass can. The completed specimen in its sealed, ^{4}He-filled can could then be transferred from the dry box to the cryostat. It was tested to ensure that the contact resistances were small (<200 $\mu\Omega$) and current independent (± 1%) at 4.12 K. The comparison resistance, made of a special Pd-Pt alloy,[1] had a nominal value of 200 $\mu\Omega$ and was mounted on the pumped ^{4}He stage of the cryostat where its temperature could be maintained at a constant value.

Two samples, K1 and K2, have been prepared and stored at room temperature for periods as long as several months between low-temperature measurements. Except for specimen K1b, the measured room-temperature resistance of each specimen was within ~3% of the value calculated from the known resistivity of potassium and the wire dimensions. Unfortunately some oxidation or other deterioration appeared to change the effective area of K1 as time passed and it was necessary to correct the measurements on K1b by 30% to obtain the expected resistivity at 77 K and higher temperatures. All resistivities obtained for K1b in this way agreed within our experimental error with the resistivity of a similar specimen, K2c, measured later. The thermal contraction of potassium has been neglected and this, combined with the accuracy of our measurements above helium temperatures, limits the accuracy of the absolute resistivities to $\simeq 1\%$, but the uncertainties in relative values below 4 K on a given specimen are $\pm 2\times10^{-15}$ Ω cm (2 fΩ cm) with a measuring current of 5 mA and half that with 10 mA.

The residual resistivity, ρ_0, of the samples decreased with age as shown in Table I. This slow annealing behavior has been observed before,[7]

TABLE I. Details of specimens.

Specimen	ρ_0 (nΩ cm)	$d\rho/dI$ (fΩ cm/mA)	I (mA)	Time after extrusion (days)
K1a	5.63	− 60 ± 2	5	2
K1b	1.50	− 7 ± 0.5	5	25
K2a	2.07	− 8.5 ± 0.5	10	45
K2b	1.50	− 4.5 ± 0.5	10	100
K2c	1.53	− 6.0 ± 0.5	10	160

yet is very surprising since Gugan[5] showed that simple defects annealed in minutes much below room temperature. It suggests that relatively gross changes, such as secondary recrystallization or possibly void agglomeration, are occurring.

The four-terminal resistivity, ρ, of each specimen had the small, temperature-independent, approximately linear current dependence shown in Table I. In all cases the resistance decreased with increasing current. The characteristics are not those due to Joule heating and are probably intrinsic to the sample. We provisionally ascribe it to size-dependent magnetoresistance in which the small self-field of the current tends to bend the electrons away from collisions with the boundaries. To eliminate complications due to the current dependence we made all further measurements at the fixed currents shown in Table I.

After subtracting ρ_0 from the measured resistivities the temperature-dependent resistivities, ρ_T, remain. The values of ρ_T/T^5 for specimens K1a, K1b, and K2c are plotted in Fig. 1 along with the calculations of Taylor, Leavens, and Shukla[9] ρ_{ph}, the resistivity due to phonon scattering, in the Bloch limit (no phonon drag) and in the limit of full phonon drag. The value of ρ_T/T^5 in the Bloch limit as $T \to 0$ K calculated by other authors[4,10] is about 40% higher, and is also indicated in Fig. 1. These experimental data and those for our other specimens are in good agreement with earlier experiments in the higher part of the temperature range.[4,5,7] The agreement appears to be sample independent, particularly since van Kempen *et al.*,[7] who measured down to 1.1 K, used quite different methods of sample preparation. That the experimental data for the well-annealed samples (K1b, K2a, K2b, K2c) fall below the Bloch curve between 3 and 2 K is undoubtedly due to the presence of phonon drag in these specimens as pointed out by van Kempen *et al.*[7] It is noteworthy that the phonon drag is stronger in the speciments with lower ρ_0, as would be expected. However, even in the purest specimens, the phonons will be brought into equilibrium at low enough temperatures by boundary scattering and ρ_T will rise once again to the Bloch limit. It is possible that the results of van Kempen *et al.*[7] could be explained in this manner. However, there is a large extra resistivity in our experimental results that cannot arise from phonon scattering alone, whichever value[4,9,10] is used for the Bloch limit. We chose to make $\rho_T = 0$ for the lowest-temperature reading in each set of measurements shown in Fig. 1 to emphasize that even with this largest possible choice for ρ_0 the extra low-temperature resistivity cannot be removed, but, although the choice of a reasonable lower value for ρ_0 would increase the lowest-temperature ρ_T values substantially, it would not significantly affect them above 2 K.

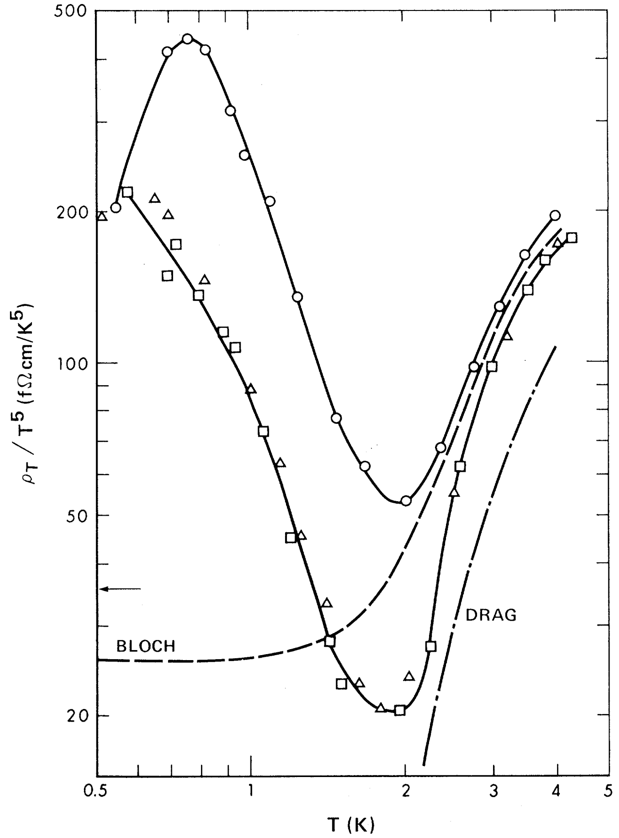

FIG. 1. Experimental data for the temperature-dependent electrical resistivity ρ_T in unannealed (○, K1a) and annealed (□, K1b; Δ, K2c) potassium. These are compared with the theoretical predictions (broken lines) of Ref. 9 for ρ_{ph} in the phonon-drag and Bloch (no drag) limits. We are grateful to Taylor, Leavens, and Shukla (Ref. 9) for unpublished data on the Bloch curve below 2 K. The arrow on the ordinate indicates the Bloch limit as $T \to 0$ K calculated by Froböse (Ref. 10) and Ekin and Maxfield (Ref. 4).

Van Kempen *et al.*[7] discuss the possibility that the low-temperature resistivity arises from electron-electron interactions which are expected to produce a resistivity proportional to T^2. To obviate the problem of the choice of ρ_0 in determining the temperature dependence of the low-temperature data, we have plotted the values of ρ vs T^n for $n = 1.0$, 1.5, and 2.0 and show those for specimen K2b in Fig. 2. For each of our specimens $n = 1.5$ fits the data better than the adjacent integral values. The slope of the straight lines does, however, vary with the residual resistivity of the specimens. If we write $\rho_T = AT^{1.5}$ then $A/\rho_0 = (86 \pm 10) \times 10^{-6}\ \mathrm{K}^{-1.5}$. It is not possible to fit the data with a single term proportional to T^2, but they may be fitted by two terms varying as low powers of T, one of which may be sample independent and similar to that calculated by Lawrence and Wilkins[11] for the electron-electron resistivity. The remaining, strongly ρ_0-dependent term could arise from the presence of electronic resonances (virtual bound states), associated by Brown[12] with linear defects, such as dislocations, in metals. Further knowledge of the dislocation density in annealed potassium specimens is needed to clarify their role in ρ_T.

Inelastic impurity scattering has had much discussion but it is generally accepted[13,14] that it is too small to be identified. Even the largest reasonable theoretical figures are an order of magnitude lower than the experimental values for ρ_T below 1 K.

A mechanism that, according to our estimates, can provide a temperature-dependent resistivity quite sufficient to account for the experimental results is the size effect associated with the Knudsen flow of electrons in the transition region where most of their collisions are with boundaries.[15] Lawrence and Wilkins[11] (see their Table I) calculate that the relaxation time for the (nonresistive) electron-electron N processes is $\tau = 1.09 \times 10^{-7}$ sec in potassium at 1 K. With the use of $V_F = 8.6 \times 10^5$ m sec^{-1}, this yields for the mean free path of the electrons $\lambda = V_F \tau = 9$ cm. If such a gas is confined to a long cylinder of radius r with diffusely scattering walls it will experience a flow resistance due to boundary scattering that varies as $\rho_0(1 + kr/\lambda)$, where k for gases[16] and for phonons in liquid helium[17] is approximately unity. Since for electrons $\lambda \propto T^{-2}$, the leading term in the temperature dependence of the resistivity will be proportional to T^2, and for $r/\lambda \simeq 0.005$, which corresponds to the potassium specimens near 1 K according to the calculations of Lawrence and Wilkins, other terms will be negligible.

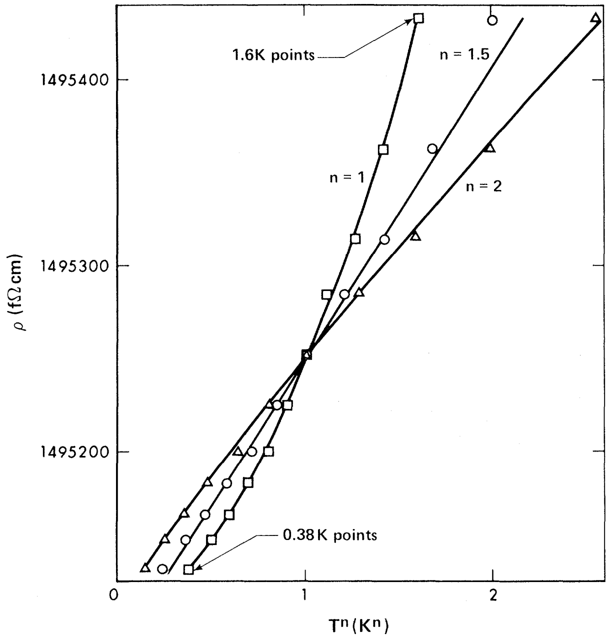

FIG. 2. Total measured resistivity (ρ) for specimen K2b plotted against T^n; $n = 1,\ 1.5,\ 2$.

Kukkonen and Smith[18] have shown that τ could be an order of magnitude smaller, and then, because a term in $(r/\lambda)^2$ may be important, $\rho_T = BT^2 - CT^4$, which is also consistent with our data. Of course, even for the purest specimen $\rho_0 = 1.5 \times 10^{-9}\ \Omega$ cm, which yields for the resistive mean free path $\lambda_0 = m/\rho_0 n e^2 = 0.15$ mm. There is, therefore, substantial scattering in addition to that at the boundaries, some of which may be off internal boundaries formed, possibly, of nets of dislocations surrounding relatively pure material. The effect of these nets may be a reduction in the effective radius of the specimen.

This suggests that in addition to experiments at lower temperatures, other avenues of investigation may be fruitful. We plan experiments on specimens of different diameter and on dilute alloys with different fractions of the residual scattering arising from point (chemical) imperfections to differentiate between the various possible scattering mechanisms.

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Nuclear Spin-Lattice Relaxation by Localized Electronic States in an Amorphous Semiconductor

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It is demonstrated that the spin-lattice relaxation rate for thallium nuclei in the glassy semiconductor $Tl_2SeAs_2Te_3$ between 130 and 300 K is limited by spin diffusion and is a thermally activated (Arrhenius) process. These facts indicate that the dominant relaxation mechanism is provided by thermally activated localized electronic states in the gap whose density can be estimated from the measured spin-lattice relaxation time.

It is widely accepted that many of the optical and electronic properties of amorphous semiconductors are determined by localized states in the forbidden gap.[1,2] Several phenomenological models have been proposed to explain the nature and energy distribution of these states, and various studies of optical and electronic properties of amorphous semiconductors, such as chalcogenide glasses, have been interpreted in terms of localized gap states. This Letter demonstrates for the first time that nuclear magnetic resonance (NMR) techniques can provide a new method of detecting and studying the localized electronic states in the gap of amorphous semiconductors. We have observed that under certain conditions thermally activated localized electronic states provide the dominant nuclear spin-lattice relaxation mechanism in semiconducting chalcogenide glasses and, when these conditions prevail, pulsed NMR techniques can be used to detect and estimate the density of these localized states.

In metals and highly conducting degenerate semiconductors, strong interactions between the nuclear spins and the conduction electrons produce a shift (the Knight shift) in the magnetic field position of the NMR and can provide the dominant relaxation mechanism[3]; the relaxation rate in these materials can be calculated from the observed Knight shift on the basis of the Korringa relation. NMR studies of highly conducting liquid semiconductors have established that the interaction of the nuclear spins with the delocalized carriers also produces an observable Knight shift.[4,5] However, in these materials the occurrence of a significant amount of carrier localization causes the spin-lattice relaxation rate to be enhanced relative to that predicted on the basis of the Korringa relation. In solid amorphous semiconductors such as chalcogenide glasses, where the electrical conductivity is much lower and some of the carriers are highly localized, no Knight shift is observed[6] and the analysis of the relaxation process developed for liquid semiconductors in Refs. 4 and 5 is not applicable. We report here detailed NMR measurements of the spin-lattice relaxation time as a function of temperature in a semiconducting