PHYSICAL REVIEW B VOLUME 10, NUMBER 11 1 DECEMBER 1974

Comparison of hyperfine fields and impurity magnetization in dilute *Pt*Co alloys

M. Ali,* W. D. Brewer, and E. Klein
Fachbereich Physik der Freien Universität Berlin, West Germany

A. Benoit, J. Flouquet, and O. Taurian
Laboratoire de Physique des Solides, Université Paris-Sud, Orsay, France

J. C. Gallop†
The Clarendon Laboratory Mullard Cryomagnetic Laboratory, Oxford, England

(Received 24 June 1974)

High-field nuclear orientation measurements in dilute *Pt*Co alloys are compared with magnetization measurements by Tissier and Tournier. The results imply the proportionality of the hyperfine field H_{hf} and the single-impurity magnetization M_s, and thus of the local magnetization M_1 and the induced part of the giant moment M_i. The saturation behavior can best be fit with a simple local spin-fluctuation model giving $H_{\mathrm{hf}}(\mathrm{sat}) = 212$ kOe and $T_K \simeq 1$ K.

INTRODUCTION

The results of hyperfine interaction measurements at impurity nuclei in metals have usually been interpreted in terms of a hyperfine field which was taken to be proportional to the local magnetization M_1. While such an assumption may be justified for spectroscopic methods such as Mössbauer effect or NMR, where the "fast relaxation" condition $1/\tau_s \gg \omega_L$ (τ_s = ionic relaxation time and ω_L = nuclear Larmor frequency) is usually fulfilled, it is not necessarily correct for nuclear-orientation (NO) experiments.[1] In the latter, one usually has $\tau_0 \gg 1/\omega_L$, T_1 and $\tau_i \ll 1/\omega_L$, T_1 where τ_0 and τ_i are the initial (oriented) state and intermediate state lifetimes and T_1 is the nuclear relaxation time. The measurement is thus effectively static and is not subject to the dynamic condition used for spectroscopic methods. The indiscriminate use of the hyperfine-field concept has sometimes led to an apparent contradiction with the results of susceptibility measurements (cf. *Cu*Mn). This discrepancy has been attributed to the nonproportionality of H_{hf} and the single-impurity moment in the weak-coupling region ($T \gg T_K$); however, it remains of interest to investigate the transition region from the situation $T > T_K$ (where the impurity spin $\vec{S}_1$ is strongly coupled to the nuclear spin $\vec{I}$) to the opposite situation $T < T_K$ (where $\vec{S}_1$ is coupled to the conduction-electron spins s.[2]) In particular, it is to be expected that in the latter situation, the impurity will have no spontaneous magnetic moment in zero applied field, but rather an induced moment which is significantly large only for applied fields $H_a > A/g\mu_\beta$. Furthermore, the spin $\vec{S}_1$ will be only slightly perturbed by the hyperfine coupling, and the hyperfine Hamiltonian will reduce to

$$\mathcal{H}_{\mathrm{hf}} = A\vec{I} \cdot \langle \vec{S}_1 \rangle = A I_z \langle S \rangle ,$$

so that one can define an effective field H_{hf} proportional to the local impurity moment (or to the local impurity magnetization M_1). We note that this latter situation always applies in magnetically ordered materials, where the ionic spin is always blocked by the strong molecular field or by collective interactions with other spins.

Since the temperature and field dependence of the magnetization $M_s(H, T)$ is not theoretically known for either Kondo or spin-fluctuation systems,[3] it is not reasonable to attempt to relate high-temperature properties to those measured at low temperatures relative to T_K; thus a comparison of NO results with magnetization data requires that both be obtained in the same temperature range. This condition can, in practice, seldom be met, since magnetization measurements over a large range of applied fields are usually only feasible at relatively high temperatures $T_M > 50$ mK, while NO experiments must be performed at $T_{\mathrm{NO}} < 20$ mK. However, if T_K is sufficiently high that both T_M and T_{NO} can be considered to be in the low-temperature limit, the condition of equal temperatures is effectively fulfilled.

The alloy system *Pt*Co, which we discuss in this paper, meets this condition since $T_K \simeq 1.5$ K,[4] while the NO experiments described here were performed in the temperature range 10–30 mK and the magnetization measurements of Tissier and Tournier[5] (TT), with which the NO results are compared, were done at 60 mK.

The comparison of the two sets of data permits us to show the proportionality of H_{hf} and M_s, the latter having been obtained by TT from an extrapolation to zero impurity concentration; the self-consistence of the results implies, as well, the correctness of the concentration analysis performed by *TT*, and also the proportionality of the magnetization M_i induced on the platinum matrix to the local impurity magnetization M_1. The proportionality constant $R = H_{hf}/M_s$ is found to be $R = -60$ kOe/μ_B. We discuss the interaction effects in more concentrated *Pt*Co samples and compare the saturation behavior of H_{hf} to a theoretical expression derived by Ishii for a singlet ground state[6] and to a simple phenomenological model based on the assumptions of the localized spin-fluctuation theory.[7]

EXPERIMENTAL

Alloys of *Pt*Co containing radioactive ^{60}Co were attached by soldering to the cold finger of an adiabatic demagnetization apparatus and cooled to temperatures in the 10-mK range in the presence of an applied field H_a. Counting of the intensity distributions of γ rays emitted in the decay of the ^{60}Co, as well as from a thermometer alloy (either *CuFe* ^{54}Mn, *Fe* ^{58}Co, or Ni^{54}Mn), as a function of temperature and applied field, then yielded the curve of $H_{eff} = H_a \pm |H_{hf}|$, assuming an effective Zeeman Hamiltonian

$$\mathcal{H}_{eff} = -g_n/\mu_n H_{eff}.$$

The sign of H_{hf} may be determined by detecting the circular polarization of the ^{60}Co γ rays or by observing the sense of the β-particle asymmetry relative to H_a; both methods were applied in this work and gave results consistent with a negative sign.[7,8]

The very dilute *Pt*Co alloys (samples 1–3) were prepared by diffusing ^{60}Co activity into commercial Pt (Johnson-Matthey, nominal purity 99.999%, and Metals Research Ltd.). The treatment and properties of these samples are shown in Table I. The more concentrated samples (samples 4–7) were kindly provided by TT and are pieces of the same alloys on which their magnetization measurements were performed. The Co concentrations were 0.041, 0.271, 0.88 and 2.58 at.% for samples 4–7, respectively. These samples were activated with ^{60}Co in the same manner as sample 1. The ^{60}Co solutions were purified by ion exchange before application to the samples. Sample 1 was studied in applied fields up to 20 kOe, while samples 2 and 3 were studied for H_a up to 72 kOe; thus the data for dilute samples covers the entire range of the magnetization measurements. The more concentrated samples were studied in fields up to 32 kOe.

RESULTS AND DISCUSSION

In this section we will first compare the NO results on the most dilute samples with the single-impurity magnetization curve obtained by TT. As noted before, this curve must be extrapolated from measurements on more concentrated samples, where interaction effects between impurities are present, since the sensitivity of the technique does not permit direct measurements on very dilute samples. This requires a model for the interaction effects as a function of total impurity concentration. The model used by TT will be discussed later.

In order to extract any useful information from comparisons of NO results and magnetization measurements, one must establish the validity of two hypotheses: (i) the hyperfine field measured in the NO experiments is indeed proportional to the local impurity magnetization; and (ii) the model used to extrapolate the magnetization data is correct. Agreement of the two curves over a large range of applied fields can be taken to confirm both these points by self-consistence.

The data are shown in Fig. 1. The solid curve is the single-impurity curve of TT multiplied by the factor $R = -60$ kOe/μ_B. The agreement is satisfactory over the entire range of applied fields. (The deviations for sample 3 in the medium-field range are most likely due to incipient interaction effects, since this was the most concentrated of the "very dilute" samples.) We note that the data for sample 1 taken at lower fields by one of us (JCG) was communicated to TT and was shown by them in support of point (ii) above. The large range of applied fields over which agreement is obtained is significant, since an accidental agreement in the low-field range, where the curvature is not strong, would not be unlikely. We may thus conclude that points (i) and (ii) are verified for this system, and that furthermore, no large orbital contribution to the magnetism is present, since the latter would be differently weighted in the NO and magnetization curves and would destroy the agreement.[9]

The situation in *Pt*Co is, however, more complex than we have thus far indicated: this system is known to possess giant moments around the Co impurities. The single-impurity magnetization M_s is therefore the sum of two contributions, the local impurity part M_1 and the part induced on the Pt lattice M_i. The NO experiments measure only the local part, i.e., $H_{hf} = R_{cp}M_1$ where R_{cp} is the hyperfine field constant for core polarization (not necessarily the free ion value). For the measured ratio R we then have

$$R = H_{hf}/M_s = R_{cp}M_1/(M_1 + M_i) = R_{cp}/(1+\alpha),$$

where α is the fraction of induced moment, $\alpha = M_i/M_1$. Thus, the constancy of R implies that α is also constant, i.e., $M_i \propto M_1$ and the induced moment can be described by a simple molecular-field model $H_m = \beta M_1$, $M_i = H_m\chi_{Pt} = \beta M_1 \chi_{Pt}$, and $M_s = M_1 + M_i = M_1(1 + \chi\beta_{Pt})$, where χ_{Pt} represents the susceptibility of the exchange-enhanced Pt conduction electron gas. These experiments are relatively sensitive to the constancy of α, since α contributes a large fraction of the total magnetization. If we take the total saturation moment to be 3.6 μ_B, as found by TT, and take the local Co moment to be 2 μ_B, about

TABLE I. Preparation of dilute *Pt*Co samples.

Sample	Activation	Nominal Co content	Resistivity ratio: $\rho(300\ \mathrm{K})/\rho(4\ \mathrm{K})$	Total magnetic[a] impurities	Fe content (atomic absorption analysis)
(1) (Metals Research)	Diffusion of dried ^{60}Co 39 h. at 1300 °C in H_2	< 1 ppm	880	37 ppm	17 ppm
(2) (Johnson-Matthey)	Diffusion of plated ^{60}Co 24 h. at 1200 °C *in vacuo*	1 ppm	1510	22 ppm	...
(3) (Johnson-Matthey)	Same as (2)	15 ppm	944	34 ppm	...

[a] From the resistivity ratios using the residual resistivity for *Pt*Fe $= 3\,\mu\Omega\,\mathrm{cm/at.}\%$ (Ref. 19).

the same as in *Pd*Co,[10] we have $\alpha = 0.8$. This in turn gives $R_{cp} = 108\ \mathrm{kOe}/\mu_B$, which is a reasonable value (e.g., R_{cp} in Co metal is $127\ \mathrm{kOe}/\mu_B$). Because of the relatively large value of α, we can be certain of its constancy to within 10% over the entire range of applied fields studied.

We have not considered the possibility of an antiferromagnetic Kondo polarization cloud off the Co sites, since *Pt*Co seems best described by a spin-fluctuation model, which does not predict such a cloud, and since efforts to find such a cloud even in "good" Kondo systems have so far been inconclusive.

We next turn to the data from the more concentrated samples. Here, interactions between the impurity moments become important, and we must consider a model for the concentration dependence of the interaction effects. The simplest model is to assume the existence of a critical distance d, within which two Co atoms interact and become magnetic. This interaction range was estimated by Crangle and Scott,[11] who assumed a uniform impurity distribution and used their value for the critical concentration for the appearance of magnetism c_{crit} extrapolated from their magnetic measurements. They obtained a value for $d = 22$ Å. A real alloy has a random impurity distribution, so that even at concentrations well below c_{crit} a certain fraction of the impurities lie within the interaction range of one another. In the model used by TT, the probability $N_1(c, Z)$ that, at concentration c, a given Co atom has no Co neighbors within the distance d (or, equivalently, among the Z nearest atoms, where Z is the total number of atoms within a sphere of radius d) is calculated. The measured magnetization is then a weighted sum of contributions from isolated impurities (with probability N_1) and from interacting impurities (probability $1 - N_1$):

$$M = M_1 N_1 + M_2(1 - N_1).$$

If the quantity M/N_1 is plotted against $(1 - N_1)/N_1$, the resulting straight lines have slopes equal to M_2, the interacting-impurity magnetization. Assuming M_2 to have a constant (saturation) value at the external fields used, the straight lines should be parallel; this condition determines the value of Z, which was found to be 180, corresponding to $d = 6.5$ Å. The intercepts on the vertical axis then give the values for $M_1 = M_s$, the single-impurity magnetization, for the various applied fields. In this manner the curve shown in Fig. 1 was obtained. The model is a rough approximation, as pointed out by TT, since it considers only two types of Co impurity and neglects, for example, the variation of the interaction strength with impurity-impurity dis-

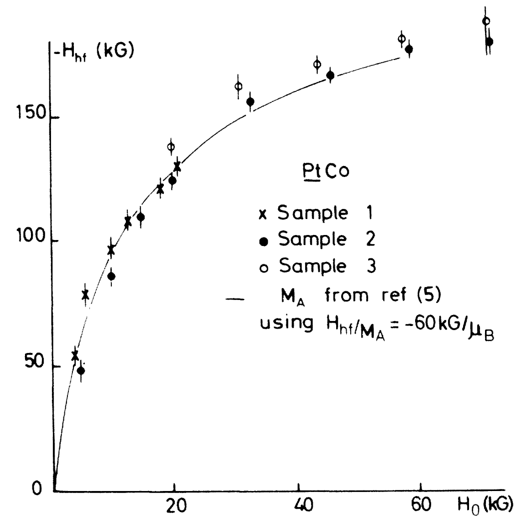

FIG. 1. Nuclear-orientation data compared to the single-impurity magnetization curve M_s obtained in Ref. 5. The latter curve has been multiplied by a factor $R = 60\ \mathrm{kOe}/\mu_B$. Errors on the NO data points are statistical.

tance within d. This is, however, not too significant for the separation of the single-impurity contribution from all contributions from interacting atoms, which are lumped together under M_2.

For the comparison of NO data and the magnetization curves from the more concentrated samples, the details of the model chosen for the interactions are in fact unimportant. This is because both sets of data were obtained from the same samples: the concentrations were identical and no extrapolation in concentration need be made. Furthermore, the γ-ray anisotropy $W(H/T)$ measured in the NO experiments is approximately linear in H/T in the range studied. Thus,

$$C H_{\text{eff}} \simeq W_{\text{expt}} \simeq \sum_i N_i W_i \simeq C \sum_i N_i H_{\text{eff}}^{(i)} ,$$

so that

$$H_{\text{eff}} \simeq \sum_i N_i H_{\text{eff}}^{(i)} \rightarrow R \sum_i N_i M_i = R M .$$

Here C is a constant depending on the anisotropy curve for the isotope measured and on the temperature, W_{expt} is the measured anisotropy at a given applied field and concentration, the index i denotes contributions from the various interacting Co species (weighted by concentration- and range-dependent factors N_i), and the arrow in the second equation implies that in this step a correction for the applied field must be made and that it is assumed that R has the same value for all Co species. A comparison of the data for $H_{\text{hf}}(H_a)$ and for $M(H_a)$ essentially tests this last assumption.

The results are shown in Fig. 2, which shows agreement between the hyperfine field points and the magnetization curves (again normalized by the factor $R = -60$ kOe/μ_B) for the two more dilute samples with c 410 and 2710 ppm, respectively. For the more concentrated samples ($c = 0.88$ and 2.58 at.%), however, a systematic deviation of the hyperfine points to lower values than the corresponding magnetization curves is seen. The deviation is larger for the more concentrated sample. This indicates that in fact, R does not have the same value for the interacting Co atoms as for isolated impurities, or, in view of the previous discussion, that the fraction α of induced moment is a function of concentration.

This is hardly surprising: as the impurity concentration increases, the giant moments begin to overlap and a greater portion of the total magnetization resides on the host lattice. This process culminates in the magnetic ordering of the sample. The two most concentrated samples are already in the ferromagnetic region; thus it is to be expected that α is somewhat larger than in the dilute samples, giving a smaller effective R value.

Another possible interpretation for the deviations in the concentrated samples is that the axial symmetry of the system is disturbed by the interactions, giving an averaging of the γ-ray anisotropy over various angles; such disalignment effects are observed, for example, in *Pd*Co.[7] In that case, however, H_{eff} shows a characteristic temperature dependence which is not observed in *Pt*Co. Also, since $T \ll T_K$ in *Pt*Co, the moments are induced parallel to H_a and no disalignment is to be expected.

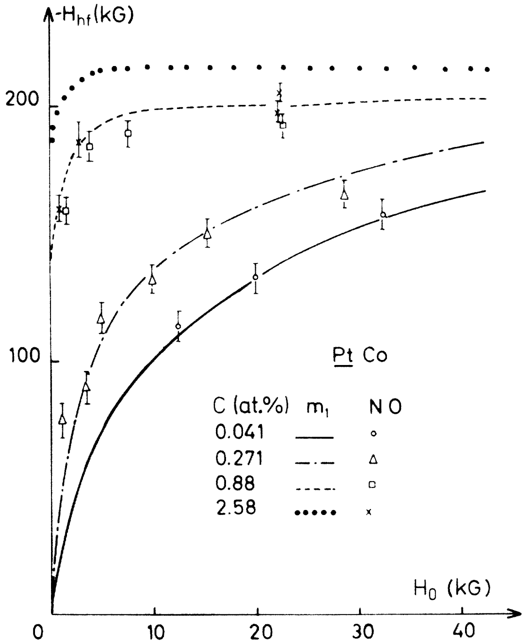

FIG. 2. Hyperfine-field points for more concentrated *Pt*Co samples compared to the magnetization curves determined in Ref. 5 for the same samples. The magnetization data were normalized by the same factor as in Fig. 1.

Finally, we will examine the saturation behavior of the hyperfine field obtained from the most dilute samples. To do this we need the value of the hyperfine field at saturation $H_{\text{hf}}(\text{sat})$. The direct measurement on the most concentrated sample gives $H_{\text{hf}}(\text{sat}) \doteq -200$ kOe; this is somewhat larger than the value -180 kOe obtained from previous NO measurements[12] and the -120 kOe determined by Mössbauer effect.[13] The explanation in the former case is undoubtedly that the applied field of 3 kOe was not sufficient to produce true saturation even in the 2-at.% sample used. In the latter case, the experimental conditions were even further from saturation and the observed field was probably due to impurity interactions. On the other hand, if we take the saturation moment μ_{sat} found by TT ($3.6\mu_B$) and normalize with the factor $R_1 = -60$ kOe/μ_B for isolated Co moments, we obtain $H_{\text{hf}}(\text{sat}) = -216$ kOe, which is larger than the directly observed value. The moment μ_{sat} was, however, derived from data on *interacting* Co atoms and thus the factor R_1 is inappropriate; the correct hyperfine constant would be somewhat smaller so the value of $H_{hf}(\text{sat})$ will tend towards the directly observed field. In any case, the choice of the saturation field is not too important, since it merely provides a vertical scale factor for the saturation curves. We thus take $H_{hf}(\text{sat}) = -200$ kOe.

In Fig. 3, the saturation curve is compared to two functions. The first is the analytic function given by Ishii[6] for a singlet ground state (Kondo state):

$$\frac{H_{hf}}{H_{hf}(\text{sat})} = \frac{g\mu_B H_a}{(g^2\mu_B^2 H_a^2 + 4k^2T_K^2)^{1/2}} = \frac{X}{(1+X^2)^{1/2}},$$

with $X = g\mu_B H_a/2kT_K$. The second is a function derived[7] from a simple model assuming a localized nonmagnetic virtual bound state of spin-$\frac{1}{2}$ without a spin-independent potential (localized-spin-fluctuation model). In this simple approximation the displacement of one spin level in a field H_a is given by

$$\delta E_\sigma = g\mu_B H_a \alpha_1,$$

where α_1 is the local susceptibility enhancement factor $\alpha_1 = 1/(1-\rho_d U)$. We use $1/kT_K = \pi\rho_d/(1-U\rho d)$ and $\rho_d = \Delta/\pi[E_\sigma^2(0)+\Delta^2] \simeq 1/\pi\Delta$ to obtain

$$\delta E_\sigma = g\mu_B H_a/2kT_K.$$

Here $E_\sigma(0)$ is the energy of the unperturbed virtual state relative to E_F [$E_\sigma(0) \simeq 0$ in this model], Δ is the width of the virtual state, ρ_d the electron density of one spin state at the Fermi level, and U the intra-atomic Coulomb repulsion of the virtual states. Applying the Friedel sum rule we obtain for the relative magnetization (hyperfine field)

$$\frac{H_{hf}}{H_{hf}(\text{sat})} = \frac{1}{\pi}\,(2\,\text{arccot}X - \pi)$$

with X defined as above. In Fig. 3, the data are plotted against XT_K and are normalized to the two functions at the point corresponding to $H_a = 10$ kOe, giving $T_K = 1.4$ K for the Ishii function and $T_K = 0.8$ K for the localized-spin-fluctuation model. The latter is seen to fit the high-field data much more satisfactorily. The disagreement with the Ishii model is not unexpected, since it is not valid near saturation[14] and fails to give the limiting value for the moment found from a perturbation calculation. The apparent success of the localized-spin-fluctuation model is completely lacking in theoretical foundation, especially since the above assumptions would also be expected to be invalid at high fields; it probably reflects the tendency of electron correlations to repel the virtual states toward the Fermi level, making the approximations applicable even in high fields. It should be mentioned that a similar semiempirical approach has been applied by Loran *et al.*,[15] Nagasawa,[16] and Souletie,[17] to relate resistivity anomalies and susceptibility measurements.

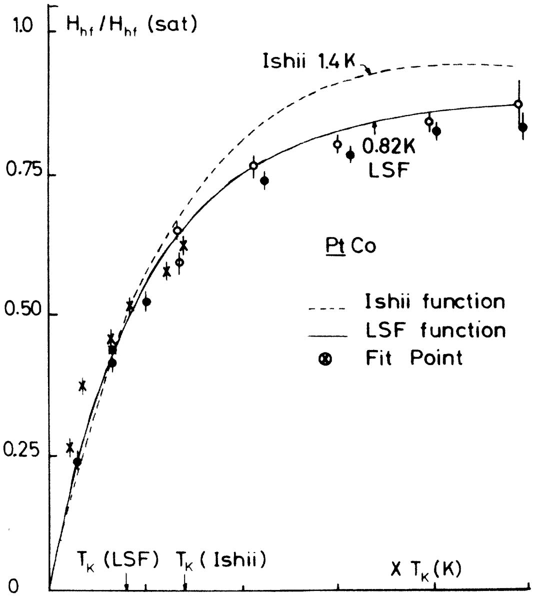

FIG. 3. Fits of $H_{hf}(H_a)$ to two theoretical expressions for the saturation behavior (see text). Dashed line: singlet state theory of Ishii; solid line: Localized spin fluctuation model (Gallop). The data were fitted to the curves at one point ($H_a = 10$ kOe) and the respective T_K values determined from this fit point. The abscissa is $XT_K = g\mu_B H_a/2k$.

The question of a spin S associated with the giant moment remains open. It is demonstrated by the susceptibility data of TT, which give an effective moment leading to an overly large saturation moment, that the effective spin $S_{eff} = 2.2$ found from the Curie constant is not that of the whole giant moment. This is also seen in the *Pd*Co system, where Mössbauer measurements[18] indicate a Brillouin function dependence for H_{hf} with $S > 2$.

We conclude that the *Pt*Co alloy system provides a nearly unique opportunity for the comparison of hyperfine and magnetization data, allowing on the one hand measurements of both types in the zero-temperature limit ($T_{expt} \ll T_K$), and on the other, almost complete restoration of the local moments with available applied fields. This is in contrast to systems like *Pd*Fe and *Pd*Co where T_K is very low so that the moments saturate in low applied fields, making an analysis of the relation between the local and induced parts of the giant moment difficult and a comparison with magnetization data meaningless because of interaction effects. Also, in systems with higher T_K like *Cu*Fe, available fields are not sufficient to approach saturation. Another likely candidate for such a comparison is the *Cu*Cr system, where, unfortunately however, good low-temperature magnetization data are still lacking.

ACKNOWLEDGMENTS

We wish to thank Dr. B. Tissier and Dr. R. Tournier for providing the concentrated *Pt*Co samples. This work was supported in part by the Bundesminister für Bildung and Wissenschaft (West Germany), the C. N. R. S. (France), and the Science Research Council (Great Britain).

---

*Present address: Physics Dept., University of Tripoli, Libya.

†Present address: National Physical Laboratory, Teddington, Middlesex, England.

[1] F. Hartmann-Boutron, J. Phys. (Paris) C1, 35, 11 (1974).

[2] J. Flouquet, J. Phys. F 1, 87 (1971).

[3] A. J. Heeger, Solid State Phys. 23, 284 (1969); J. Kondo, *ibid.* 23, 184 (1969).

[4] The value 1.6 K is obtained from the initial slope of the hyperfine field (Ref. 12) and 1.65 K from the susceptibility measurements (Ref. 5).

[5] B. Tissier and R. Tournier, Solid State Commun. 11, 895 (1972).

[6] H. Ishii, Prog. Theor. Phys. 40, 578 (1970).

[7] J. C. Gallop, D. Philos. thesis (Oxford, 1970) (unpublished).

[8] M. Ali, Diplomarbeit (Freie Universität, Berlin, 1972) (unpublished).

[9] J. Boysen, W. D. Brewer, and J. Flouquet, J. Phys. (Paris) C1-35, 5 (1974).

[10] G. G. Low and T. M. Holden, Proc. Phys. Soc. Lond. 89, 119 (1966).

[11] J. Crangle and W. R. Scott, J. Appl. Phys. 36, 921 (1965).

[12] J. C. Gallop and I. A. Campbell, Solid State Commun. 6, 831 (1968).

[13] T. Ericksen, M. T. Hirvonen, T. E. Katila, and P. E. Reivari, *Proceedings of the Twelfth International Conference on Low-Temperature Physics*, Kyoto, 1970, (Academic Press of Japan, Tokyo, 1971), p. 765; T. Ericksen, M. T. Hirvonen, T. E. Katila, and V. K. Typpi, Solid State Commun. 8, 765 (1970).

[14] B. Giovannini, R. Paulson, and J. R. Schrieffer, Phys. Lett. 23, 517 (1966).

[15] J. W. Loram, R. J. White, and A. D. C. Grassie, Phys. Rev. B 5, 3659 (1972).

[16] H. Nagasawa, Solid State Commun. 10, 33 (1972).

[17] J. Souletie, J. Low Temp. Phys. 7, 141 (1972).

[18] M. P. Maley, R. D. Taylor, and J. L. Thompson, J. Appl. Phys. 38, 1249 (1967).

[19] D. K. C. McDonald, Proc. R. Soc. Lond. 266, 161 (1962).