g Value of Potassium Conduction Electrons

W. M. WALSH, JR., L. W. RUPP, JR., AND P. H. SCHMIDT
Bell Telephone Laboratories, Murray Hill, New Jersey
(Received 8 September 1965)

Spin resonance of conduction electrons has been observed near 12 Gc/sec in sheets of vacuum-distilled potassium metal in the temperature range from 1.3°K to room temperature. Linewidths on the order of, or less than, one gauss at liquid-helium temperatures permit an accurate g-value determination: $g_K = 1.9997(8) \pm 0.0001$. The experimental g shift is in close agreement with values recently calculated by Bienenstock and Brooks neglecting polarization of the ion cores. Variations of line shape and apparent intensity with the orientation of the applied magnetic field relative to the sample plane have been observed at the lowest temperatures.

I. INTRODUCTION

THE spin resonance of conduction electrons in metallic potassium has previously been observed both in bulk[1,2] and particulate[3,4] specimens. Excessive linewidth resulting from impurity or phonon scattering has, however, prevented an accurate determination of of the g shift of this spin system. Such a measurement is of interest as an experimental test of the calculations of Bienenstock and Brooks.[5] Using bulk planar specimens of highly purified metal we have observed linewidths considerably less than a gauss in the liquid-helium temperature range and have, therefore, been able to measure the potassium g shift to $\pm 4\%$ accuracy.

In addition, both the shape and the apparent intensity of the narrow conduction electron spin resonance (CESR) line observed at very low temperatures are found to depend on the orientation of the applied magnetic field with respect to the sample surface.

Experimental details are outlined in the following part of the article. Section III is devoted to the g-shift measurement while the geometrical effects are presented in Sec. IV.

II. EXPERIMENTAL DETAILS

The potassium used in these experiments was obtained from the Mine Safety Appliances Research Corporation, Callery, Pennsylvania, with a nominal purity of 99.95%. This starting material was further purified by vacuum distillation. Details of the process will be published elsewhere.[6] Spectrochemical analysis reveals no measurable impurities in the distillate, i.e., levels of a part-per-million or less of detectable contaminants. Resistivity ratio measurements between room temperature and 4.2°K yield values close to 8000 for the distilled metal, the ratio increasing to ~13 000 at 1.3°K.

Samples for the microwave experiments are prepared by rolling out freshly etched pieces of the reactive bulk metal between layers of Parafilm[1] under degassed mineral oil (Nujol). Typical specimen thicknesses are 0.2 mm. Rectangular samples are cut from the sheet with a stainless steel blade and are then pressed onto an inner face of a $\frac{1}{2}\lambda_g$ rectangular waveguide cavity resonant near 12 kMc. As soon as possible after sample installation the cavity and its associated waveguide feed are evacuated to $\lesssim 10^{-2}$ Torr. The assembly is then cooled to 77°K in periods ranging from a minute to several hours. Further temperature reduction is effected quite rapidly. No marked deterioration (discoloration or loss of metallic sheen) has been observed of samples held in vacuum for periods up to a week, whereas a few hours suffice for samples to become markedly "tarnished" when stored under oil at room temperature or in liquid nitrogen.

The microwave spectrometer is a conventional Magic-Tee bridge using homodyne diode detection. Magnetic-field modulation at 165 cps may be used in the case of strong, narrow signals to display the absorption-versus-field curve directly on an oscilloscope after selective preamplification. Standard phase-sensitive demodulation techniques are used to record the field derivative of weaker changes in cavity loss. Typical driving power levels are ~10 to 200 mW with loaded-cavity Q values of ~2000.

An unexpected result of the sample encapsulation and mounting technique is the existence of appreciable microwave magnetic-field intensity on the sample face which is nearly, but not quite, in contact with the cavity sidewall because of the insulating Parafilm layer. In fact, CESR signals in this configuration are at least five times as intense as those obtained from samples of equal nominal area which are exposed to the microwave field on one face only. The latter situation was assured by embedding the sample in a recess milled into the cavity wall, a Parafilm cover then being pressed over the exposed face to retard corrosion. We believe the enhanced signal intensity of the "suspended" metal sample to result from propagation of a coaxial TEM mode which uses the sample as a very-far-off-center conductor and retains the microwave magnetic-field polarization of the waveguide cavity. Such a mode would have most of its intensity confined to the narrow space between the "center" conductor and the nearest part of the outer conductor (the waveguide cavity). Thus

[1] G. Feher and A. F. Kip, Phys. Rev. **98**, 337 (1955).
[2] J. E. Cousins and R. Dupree, Phys. Letters **14**, 177 (1965).
[3] R. A. Levy, Phys. Rev. **102**, 31 (1956).
[4] R. C. McMillan, J. Phys. Chem. Solids **25**, 773 (1964).
[5] A. Bienenstock and H. Brooks, Phys. Rev. **136**, A784 (1964).
[6] P. H. Schmidt, J. Electrochem. Soc. (to be published).

we obtain a significant improvement in effective filling factor of the waveguide cavity by the sample because of the "loading" effect of the coaxial mode. While certainly useful as a means of improving the spectrometer sensitivity, the existence of comparable microwave field intensities on both faces of the sample must be kept in mind when considering the rather strange line shapes observed at low temperature (Sec. IV).

The experimental geometry indicated in Fig. 1 has been used to compare the g value of potassium with that of metallic lithium which is essentially equal to that of the free electron.[1,7] The lithium reference samples were prepared and mounted in the same manner as that used for potassium. An oscilloscope display of the two resonances versus magnetic field at 4.2°K is shown in Fig. 2. Both lines have the asymmetric shape expected of resonance in a metal under anomalous skin effect conditions, i.e., where the carrier mean free path exceeds the penetration depth of the microwave fields.[1,8]

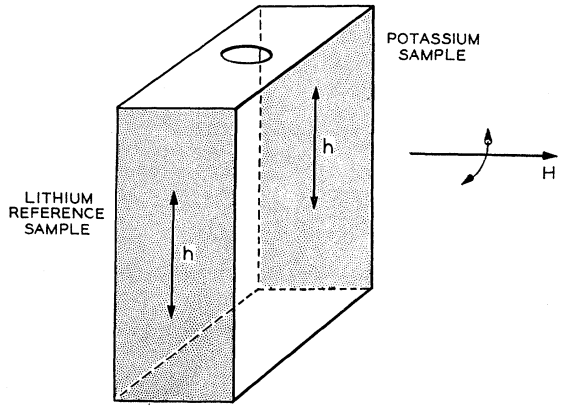

FIG. 1. A typical experimental geometry: sheet samples of potassium and lithium in Parafilm are pressed on opposite vertical sidewalls of a TE_{101} cavity in order to measure relative g values. The applied field **H** may be rotated in the horizontal plane for examination of tilt effects.

An initial experiment performed with the potassium sample placed on the horizontal end wall of the cavity permitted the applied field to be rotated with respect to the microwave magnetic-field-polarization direction on the sample. The potassium resonance intensity decreased to an unobservable level as the microwave and static magnetic fields were aligned, thus confirming the magnetic dipole character of the transition.

It is necessary to recognize that, while all samples of the redistilled metal which have been examined exhibit spin resonance, the width of the line and, to some extent, its shape (degree of asymmetry) at any temperature vary from sample to sample and, for a given sample, vary with previous thermal history. Such hysteresis presumably results from strains and corrosion unavoidably present as a result of the imperfect sample encapsulation procedure. In view of this lack of precise reproducibility the linewidth data displayed in Fig. 3 must be considered as upper bounds. Under such circumstances we will not attempt any serious discussion of transverse spin relaxation time (T_2) versus temperature of the kind recently presented for conduction electron spin resonance in sodium.[9] The dashed line labeled $T^{1.4}$ in Fig. 3 merely indicates the trend of the data.

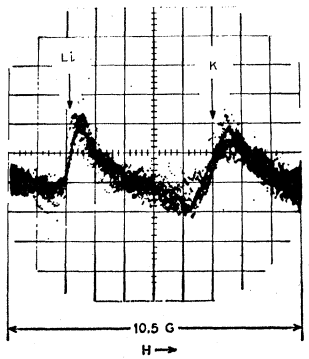

FIG. 2. An oscilloscope photograph of conduction electron spin resonance absorptions due to K and Li at 4.2°K and 11.750 kMc/sec. The geometry of Fig. 1 was used with **H** in the plane of the samples. Sample areas were equal within 5%. The field modulation amplitude at the samples was calibrated using proton nuclear magnetic resonance.

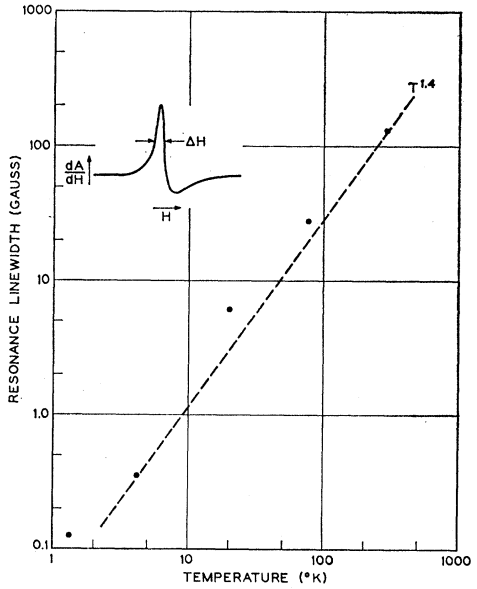

FIG. 3. Crude linewidth-versus-temperature data for potassium CESR. The data points are considered to be upper bounds due to lack of detailed reproducibility as discussed in the text. The linewidth is defined as the full width at half-height of the positive slope of the resonance. The dashed line labeled $T^{1.4}$ merely indicates the trend of the data and has no theoretical significance.

[7] R. J. Pressly and H. L. Berk, Bull. Am. Phys. Soc. **8**, 345 (1963); Phys. Rev. **140**, A1207 (1965).
[8] F. J. Dyson, Phys. Rev. **98**, 349 (1955).
[9] F. Vescial, N. S. VanderVen, and R. T. Schumacher, Phys. Rev. **134**, A1286 (1964).

III. THE g VALUE

Despite the lack of precise reproducibility in line shape and width mentioned above, the CESR linewidth of our redistilled potassium in the liquid-helium temperature range is consistently less than one gauss thus permitting the resonance field to be specified to within ± 0.2 gauss or less in a field of ~ 4200 G. The magnetic field is measured using nuclear magnetic resonance of protons in water located externally to the spin resonance Dewar assembly. Both nuclear resonance and microwave frequencies are determined by an electronic counter. A slight correction (~ 4 parts in 10^4) for the different positions of the proton and metal samples in the magnet gap is calibrated in a separate experiment using a paramagnetic resonance of known g value. If ν_μ and ν_ρ are the microwave and (corrected) proton frequencies measured in Gc/sec and Mc/sec, respectively, the g value is given by

$$g = 3.0420\, \nu_\mu/\nu_\rho . \tag{1}$$

Since, in fact, it is the shift of the potassium CESR with respect to that of the free electron ($g_0 = 2.00232$) which is of interest, an alternative (but fundamentally equivalent) method of measurement has also been used. It consists in determining the difference, $\delta H = H_K - H_{Li}$, between the resonance fields H_K and H_{Li} of conduction electron spins in potassium and lithium samples simultaneously present in the experimental cavity and symmetrically located in the magnet gap. Since, to the accuracy of interest here, the lithium g shift is zero, such a measurement yields the potassium g shift directly:

$$g_K - g_0 \equiv g_K - g_{Li} \simeq -(\beta/h\nu_\mu) g_{Li}^2 \delta H . \tag{2}$$

In Eq. (2), β is the Bohr magneton and it is apparent that only moderate precision is required in the determination of ν_μ and δH. A further advantage of this direct comparison is that the unknown and reference signals have similar line shapes and widths thus reducing the importance of any uncertainty in the exact fields for resonance due to line asymmetry (see Fig. 2).

The two techniques described above yield results consistent to within the stated accuracy

$$\begin{aligned} g_K &= 1.9997(8) \pm 0.0001 , \\ g_K - g_0 &= -0.0025(4) \pm 0.0001 . \end{aligned} \tag{3}$$

Undoubtedly greater precision could be attained by performing the experiment at higher microwave frequencies or by careful interpretation of the line shape, but there is little need for such refinement at present in view of theoretical uncertainties to be discussed below.

The g value reported here differs from those measured by McMillan in the temperature range 100–450°C (1.9982 ± 0.0005),[4] and by Cousins and Dupree at room temperature (1.9976 ± 0.0026).[2] It is likely that these discrepancies are due to the broader lines observed in the higher temperature experiments rather than to any appreciable temperature dependence of the g shift. We have not made any serious attempt to measure the g value above 4.2°K.

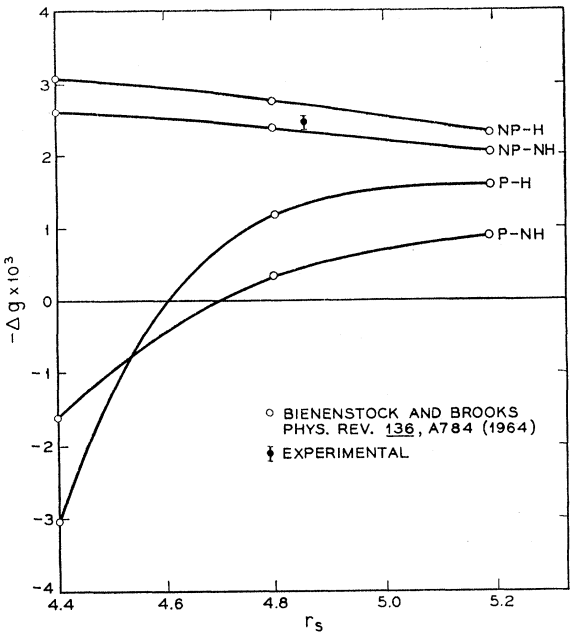

FIG. 4. Theoretical values of the potassium g shift computed by Bienenstock and Brooks for various values of the Wigner-Seitz sphere radius. The labels H or NH and P or NP correspond, respectively, to inclusion or neglect of a Hartree electron-electron interaction potential and a core-polarization correction. It is clear that the experimental point lies nearest the values calculated ignoring the core-polarization correction.

Recently, Bienenstock, and Brooks[5] have calculated the g shifts of the alkali metal conduction electrons using the general theory of Yafet.[10] Their results for potassium, as well as our experimental number, are shown in Fig. 4. The value of the Wigner-Seitz radius for potassium at low temperature is 4.86 in units of the Bohr radius, based on the x-ray data of Barrett.[11] Four theoretical curves are present in the figure corresponding to inclusion or neglect of a Hartree electron-electron interaction potential (H or NH) and of a core-polarization correction (P or NP). Rather good agreement with the experimental g shift is found if the core-polarization correction is ignored. There is little to choose between the calculated values with or without the Hartree potential. This situation is similar to that found in the case of sodium CESR save that for potassium the adverse effect of the core polarization is much more pronounced. It is apparent that if the theoretical calculations should be revised in the future, potassium provides an extremely good experimental check since its g shift is large enough to be measured with considerable accuracy.

[10] Y. Yafet, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1963), Vol. 14, p. 1.
[11] C. S. Barrett, Acta Cryst. 9, 761 (1956).

IV. LINE SHAPE AND APPARENT INTENSITY

In addition to modest hysteresis in the CESR linewidth and asymmetry versus temperature mentioned earlier, we have observed more interesting effects which depend on the angle made by the static magnetic field with the plane of the sample. These geometrical effects are observed only at the lowest attainable temperature (1.3°K) which leads to the smallest resonance linewidths. Since it is necessary to operate at appreciably reduced microwave power (5 mW or less incident on the cavity) in order to avoid sample heating as well as incipient "day" shifting of the line position,[12,13] the field derivative of the resonance is recorded in these experiments. As illustrated in Fig. 5, the differentiated line is most intense when the applied field lies in the plane of the sample. The width at half height of the positive slope peak is 0.13 G in this trace, corresponding to a transverse relaxation time T_2 of $\sim 0.8 \times 10^{-6}$ sec.[1] As the field is tilted a few degrees out of the sample plane the line initially splits into two partially resolved components. Upon further increase of the tilt angle the low-field component rapidly loses intensity and is not observed beyond 12°. The remaining component also loses intensity, though more slowly, and is barely detectable beyond 30° of tilt. The experiment has been repeated several times using different samples with similar results though the CESR lines are more typically 0.2–0.3 G wide which makes the splitting phenomenon almost unobservable. The over-all decrease in signal intensity with increasing tilt angle is, however, consistently reproducible.

The loss of signal intensity can be qualitatively understood when it is realized that at low temperature in such pure potassium the mean free path of the conduction electrons is ~0.5 mm, sufficient for completion of ~6 cyclotron orbits about the magnetic field required to observe spin resonance before scattering takes place. This estimate is confirmed by our observation of Azbel'-Kaner cyclotron resonance variations in the sample's surface impedance as the field is swept from 0 to 6 kG.[14] Under such circumstances carrier and, therefore, spin diffusion are inhibited transverse to the applied magnetic field because the cyclotron motion traps the carriers on the flux lines. Diffusion along the magnetic field is unaffected. As Dyson points out,[8] the spins which re-enter the microwave skin depth at random intervals over their entire coherent precision lifetime (T_2) contribute most to the observed sharp central resonance line. It is therefore reasonable that we should see the most intense signal in the geometrical configuration which most effectively prevents diffusion away from the sample surface. As the field is tilted away from the sample plane, diffusion along the field will carry spins out of the microwave penetration region (the anomalous skin depth modified by the Azbel'-Kaner cyclotron resonance phenomenon) and therefore statistically fewer of them will be able to interact with the radiation fields over their entire precession lifetimes. This anisotropic diffusion model has been used by Azbel', Gerasimenko, and Lifshitz[15] to calculate the tilt dependence of the resonance intensity. Direct comparison with their theory is not profitable at present, however, due to the line splitting observed in our experiments. The splitting may be an artifact arising from excitation of both faces of the thin sample. Further experiments are planned in order to study the CESR line shape and intensity under cyclotron resonance conditions.

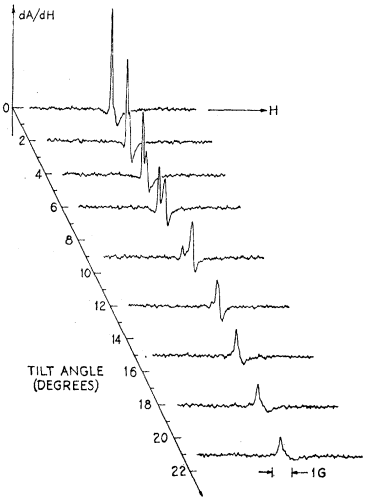

FIG. 5. The differentiated potassium CESR line as a function of the angle made by the magnetic field with the sample plane. The traces were taken at 1.3°K. The decrease in signal intensity as the tilt angle increases is attributed to anisotropic spin diffusion induced by the applied magnetic field under long mean-free-path conditions. The line splitting observed over the first 10° of tilt is not understood.

CONCLUSIONS

We have examined the conduction electron spin resonance in very pure bulk potassium metal. The measured g shift is in good accord with the theoretical calculations of Bienenstock and Brooks[5] if core-polarization effects are neglected. The resonance line shape and intensity are found to depend on the angle of tilt between the applied magnetic field and the plane of the sample at pumped helium temperatures. The observed decrease in line intensity as the tilt angle increases is qualitatively comprehensible using the concept of anisotropic carrier diffusion under cyclotron resonance conditions. It is, however, not possible at present to make direct comparison with the theory of Azbel', Gerasimenko, and Lifshitz[15] because the resonance line splits as the tilt angle increases.

[12] A. W. Overhauser, Phys. Rev. **92**, 411 (1953).
[13] M. Gueron and Ch. Ryter, Phys. Rev. Letters **3**, 338 (1959).
[14] C. C. Grimes and A. F. Kip, Phys. Rev. **132**, 1991 (1963).
[15] M. Ya. Azbel', V. I. Gerasimenko, and I. M. Lifshitz, Zh. Eksperim. i Teor. Fiz. **32**, 1212 (1957) [English transl.: Soviet Phys.—JETP **5**, 986 (1957)].