T_K in the range 0.05–0.2 K, it is possible to obtain again a good agreement with the experimental data by a slight adjustment of Δ. On the other hand for $T_K > 1$ K we obtain a poor agreement with the experimental points, particularly in the low-temperature region, even if we allow a Δ variation in the range 30–300 K.

Our calculations unquestionably show the importance of the crystal-field splitting for the magnetic susceptibility of Kondo systems and suggest that crystal fields should play a prominent role also for other properties of the Kondo systems. This possibility, as well the extension of the theory to other crystal-field symmetries, is at present under examination.

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[1]K. S. Kim and M. B. Maple, Phys. Rev. B 2, 4696 (1970).
[2]W. Gey and E. Umlauf, Z. Phys. 242, 241 (1971).
[3]T. Sugawara and H. Eguchi, J. Phys. Soc. Jap. 26, 1322 (1969).
[4]J. J. Wollan and D. K. Finnemore, Phys. Lett. 33A, 299 (1969).
[5]J. Flouquet, Phys. Rev. Lett. 27, 515 (1971).
[6]A. S. Edelstein, Phys. Rev. Lett. 20, 1348 (1968).
[7]A. S. Edelstein, L. R. Windmiller, J. B. Ketterson, G. W. Crabtree, and S. P. Bowen, Phys. Rev. Lett. 26, 516 (1971).
[8]Recently Edelstein *et al.* [in *Magnetism and Magnetic Materials—1971*, AIP Conference Proceedings No. 5, edited by C. D. Graham, Jr., and J. J. Rhyne (American Institute of Physics, New York, 1973), p. 558] pointed out the possible importance of crystalline field effects in the susceptibility and that the most likely value of T_K appears to be < 1°K.
[9]S. Yoshida and T. Sugawara, Phys. Lett. 30A, 422 (1969).
[10]T. Sugawara and S. Yoshida, J. Low Temp. Phys. 4, 657 (1971).
[11]F. E. Maranzana, Phys. Rev. Lett. 25, 239 (1970).
[12]K. H. J. Buschow, H. J. Van Daal, F. E. Maranzana, and P. B. Van Aken, Phys. Rev. B 3, 1662 (1971).
[13]H. J. Van Daal, F. E. Maranzana, and K. H. J. Buschow, J. Phys. (Paris), Suppl. 32, 424 (1971).
[14]B. Cornut and B. Coqblin, Phys. Rev. B 5, 4541 (1972).
[15]E. Borchi and S. De Gennaro, to be published.
[16]T. Sugawara and H. Eguchi, J. Phys. Soc. Jap. 23, 965 (1967).
[17]T. Murao and T. Matsubara, Progr. Theoret. Phys. 18, 215 (1957).
[18]H. Miwa, Progr. Theoret. Phys. 34, 1040 (1965).
[19]K. Yosida and A. Okiji, Progr. Theoret. Phys. 34, 505 (1965).
[20]J. Kondo, in *Solid State Physics*, edited by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic, New York, 1969), Vol. 23.
[21]R. Kubo and K. Tomita, J. Phys. Soc. Jap. 9, 888 (1954).
[22]Here we neglect possible Kondo sidebands (see Ref. 11) which appear to be of little importance in the magnetic susceptibility case.

High- and Low-Field Limits for the Hall Coefficient of Potassium

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The Hall coefficient (R) for *homogeneous* potassium single crystals was measured at 4.2°K in magnetic fields (H) up to 85 kG. Above 15 kG, R approached H-independent values in excellent agreement with free-electron calculations. Thus, the Fermi surface must be simply connected. Below 15 kG, R exhibited weak H dependence stemming almost unambiguously from scattering anisotropy (due predominantly to phonons). At low H, R is compared with pseudopotential calculations. Correlations between R and magnetoresistance are identified for either scattering or inhomogeneity phenomena.

A recent commentary[1] concerning the anomalous linear magnetoresistance (MR) of potassium (K) concluded with the challenge "... because so long as there are doubts about the behavior of potassium, there must be doubts about our fundamental understanding of metals." Analogously, the anomalous decrease of the Hall coefficient (R) at high magnetic fields (H) presents an equivalent challenge. Traditional microscopic theories[2] for *homogeneous*[3] conductors with simply connected Fermi surfaces (FS) rigorously predict that R must approach an H-independent value ($R_\infty = -1/ne$; n = electron density) in the high-field limit where $\omega_c\tau \gg 1$, ω_c being the cyclotron frequency and τ the relaxation time. Thus for K, In, and Al, whose FS are generally believed

to be simply connected, R should accordingly become H independent at high H. But this prediction disagrees with experimental results[4-6] at high H where R decreases monotonically with increasing H, even though $\omega_c\tau \gg 1$. For In[5] and Al,[5,6] these observed anomalous decreases of R have been generally weak. However, for K,[4,5] very striking decreases of R (up to 12% at $\omega_c\tau = 350$) have been observed which seemingly conflict with (1) the common belief[7] that K is the prototype free-electron metal, and (2) de Haas–van Alphen results[8] which directly measure an almost perfectly spherical FS for K. Many nontraditional explanations have been proposed for the anomalous high-field behaviors of R and/or MR due to either FS[9,10] or scattering[11,12] or inhomogeneity[13] effects.

In this Letter, experimental evidence[14] is presented for the H independence of R at high transverse H for K single crystals which were characterized to be *homogeneous* as defined below.[3] These results were obtained directly from classical dc four-probe measurements (absolute accuracy ~1%; resolution ~0.02%) at 4.2°K up to $\omega_c\tau = 250$ on three samples with resistivity ratios between 300 and 4.2°K ($\rho/\rho_{4.2}$) of 2560, 3220, and 4700. The voltage between the Hall probes (V_R) was continuously recorded as H was changed from −85 to +85 kG. Our previous experiences with the anomalous linear MR showed the crucial importance of minimizing the numerous sources of both gross and subtle macroscopic inhomogeneities.[15] Therefore, concerted efforts were made to avoid these pitfalls in our present measurements.

The samples (2 mm diam; ~1 m long) were prepared by filling evacuated clear polyolefin tubing with freshly vacuum-distilled molten K. These encapsulated samples were then slowly solidified in a temperature gradient. The Hall probes were point probes made of K only, which were formed during the filling process in accurately positioned small holes diametrically opposed in the tubing wall. Over very large regions near the Hall probes, these samples had very uniform cross sections with no contraction voids and were also single crystals with visible blaze planes. The current, MR, and Hall probes were all well separated. Between the MR probes, the samples were uniform single crystals except near the MR probe furthest from the Hall probes where a few small contraction voids and large crystallites existed.

Babiskin and Siebenmann[13] (BS) previously observed for K not only the usual anomalous linear MR at high H, but additionally three distinct saturating MR behaviors at lower H. In order to achieve consistency between these results and the predictions of both the traditional microscopic theories[2] for homogeneous conductors and the macroscopic theories[16] dealing with inhomogeneous conductors, BS proposed a heuristic model[13] which essentially extends Matthiessen's rule from $H = 0$ to high H. In this BS model, the three saturating MR behaviors were attributed to the anisotropy of microscopic scattering mechanisms (phonons, residual defects, and size effects) which occur microscopically on a scale smaller than the mean free path (λ_0). However, the anomalous linear MR was attributed to macroscopic inhomogeneities,[15] which occur macroscopically on a scale $> \lambda_0$ and cause H-dependent redistributions of the current streamlines. (We previously[13] chose λ_0 to indicate the approximate midpoint of the transitional range of dimensions which separates predominantly microscopic from predominantly macroscopic phenomena. Although this choice of λ_0 is appropriate at $H = 0$, it is not appropriate for transverse H for which we henceforth replace λ_0 by D_c, the mean cyclotron diameter.)

The homogeneity characteristics of our samples were deduced by analyzing their MR according to the BS model[13] as follows: (1) At high H, their linear MR slopes (S) were very small [$S < 5\times10^{-4}$; $S = (\Delta\rho_H/\rho_0)(\omega_c\tau)^{-1}$; $\Delta\rho_H/\rho_0$ is the MR increase]. These small slopes characterize these samples as containing essentially no significant macroscopic inhomogeneities on a scale $> D_c$, except for the few small voids and crystallite boundaries between the MR probes. Consequently, we emphasize that these samples were even more homogeneous near the Hall probes where no voids or crystallite boundaries existed. (2) At lower H, the $\Delta\rho_H/\rho_0$ values due to their residual MR saturations[13] were also very small ($\Delta\rho_H/\rho_0 < 0.005$). Thus, these samples can be characterized as having an essentially uniform distribution of residual defects on a scale $< D_c$. (3) At 4.2°K, the $\Delta\rho_H/\rho_0$ values due to their phonon MR saturations[13] (occuring at ~15 kG) were much greater than those due to the residual and size-effect saturations.[13]

The continuous recordings of V_R versus H at 4.2°K appeared to be straight lines from −85 to +85 kG to within the recorder pen-line width. Since the Hall probes were accurately positioned, no resistive or MR voltage was detected [i.e., $V_R = 0$ at $H = 0$ and $V_R(+H) = -V_R(-H)$]. Thus, V_R

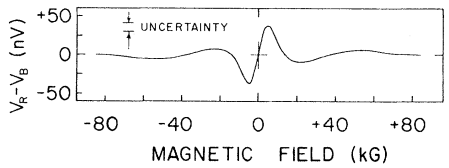

FIG. 1. Deviations from linearity of V_R versus H for a $\rho/\rho_{4.2}=4700$ K sample at 4.2°K.

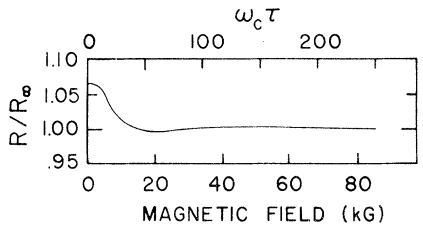

FIG. 2. Normalized plot of R/R_∞ versus $\omega_c\tau$ (and H) for a $\rho/\rho_{4.2}=4700$ K sample at 4.2°K.

is the odd-functioned Hall voltage alone. This apparent linearity of V_R was examined more closely using a linear bucking technique where a bucking voltage (V_B), accurately proportional to H with an adjustable slope, was subtracted from V_R. After setting $V_B=V_R$ at -85 kG, the greatly amplified odd-functioned deviations from linearity of V_R (i.e., V_R-V_B) from -85 to $+85$ kG shown in Fig. 1 were obtained from continuous recordings at 4.2°K for the $\rho/\rho_{4.2}=4700$ sample. Figure 1 demonstrates that V_R is significantly nonlinear below ~15 kG, but its deviations from linearity above ~15 kG are within the measurement uncertainty.

Above ~15 kG, the absolute R values for our three samples were sample independent to ~1% with an average value of -43.9×10^{-11} m^3/C. This value agrees closely with the one-electron-per-atom values for R_∞ of -43.8 and -44.6×10^{-11} m^3/C, which were calculated respectively from the 4.2°K density[17] and the 5.2°K lattice constant.[18] While this absolute agreement is significant, what is more important is that the relative values of R are essentially H independent above ~15 kG and are constant to ~0.1% between 65 and 85 kG. (Because of the constant uncertainty of V_R-V_B in Fig. 1, the relative accuracy of R increases with H from a rather indeterminate level at very low H to ~0.1% at 85 kG.) Figure 2 clearly shows this H independence of R at high H in the the normalized plot of R/R_∞ versus both $\omega_c\tau$ and H, where $R_\infty=R$ at 85 kG.

Based on the charge-density–wave model which yields a multiply connected FS for K, Overhauser[9] calculates a decreasing R above a magnetic breakdown field of 54 kG, which agrees with anomalous experimental results.[4] However, in Fig. 2, our H-independent results for R at high H disagree diametrically with H-dependent results[4] and also do not support Overhauser's model. Instead, our results support the usual conclusion[7,8,13] that the FS of K is indeed simply connected.

Concerning our low-field results, we redefine R/R_∞ as r, which is the Hall-angle mixing factor described by Allgaier.[19] At low H, $r\neq1$ because of FS and/or scattering anisotropy, while at high H, $r\to1$ because it depends only on the FS volume rather than FS and scattering anisotropy. Allgaier's[19] extension of earlier works on r at low H shows that scattering anisotropy alone always makes $r>1$, while FS anisotropy alone always makes $r<1$ provided that the FS anisotropy is not strongly energy dependent. Since the FS anisotropy for K is very weak[8] and is also weakly energy dependent, it causes only a negligible drop of r below unity. Therefore, our entire result in Fig. 2 of $r>1$ up to ~15 kG can be attributed almost unambiguously to scattering anisotropy alone.

Concerning the nature of the scattering anisotropy, our 4.2°K results of a decreasing r up to ~15 kG and a scattering-independent r above ~15 kG correlate closely with our phonon MR results[13] at 4.2°K of an increasing $\Delta\rho_H/\rho_0$ up to its saturation, also at ~15 kG. This phonon MR saturation originates from the formation of "hot-spot" bands[11,13] on the FS which is associated with the increase of umklapp scattering with increasing H. Therefore, we conclude that the decreasing r up to ~15 kG stems predominantly from this same source of electron-phonon scattering anisotropy.

In the low-field limit where $\omega_c\tau\ll1$ and $r\to r_0$ as $H\to0$, the r_0 value of ~1.07 at 4.2°K shown in Fig. 2 is our estimate of r_0 extrapolated from r values at higher H due to the measurement uncertainty at very low H. This estimated r_0 stems predominantly from electron-phonon scattering anisotropy, but also includes small contributions from the anisotropies due to the FS, residual defects, and size effects. Hayman and Carbotte[20] have recently calculated the temperature dependence of r_0 for K using the measured phonon spectrum and various proposed pseudopotential form factors. They determined that the magnitude of r_0 due to electron-phonon scattering anisotropy was indeed >1 and was very sensitive to the form of the pseudopotential used. The four

different form factors that they used led to the values 1.10, 1.24, 1.74, and 3.85 for r_0 at 4.2°K. Thus, our estimated experimental r_0 value of 1.07 clearly favors the calculated[20] r_0 value of 1.10 for the proposed Ashcroft pseudopotential.

Both the high- and low-field aspects of our results on R for *homogeneous* K single crystals are in excellent accord with traditional microscopic theories.[2] Therefore, we conclude that the anomalous high-field behaviors of R and MR are not characteristics of *homogeneous*[3] conductors. Furthermore our results cannot support any of the nontraditional FS[9,10] or scattering[11,12] explanations proposed for the anomalous high-field behaviors of R and/or MR, which essentially assume homogeneous conductors. We have carried out a detailed examination of the anomalous results for K and for many other metals as well as semiconductors. This examination showed that the anomalous behaviors of R and MR can be systematically correlated with each other and with the presence of many sources for macroscopic inhomogeneities on a scale $>D_c$. Therefore, based on the microscopic and macroscopic postulates of the BS model[13] for MR which we now extend correspondingly to R, we adopt the following heuristic standpoint: (1) At lower H, the H dependence of R and the corresponding saturating MR behaviors stem predominantly from the anisotropy of microscopic scattering mechanisms on a scale $<D_c$ and from FS anisotropy. Thus D_c and N_c are *position independent*[3] if not overwhelmed by macroscopic inhomogeneities.[15] (2) At high H, the anomalous H-dependent decrease of R and the corresponding linear MR increase stem predominantly from macroscopic inhomogeneities[15] on a scale $>D_c$ which cause D_c and N_c (mostly N_c for K) to become increasingly *position dependent*[3] with increasing H. This, in turn, causes H-dependent redistributions of the current streamlines of a magnetohydrodynamic nature.

Our standpoint concerning inhomogeneities for simple metals is not entirely new, since many of its aspects have long been well recognized in semiconductors.[21] The influence of known inhomogeneities on the high-field behavior of R and MR have been extensively studied[21] in such high-mobility semiconductors as InSb whose FS is nearly isotropic. However, inhomogeneity effects have not received adequate attention in metals, since the strong FS anisotropies for most metals have generally masked these subtle "anomalous" effects as well as the elusive scattering effects. But for simple metals (especially for K), these inhomogeneity and scattering effects are unmasked and can be unscrambled by high-field studies.

A detailed paper on this general subject will be published elsewhere. We thank R. S. Allgaier and S. M. Bhagat for illuminating discussions.

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[1]Anonymous, Nature (London) 235, 61 (1972).

[2]See, e.g., C. M. Hurd, *The Hall Effect in Metals and Alloys* (Plenum, New York, 1972).

[3]A conductor is broadly define here to be homogeneous if the spatial variations of the electron densities (n) and/or scattering rates ($1/\tau$) occur microscopically on a scale smaller than the path dimensions covered by the electron trajectories during their lifetimes. At $H=0$ the mean free path (λ_0) is 150 μm for K with $\rho/\rho_{4.2}=5000$. At high transverse H, the paths are localized to orbital trajectories whose mean cyclotron diameter (D_c) equals 1 μm at 98.7 kG for K and whose number of completed orbits (N_c) equals $\omega_c\tau/2\pi$. Since these trajectories sample the effects of many spatial variations, λ_0, D_c, and N_c will all be essentially *position independent* throughout a homogeneous conductor. Conversely for inhomogeneous conductors, macroscopic inhomogeneities can cause these spatial variations to occur macroscopically over dimensions $>D_c$ at a given H or even $>\lambda_0$. Now since the trajectories sample the local variations, λ_0, D_c, and N_c will be *position dependent*. Furthermore, as D_c decreases with increasing H, the increasing position dependence of D_c and N_c causes current streamline redistributions. Since $D_c \propto n^{1/3}/H$, D_c is less position dependent than N_c in metals and vice versa in semiconductors.

[4]P. A. Penz, Phys. Rev. Lett. 20, 725 (1968); P. A. Penz and R. Bowers, Phys. Rev. 172, 991 (1968).

[5]J. C. Garland and R. Bowers, Phys. Rev. 188, 1121 (1969).

[6]T. Amundsen and P. Seeburg, J. Phys. C: Proc. Phys. Soc., London 2, 694 (1969).

[7]M. J. G. Lee, Crit. Rev. Solid State Sci. 2, 85 (1971).

[8]D. Shoenberg and P. J. Stiles, Proc. Roy. Soc., Ser. A 281, 62 (1964).

[9]A. W. Overhauser, Phys. Rev. Lett. 27, 983 (1971), and Phys. Rev. B 3, 3173 (1971).

[10]P. M. O'Keefe and W. A. Goddard, III, Phys. Rev. Lett. 23, 300 (1969).

[11]R. A. Young, Phys. Rev. 175, 813 (1968).

[12]L. M. Falicov and H. Smith, Phys. Rev. Lett. 29, 124 (1972).

[13]J. Babiskin and P. G. Siebenmann, Phys. Rev. Lett. 27, 1361 (1971), and Phys. Kondens. Mater. 9, 113 (1969).

[14]See also P. G. Siebenmann and J. Babiskin, Bull. Amer. Phys. Soc. 17, 236 (1972); D. E. Chimenti and B. W. Maxfield, Bull Amer. Phys. Soc. 17, 279 (1972).

[15]The following sources for macroscopic inhomogenities were encountered either by the authors or other workers: end effects due to current probes; cross sectional and conductivity variations due to nonideal potential probes; contraction voids; any other nonuniform variation of the sample cross section or local conductivity; extrusion defects; conductivity aggregates; impurity clusters and arrays; grain boundaries and subboundaries; dislocation arrays and gradients; slip planes; crystal-growth imperfections such as cores, facets, and striations; carrier concentration or mobility gradients; strain gradients and inhomogeneous strain fields; surface corrosion; surface damage.

[16]C. Herring, J. Appl. Phys. 31, 1930 (1960); H. L. Frisch and J. A. Morrison, Ann. Phys. (New York) 26, 181 (1964); H. J. Lippmann and F. Kuhrt, Z. Naturforsch. 13A, 462 (1958); J. S. Lass, J. Phys. C: Proc. Phys. Soc., London 3, 1962 (1970).

[17]C. A. Swenson, Phys. Rev. 99, 423 (1955).

[18]S. A. Werner *et al.*, Phys. Rev. 186, 705 (1969).

[19]R. S. Allgaier, Phys. Rev. B 2, 3869 (1970).

[20]B. Hayman and J. Carbotte, Phys. Rev. B 6, 1154 (1972).

[21]See, e.g., R. T. Bate, in *Semiconductors and Semimetals*, edited by R. K. Willardson and A. C. Beer. (Academic, New York, 1968), Vol. 4. (See also references to A. C. Beer; H. Weiss; S. M. Puri; and T. H. Geballe).

New Type of First-Order Phase Transition in Ferroelectric Thin Films

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It is shown that the depolarization field in a ferroelectric thin film changes the order of the phase transition as well as the magnitude of the polarization and transition temperature.

Previous discussion[1-3] has been concerned with the order of a phase transition as determined by the number of order parameters in Landau's theory[4] of phase transitions and by model calculations that go beyond the Landau theory. Anderson and Blount[1] have pointed out that a first-order transition is possible when only strain is involved since the third-order term in strain does not generally vanish in the free-energy expansion. Pytte[2] as well as Gillis and Koehler[3] have discussed the results of model calculations that go beyond the Landau theory. They point out that the self-consistent field theory can lead to a first-order transition when the only anharmonicity is of fourth order, whereas the Landau-Lifshitz-Devonshire[4] theory predicts a second-order transition when only fourth-order anharmonic terms are considered. The present paper will describe *a new type of first-order phase transition* in a unidomain ferroelectric thin film which is also characterized by an anharmonicity of only fourth order in the polarization. For the system under consideration, namely, intrinsic semiconducting electrodes placed externally on the ferroelectric thin film, the modification of the order of the transition can be shown to result from the additional order parameter that results from the compensating charge in the electrode.

The concept of a depolarization field[5-8] has been around for quite some time now, and it is well realized that it can play a dominant role in ferroelectric crystals of small dimensions. In what follows it will be shown that a second-order ferroelectric transition in bulk is transformed to a first-order transition in thin films under the influence of the depolarization field.

In the study of ferroelectric bulk properties one assumes that the polarization is fully compensated and consequently the depolarization field is set equal to zero. Without compensation, the depolarization field for values of the polarization of approximately 1 $\mu C/cm^2$ would be on the order of 10^7 V/cm. This is about 2 orders of magnitude more than the stability of the polar state would allow. Since close cancelation of the polarization is necessary for stability, the properties of the electrodes, in which the compensation charge is accomodated, play an important role. It will be shown that the presence of the depolarization field leads to reduction in polarization values and depression of transition temperature in thin films when compared with the bulk value. Below a certain "transition length" the ferroelectric state becomes thermodynamically unstable. Quantitative results will be provided for triglycine sulphate (TGS).