COMMENTS AND ADDENDA

The Comments and Addenda section is for short communications which are not of such urgency as to justify publication in Physical Review Letters and are not appropriate for regular Articles. It includes only the following types of communications: (1) comments on papers previously published in The Physical Review or Physical Review Letters; (2) addenda to papers previously published in The Physical Review or Physical Review Letters, in which the additional information can be presented without the need for writing a complete article. Manuscripts intended for this section may be accompanied by a brief abstract for information-retrieval purposes. Accepted manuscripts will follow the same publication schedule as articles in this journal, and galleys will be sent to authors.

Nuclear Magnetic Resonance in Solid and Liquid Copper†

R. L. Odle and C. P. Flynn
Department of Physics and Materials Research Laboratory, University of Illinois, Urbana, Illinois 61801
(Received 1 February 1971)

Two recently published and mutually discrepant sets of data giving the Knight shift in solid and liquid Cu are shown to be compatible with earlier results in those temperature ranges for which each recent set is apparently reliable. Recent diffusion data are also discussed.

In a brief note published some years ago, Odle and Flynn[1] reported values for the Knight shift of Cu in solid and liquid Cu at high temperatures and for Sb in liquid Sb. The Sb results have since been confirmed,[2] but doubt has been cast on the Cu results by two much more extensive studies[3,4] which agree fully neither with each other nor with the original work. It is important that this matter be resolved because of the unusually large Knight-shift change undergone by Cu at its melting point,[1] and the interpretation of this shift[1] as originating partly in the elimination of p-like necks on the Fermi surface. The explicit results of the earlier work are presented in this note. These agree with the two sets of later results where each is apparently reliable, and the composite data appear to confirm our earlier conclusions.

Figure 1 shows the data of Odle and Flynn (OF), together with those of El-Hanany and Zamir (EZ) and of Warren and Clark (WC), fitted together in the liquid at the melting point where the results are in best accord. It should be noted that each set does contain the inherent possibility of small absolute shifts owing to the choice of differing reference standards and to the difficulty of absolute field calibration inside furnaces at these elevated temperatures. All major discrepancies originate in the anomaly observed by EZ at about 1000 °K and in three points taken by WC at temperatures immediately below the melting point.

The anomaly at 1000 °K occurs at the linewidth transition.[5] It most probably originates in apparatus adjustments enforced by the transition or in skin-effect shifts[6] due to imperfect sample construction. Neither the susceptibility[7] nor the spin-lattice relaxation rate[3,4] of Cu shows any signs of an anomaly having this order of magnitude near 1000 °K. In the alternative recent data[3] the discrepancy below the melting point was accompanied by substantially accelerated relaxation of an imperfectly reproducible nature and has been ascribed[4] to sample contamination. Difficulties con-

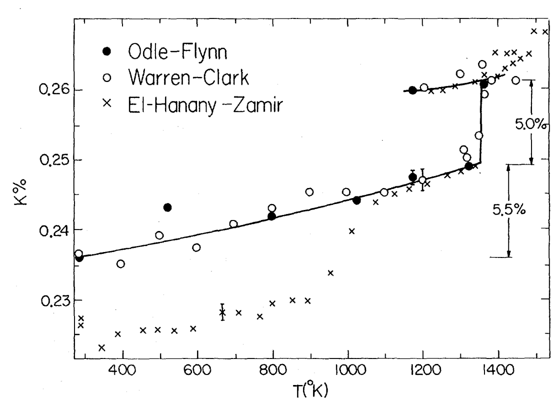

FIG. 1. Knight shift of Cu as a function of temperature according to several reports. The data from various sources are fitted together just above the melting point. Error bars indicate the typical experimental uncertainties quoted by WC and EZ, and the estimated uncertainties for $T > 1100$ °K in the OF data.

nected with sample structure can be avoided by careful preparation and encapsulation techniques described elsewhere.[8]

The assembled data are consistent with changes in K of 5.5% from room temperature to the melting point and a further 5.0% at the melting transition. These compare favorably with the values (5.0 ± 1.5) and (5.1 ± 0.3)% we reported previously (the latter value was obtained as the mean of repeated measurements). The absolute Knight shift at room temperature in Fig. 1 agrees with accepted values for Cu,[9] of which the higher (~ 0.236) are probably the more reliable, owing to skin-effect shifts.

We note further that the relaxation rates measured by EZ confirm the motional narrowing observed by Flynn and Seymour[5] (FS), and allow an estimate to be made of the activation energy Q for self-diffusion. The result, $Q = 2.04 \pm 0.02$ eV, appeared to be in better agreement with existing radio-tracer studies than the value of $Q = 2.08_5 \pm 0.04$ eV obtained by FS from absolute diffusion rates and an estimated D_0 (the diffusion rates of EZ and FS agree where they overlap). Results derived from direct observation of T_2 should indeed be the more precise. Unfortunately, recent more accurate tracer studies[10] give $Q = 2.19 \pm 0.01$ eV. This tends to confirm the impression that nuclear-magnetic-resonance (NMR) methods (except perhaps those using temperature ranges extended by the Ailion-Slichter[11] or related methods) do not compare in accuracy or reliability with alternative radio-tracer techniques when suitable isotopes are available.

Note added in manuscript. We have been notified through a publication of the Israel Atomic Energy Commission that further investigations by EZ confirm our belief that their published Knight-shift data contain substantial systematic errors. It appears that the anomaly at ~ 1000 °K is indeed an experimental artifact. The 7% discrepancy between their NMR results and the tracer values of the activation energy for self-diffusion in copper has not, as yet, been explained.

†Work supported in part by the Advanced Research Projects Agency under Contract No. HC 15-67-C-0221.

[1]R. L. Odle and C. P. Flynn, J. Phys. Chem. Solids 26, 1685 (1965).

[2]W. W. Warren and W. G. Clark, Phys. Rev. 177, 600 (1969).

[3]W. W. Warren and W. G. Clark, Phys. Rev. B 1, 24 (1970).

[4]U. El-Hanany and D. Zamir, Phys. Rev. 183, 809 (1969).

[5]C. P. Flynn and E. F. W. Seymour, Proc. Phys. Soc. (London) 77, 922 (1961).

[6]A. C. Chapman, P. Rhodes, and E. F. W. Seymour, Proc. Phys. Soc. (London) B70, 345 (1957).

[7]J. Bensel and J. A. Gardner, J. Appl. Phys. 41, 1157 (1970).

[8]J. A. Gardner and C. P. Flynn, Phil. Mag. 15, 1233 (1967).

[9]W. D. Knight, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1956), Vol. 2; H. S. Gutowski and B. R. McGarvey, J. Chem. Phys. 20, 1472 (1952).

[10]S. J. Rothman and N. L. Peterson, Phys. Status Solidi 35, 305 (1969).

[11]D. Ailion and C. P. Slichter, Phys. Rev. 135, A109 (1964).

PHYSICAL REVIEW B VOLUME 4, NUMBER 9 1 NOVEMBER 1971

Healing Length of the Superconducting Order Parameter*

A. E. Jacobs
Department of Physics, University of Toronto, Toronto 181, Ontario, Canada
(Received 10 May 1971)

We calculate the healing length of the superconducting order parameter near $T = T_c$ by means of a variational method based on the Neumann-Tewordt expression for the free energy of an inhomogeneous superconductor. The result for the correction to the Ginzburg-Landau healing length near $T = T_c$ indicates that the healing takes place over distances of the order of the coherence length at all temperatures, in disagreement with a recent calculation which predicts healing over atomic distances at low temperatures.

I. INTRODUCTION

The problem of a superconductor in contact with a magnetic material is one of current interest. Because of the large pair breaking, the superconducting order parameter $\Delta(\vec{r})$ is assumed to vanish in the magnetic material; the boundary condition on $\Delta(\vec{r})$ in the superconductor is taken to be $\Delta(\vec{r}) = 0$ at the interface. To obtain qualitative predictions for the properties of this system, one can take $\Delta(\vec{r})$ to jump at the interface to the value (Δ_∞) characteristic of wholly superconducting material