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THE CONDUCTION ELECTRON SPIN DENSITY AROUND Fe IMPURITIES IN Cu ABOVE AND BELOW T_K*

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ABSTRACT

We have observed the nuclear resonances of five shells of Cu atoms which are near neighbors to single Fe atoms in dilute alloys of CuFe. The resonance positions show that the conduction electron spin polarization oscillates with distance from the Fe impurity. We follow four of the resonances from 300 K to well below the 29 K Kondo temperature, finding that for all four the spin density has the same temperature dependence as the magnetic susceptibility. These data show that contrary to some speculation there is no drastic change in the spatial polarization associated with the "Kondo condensation."

Considerable effort, both theoretical and experimental, has gone into determining the nature of the ground state of a Kondo system[1,2,3] but to date important questions remain unresolved. The classic Kondo system is a dilute alloy of <u>Cu</u>Fe. Polarization of the Fe by application of an external magnetic field, H, induces a spin polarization $\sigma(r)$ in the conduction electrons at a distance r from the Fe atom.

The essence of the controversy is whether $\sigma(r)$ is given by Eq.(1a) or (1b) (we consider H low enough for linear response).

$$\frac{\sigma(r,T)}{H} = \chi_s(T)\,f(r) \qquad (1a)$$

$$\frac{\sigma(r,T)}{H} = \chi_s(T)\,g(r,T) \qquad (1b)$$

where $\chi_s(T)$ is the Fe spin susceptibility at temperature T. χ_s for Fe in <u>Cu</u>Fe is closely fit by a Curie Weiss law, $\chi_s = C/(T+T_K)$ where C is a constant, and T_K is the Kondo temperature of 29 K.[4] For Eq.(1a) the shape of $\sigma(r)$ is given by f(r) and does not change with temperature, though the magnitude of σ/H at any r tracks χ_s as T is varied. For Eq.(1b) the shape function g is also a function of T so the shape changes, presumably as T crosses T_K. The shape change is said to be a manifestation of the "Kondo condensed state."[3]

Muller-Hartmann's[5] theoretical predictions support Eq.(1a), but Heeger <u>et al</u>., using the Kondo-Applebaum theory, concluded Eq.(1b) was needed, and supported this contention with observations of the Cu NMR line-width.[6] Potts and Welsh[7] confirmed these experimental results. On the other hand, neutron diffraction studies of Stassis and Shull[8] and NMR studies of Nagasawa and Steyert[9] support Eq.(1a). Recent Mössbauer results of Steiner <u>et al</u>.[10] support Eq.(1b).

We have directly measured $\sigma(r,T)$ at 4 distinct shells of neighbors to isolated Fe atoms in dilute alloys of CuFe from temperatures well below to well above T_K, and find that Eq.(1a) is correct.

The experiments are similar to those described previously[11,12,13] in which one observes the nuclear magnetic resonance spectrum of the host Cu nuclei. In addition to the large main Cu resonance due to atoms far from the Fe impurities, we observe five small satellite resonances which we attribute to Cu atoms which are near neighbors to single Fe impurities. Elementary theory shows that the splittings of the satellite resonances from the main Cu resonance are proportional to the conduction electron spin density at these neighboring sites. We find that splittings are independent of concentration for the concentrations studied: 500, 830, 1000, and 5000 ppm. They are linear in external magnetic field at all temperatures and fields studied showing electric quadrupole effects are small, and that we have not induced any changes of state by application of H. The field dependence at 300 K is shown in Fig. 1. The intensity of the satellites varies nearly linearly with concentration showing that they arise from single Fe atoms, not pairs or larger clusters.

No firm identification of which satellite corresponds to which shell of Cu neighbors around the Fe can be made at this time. However, some identification information is available. For example, satellite A at room temperature exhibits the asymmetry characteristic of a direct dipole-dipole interaction between a Cu shell of neighbors and the Fe moment.[11] From this asymmetric shape, one determines that the dipolar coupling constant for satellite A is $\chi_o/r^3 = (1.2 \pm .25) \times 10^{-3}$, where χ_o is the susceptibility of the Fe atom in emu/atom and r is the distance from the Fe impurity to the shell of neighbors that gives rise to satellite A. Using $\chi_o = .95 \times 10^{-26}$ emu/atom at 300 K,[14] one obtains $r = (2.0 \pm .15)\mathring{A}$. Since the first neighbor distance is $2.55\mathring{A}$, we believe satellite A is probably the first neighbor. Satellite M is probably the second neighbor since it is slightly broader than all the other satellites except A and also is at least two times smaller in relative intensity. Satellites B and C, which are comparable to each other in intensity and at least twice as intense as M, are most likely from the 3rd, 4th, or 5th shells. Satellite N is too close to the main Cu resonance to get a reliable intensity measurement.

The breadth of all the satellites increased with decreasing temperature. As a result, we could not observe A at or below 77 K. We followed satellite B down to 1.4 K at 9.5 kG and down to 17 K at 25 kG. We followed M down to 20 K at 9.5 kG and down to 30 K at 25 kG. All splittings were linear in field in contrast to the linewidth results reported earlier. We followed C down to 4.2 K at 25 kG, and N to 10 K at 25 kG. The data below 77 K is from an 830 ppm sample except for a few points at 25 kG on satellites B, C, M, and N and 9.5 kG on satellite B which were done on a 500 ppm sample.

Since the splittings of the satellites from the main line, ΔH, are proportional to H, it is convenient to define the quantity $\Delta K = \Delta H/H$ as a measure of the splittings in analogy to the usual Cu Knight shift K. It is easy to show that $\sigma(r,T)/H \propto \Delta K(r,T)$, so that the temperature dependence of ΔK tells how $\sigma(r,T)/H$ varies with temperature at each position r. If ΔK fits a Curie-Weiss law, a plot of $1/\Delta K$ (or $K/\Delta K$) vs. T would be a straight line with an intercept at $-\theta$, where θ is the Curie-Weiss temperature.

Fig. 2 shows a plot of $K/\Delta K$ vs. T. The straight lines, which are least squares fits of the data, obey a Curie-Weiss law with θ's of 29.2 ± 2.4 K for B, 27.6 ± 4.0 K for C, 29.2 ± 2.3 K for M, and 29.3 ± 7.1 for N.

Fig. 3 shows $\Delta K/K$ vs. $1/(T+29)$ to emphasize the low temperature points. The fact that the straight line fits the data shows that $\Delta K/K$ tracks χ_s with T.

We therefore conclude that Eq.(1a) describes the results, and that the entire manifestation of the Kondo effect on σ is through its effect on the susceptibility with no extra "Kondo compensation" in the conduction electron spin cloud.

These results agree with the neutron diffraction studies.[8/] Can they be reconciled with the NMR linewidth[6,7/] and recent Mössbauer studies?[10/] We believe they can.

As was first pointed out by Tholence and Tournier,[4/] clusters of two or more Fe atoms have a lower T_K than singles, and make a large contribution to the susceptibility. Since the satellite splittings are spectroscopic measurements, they pick out only one kind of species--in this case isolated Fe's. But linewidths should include effects of higher clusters. Lang et al.[11/] found in CuCo that the splittings and linewidths had different temperature dependences, and accounted for the linewidths quantitatively in these terms. We believe, therefore, the CuFe linewidth anomaly is measuring clustering effects, and does not conflict with our results.

Steiner et al. disagree with our result. Their Fig. 2, which is a plot of H/H_{hf} vs. T where H_{hf} is the hyperfine field, would suggest

$\theta \cong 17$ K, a strong disagreement both with χ and with our results. They point out that their data is sensitive to the presence of a temperature independent hyperfine field. They conclude from the data of others at high temperatures that there is no such field. However, if one confines one's attention solely to their data in their Fig. 3, which is a plot of H_{hf}/H vs. $1/(T+29)$, one sees it fits a straight line with a high temperature intercept different from zero (apart from the very low temperature region where they demonstrate the T^2 dependence of $1/H_{hf}$). The other Mössbauer data they show also fit a straight line, but probably with a high temperature intercept roughly equal to zero. That is, the Mössbauer data fit a picture of a small (possibly zero) positive orbital H_{hf} independent of temperature, with a large negative spin H_{hf} varying as $1/(T+29)$ in agreement with our result. We propose this alternative interpretation of their data which then brings all experiments into agreement.

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REFERENCES

1. J. Kondo, in Solid State Physics, edited by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic Press, New York, 1969), Vol. 23.

2. A. Narath, Crit. Rev. Solid State Sci. 3, 1 (1972).

3. A. J. Heeger, in Solid State Physics, edited by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic Press, New York, 1969), Vol. 23.

4. J. L. Tholence and R. Tournier, Phys. Rev. Lett. 25, 867 (1970).

5. E. Müller-Hartmann, Z. Phys. 223, 277 (1969).

6. D. C. Golibersuch and A. J. Heeger, Phys. Rev. 182, 584 (1969); A. J. Heeger, L. B. Welsh, M. A. Jensen, and G. Gladstone, Phys. Rev. 172, 302 (1968).

7. J. E. Potts and L. B. Welsh, Phys. Rev. B5, 3421 (1972).

8. C. Stassis and C. G. Shull, Phys. Rev. B5, 1040 (1972).

9. H. Nagasawa and W. A. Steyert, J. Phys. Soc. Japan 28, 1202 (1970).

10. P. Steiner, W. V. Zdrojewski, D. Gumprecht, and S. Hüfner, Phys. Rev. Lett. 31, 355 (1973).

11. D. V. Lang, J. B. Boyce, D. C. Lo, and C. P. Slichter, Phys. Rev. Lett. 29, 776 (1972); D. V. Lang, D. C. Lo, J. B. Boyce, and C. P. Slichter, to be published.

12. D. C. Lo, D. V. Lang, J. B. Boyce, and C. P. Slichter, Phys. Rev. B8, 973 (1973).

13. J. B. Boyce, T. J. Aton, and C. P. Slichter, to be published.

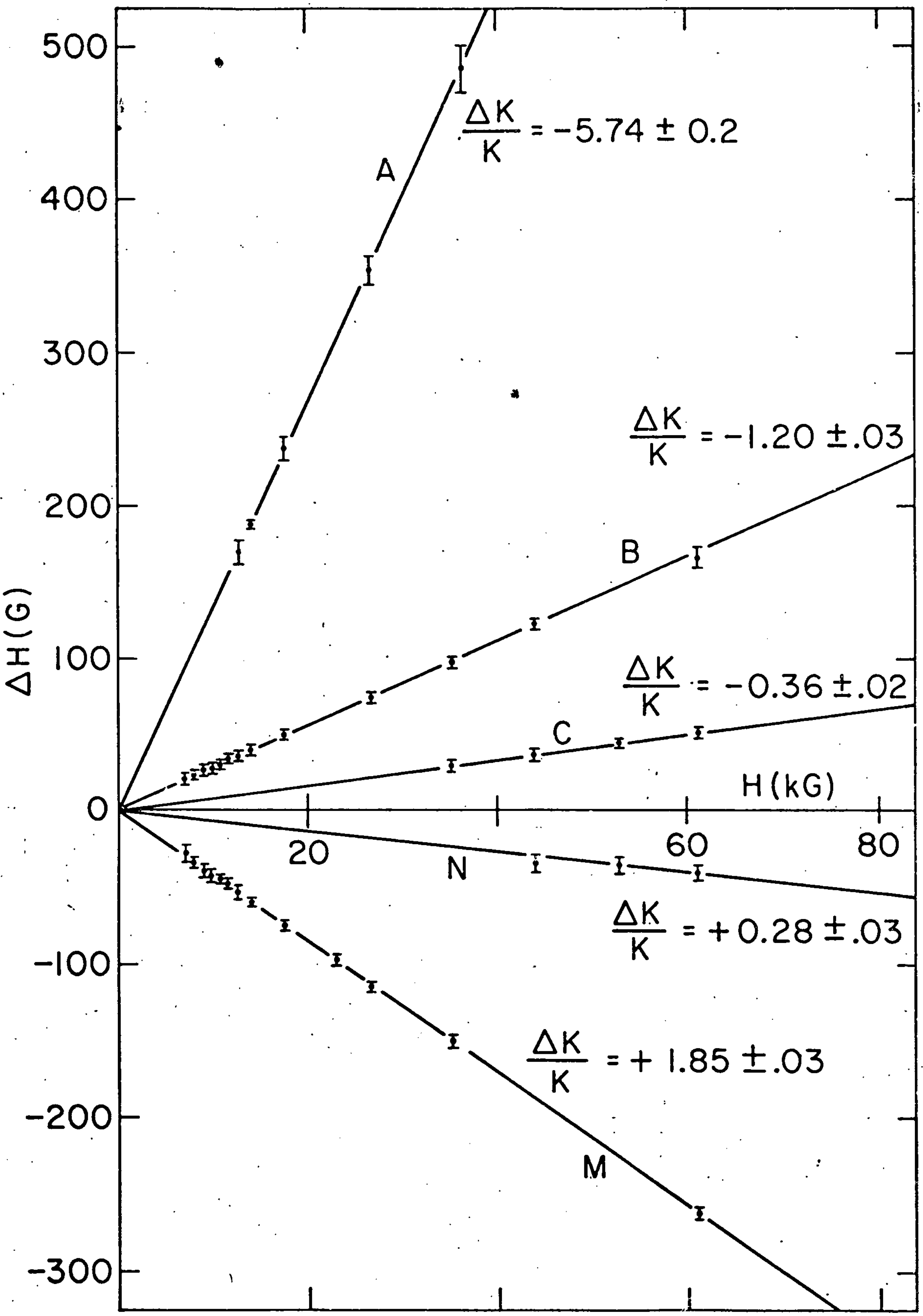
14. C. M. Hurd, J. Phys. Chem. Solids 28, 1345 (1967).

FIGURE CAPTIONS

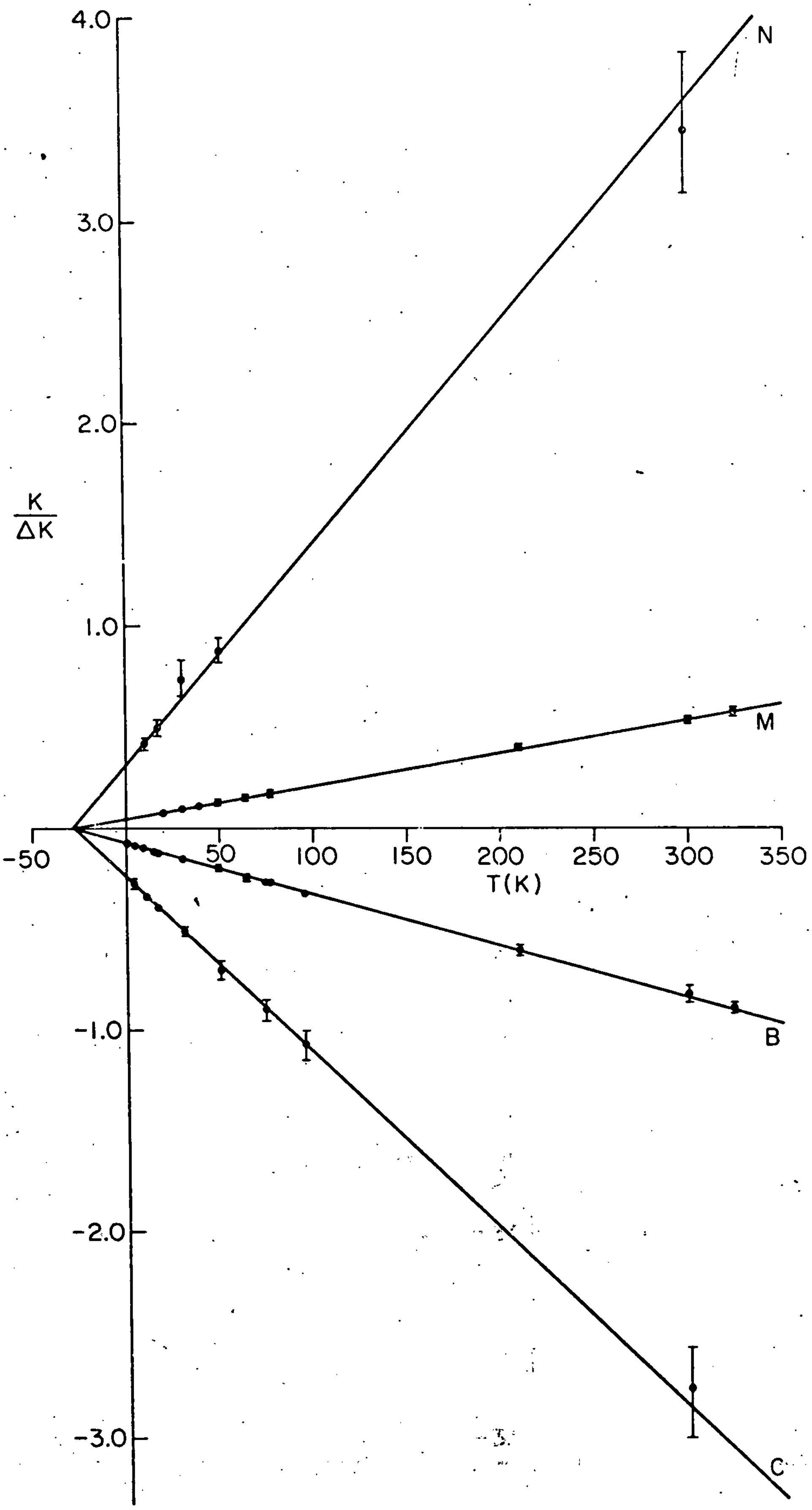
Fig. 1: Magnetic field dependence of satellite separations from main Cu^{63} resonance at 300 K. Shift of satellite, ΔH, in Gauss from the Cu^{63} resonance vs. applied field H. The $\Delta K / K$ for satellite A includes a direct dipole-dipole contribution of $-.5 \pm .1$ so that the isotropic part of $\Delta K/K|_A = -5.24 \pm .3$.

Fig. 2: $K/\Delta K$ vs. temperature for four of the satellites. The straight lines are least squares fits to the data.

Fig. 3: The Knight shifts vs. $1/(T+29)$ for four of the satellites. No additional polarization is seen to form below $T_K = 29$ K.



500
400
300
200
100
0
-100
-200
-300
ΔH (G)
H (kG)
20
60
80
A
B
C
N
M
ΔK/K = −5.74 ± 0.2
ΔK/K = −1.20 ±.03
ΔK/K = −0.36 ±.02
ΔK/K = +0.28 ±.03
ΔK/K = + 1.85 ±.03


4.0
3.0
2.0
1.0
-1.0
-2.0
-3.0
K/ΔK
-50
50
100
150
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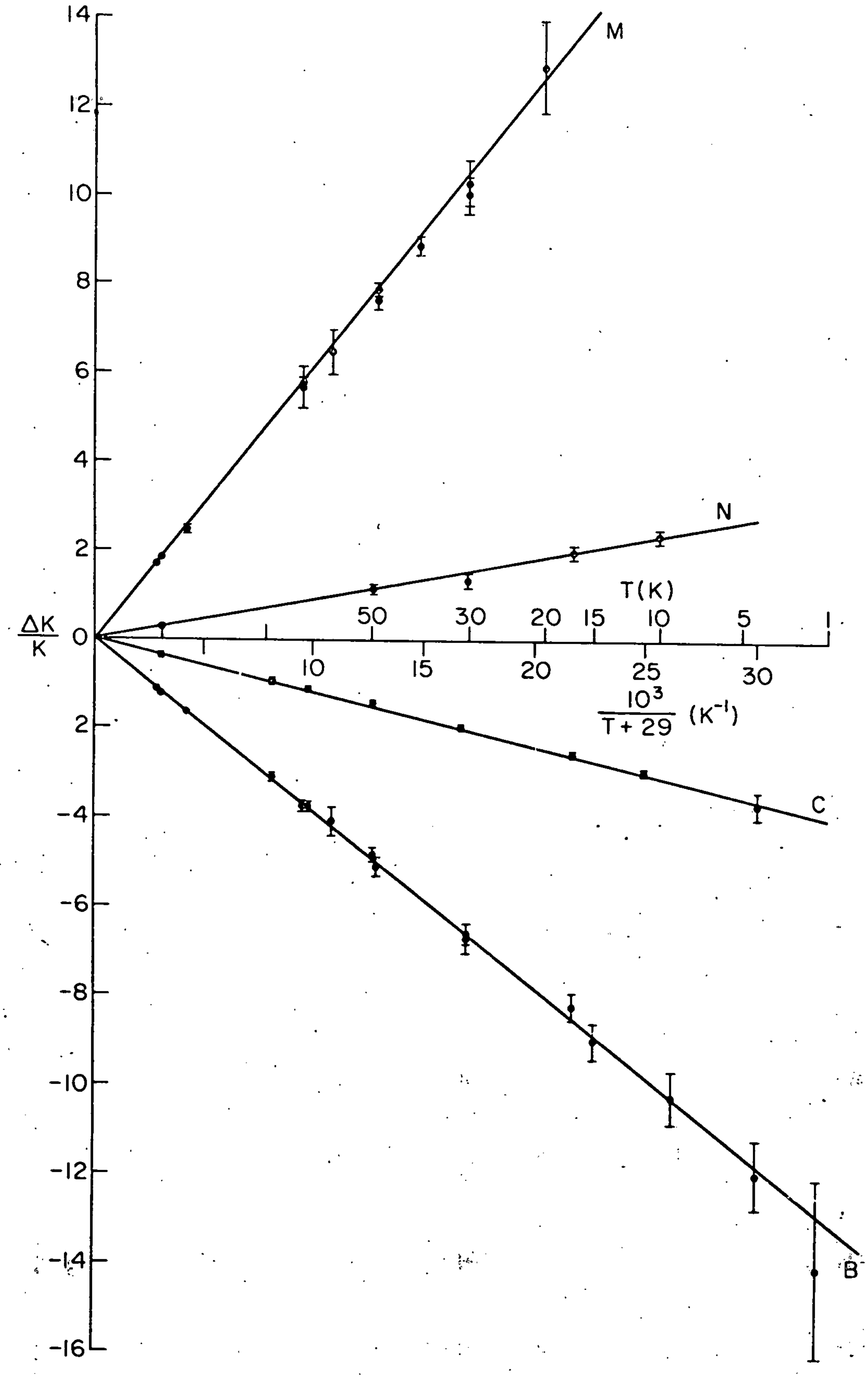
300
350
T(K)
N
M
B
C



M
N
C
B
ΔK/K
T(K)
50
30
20
15
10
5
1
10
15
20
25
30
10³/(T + 29) (K⁻¹)
14
12
10
8
6
4
2
0
2
-4
-6
-8
-10
-12
-14
-16