PHYSICAL REVIEW B VOLUME 30, NUMBER 9 1 NOVEMBER 1984

Normal-state magnetic susceptibility as a structural probe in an amorphous superconducting Zr-Co alloy

Ö. Rapp and L. Hedman
Department of Solid State Physics, The Royal Institute of Technology, S-100 44 Stockholm, Sweden

(Received 23 January 1984; revised manuscript received 29 May 1984)

Amorphous $Zr_{65}Co_{35}$ alloys were prepared by melt spinning with different cooling rates. The x-ray diffraction patterns, superconducting transitions, and normal-state magnetic properties were studied. The differences in x-ray results and superconducting T_c's between these samples were small. The temperature and field dependence of the magnetic susceptibility were both found to vary significantly with cooling rate. This is interpreted in terms of the effect of varying cooling rate on Co-rich clusters.

I. INTRODUCTION

The basic fact that a glass is not a unique, well-defined structure has received increased attention only gradually for metal glasses. A reason may be that it is still too difficult a question to ask how the microstructure of a glass affects the physical properties. There is mostly an unfortunate division in the literature between papers dealing only with structural characterization of glasses and those dealing only with physical properties.

Nevertheless, several methods have been attempted to correlate physical and structural properties. One possibility is to prepare samples of similar composition by different methods. Another approach is to allow the structure of a given sample to relax by a suitable heat treatment. A third method is to liquid-quench samples of similar composition and use different cooling rates. Only in a few cases, however, is there a physical understanding why a certain structural change leads to the observed change of a measured property. A detailed description of the relevant structural changes would seem to be beyond the present possibilities.

In this paper we report on some effects of structural changes in a metal glass induced by different cooling rates in melt spinning. X-ray diffractograms are obtained, the superconducting transition temperature T_c is measured, and the temperature and field dependence of the normal-state magnetic susceptibility χ are studied. $Zr_{65}Co_{35}$ is chosen for this investigation since it is easily formed in melt spinning, has a convenient T_c, and contains a large fraction of a magnetic element. With different cooling rates there are significant differences only in χ, however, particularly in its field dependence, while T_c remains largely unaffected. This experiment permits a simple physical interpretation of the relation between χ and cooling rates in terms of the different distributions and sizes of small Co-rich clusters.

II. EXPERIMENTAL TECHNIQUES

The samples were prepared from Zr of 99.8 wt. % nominal purity (Alfa Ventron) and Co of 99.998 wt. % nominal purity (Johnson and Mattey). Appropriate quantities were arc-melted several times under reduced pressure of Ar gettered by molten Zr. The weight losses in this process were small. Attributing them to losses only of Co gives the following series of nominal compositions for the different samples with sample thickness in μm, Zr concentration in at. %: (20,64.62), (30,64.58), (50,64.62).

Melt spinning was performed by melting the samples in an induction furnace and pressurizing the liquid by Ar gas through an orifice onto a rotating drum. Oxidation of the samples was prevented by pouring liquid nitrogen into a large container below the apparatus just prior to melting so that the drum was surrounded by nitrogen gas. It proved to be difficult to control the thickness of the ribbons reliably by varying the ejection pressure and wheel speed.[1] By a series of different attempts it was possible to obtain ribbons of sufficient quantities and homogeneity.

The thickness of the ribbons was measured with a micrometer. This procedure overestimates the true thickness by a small fraction due to the roughness of one surface. The results for the samples used were 22±4, 31±2, and 50±2 μm. The scatter includes measurement errors and variations along the length of the samples. Due to these uncertainties the samples are designated by their thickness as 20, 30, and 50 μm, respectively. The widths of these ribbons were approximately 0.2, 1, and 1 mm, respectively.

A rotating drum of copper was used for the 20- and 30-μm samples and a stainless-steel cylinder for the 50-μm sample. The cooling rate of this latter sample was therefore presumably even lower than a comparison between the different thicknesses would suggest.

Pieces of each sample were examined by Mo $K\alpha$ radiation at room temperature. The instrument was equipped with a curved monochromator of LiF in the diffracted beam, a scintillation counter, a pulse height analyzer, and a step scanning control. Readings were taken for 100 s at steps of 0.1° in θ.

The superconducting transition temperature was measured resistively by a dc technique with four edges of Cu pressed onto the sample surface. The measuring current was a few mA. The temperature was obtained from a calibrated carbon resistor.

The magnetic susceptibility was measured as a function of field up to 1.3 T and temperature in the range 4—300 K. A Faraday method was used. Several pieces of each sample of length $\simeq 1$ cm were bent into a *V* form and suspended by a calibrated gold wire. For the 20-μm sample 12 such pieces were required for a sample mass of 6 mg. With such small masses the accuracy of the measurements is somewhat reduced and amounts to approximately 1%.

III. RESULTS AND DISCUSSION

The x-ray results are shown in Fig. 1. k is the magnitude of the scattering vector, $k = 4\pi \sin\theta/\lambda$. These spectra show that the samples are x-ray amorphous. The value of k at the first peak, k_p, is within 2.60 ± 0.01 Å^{-1} in all cases. Thus there are no appreciable differences in the nearest-neighbor distance for these samples. This value of k_p is in agreement with those reported previously[2,3] for $Zr_{64}Co_{36}$.

Other differences between the different samples are also small, smaller, e.g., than those observed after thermal relaxation of an amorphous Zr-Cu alloy,[4] where the half width of the first peak decreased by 4% after relaxation. In the present case the half width of the first peak is 0.50 ± 0.01 Å^{-1} for the 20- and 30-μm samples and 0.49 ± 0.01 Å^{-1} for the 50-μm sample.

The superconducting T_c was found to be within 2.67 ± 0.05 K for all samples. The widths of the transitions, which increased with increasing cooling rate, were in the range 6—20 mK. The result for T_c is in agreement with previous reports such as 2.65 K for a similarly prepared alloy[5] using high-purity Zr, 2.70 K obtained by Babić *et al.*,[6] and 2.71 K from interpolation in the results reported by Altounian and Strom-Olsen.[7] On the other hand, Karkut and Hake[8] found $T_c \sim 2.5$ K. As they pointed out, such a low value is possibly due to impurities.

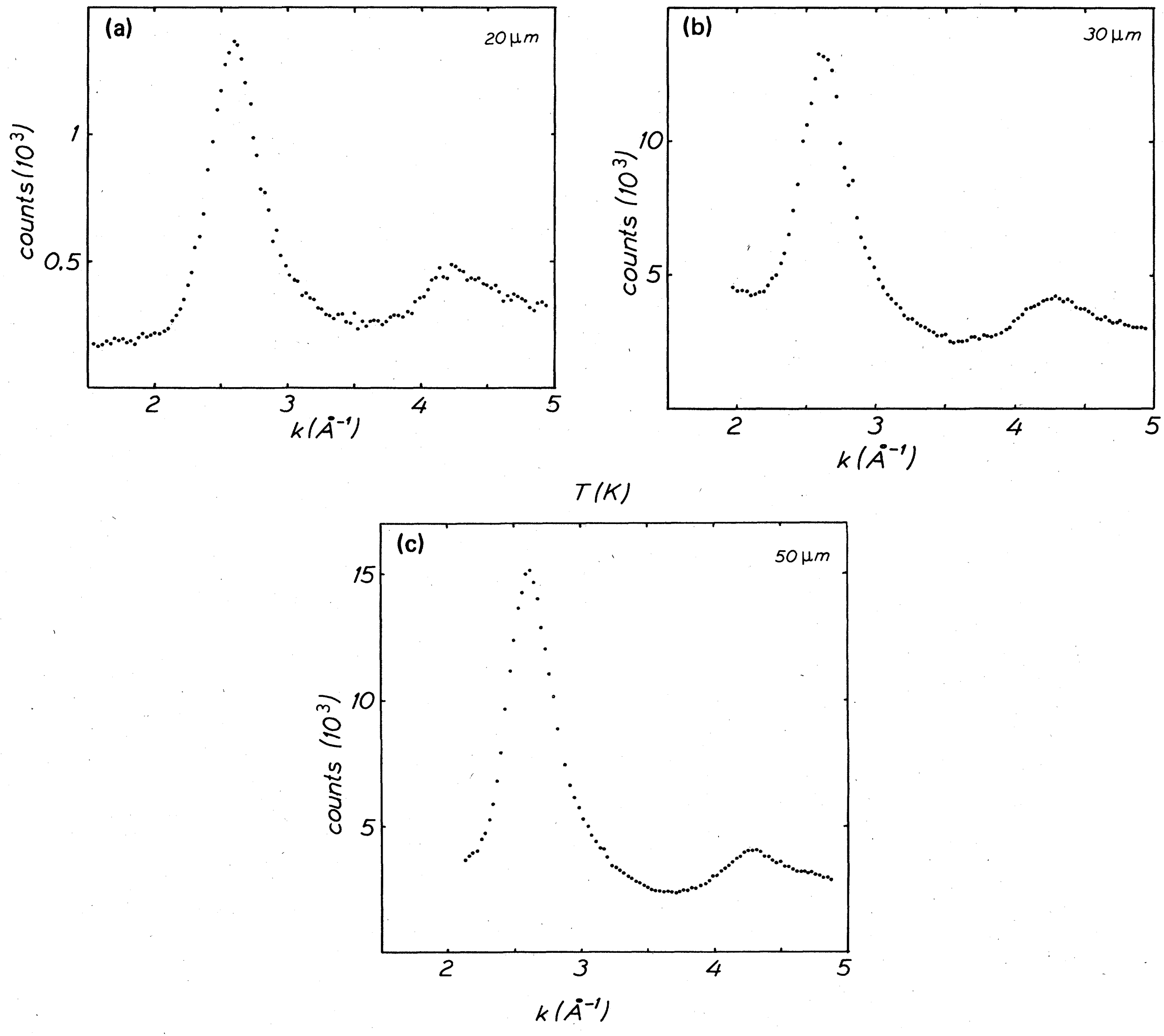

FIG. 1. X-ray diffractograms of $Zr_{65}Co_{35}$ for (a) 20-μm, (b) 30-μm, and (c) 50-μm thick samples. k is the magnitude of the scattering vector $= 4\pi \sin\theta/\lambda$.

The range of T_c variation for the present samples is small. For instance, the effect of relaxation experiments is generally[4,9] to decrease T_c irreversibly by 0.2—0.3 K. Furthermore, T_c in Zr-Co alloys varies appreciably with composition. It decreases linearly with Co concentration in this concentration region[7,10] by about 0.12 K/at. %. These observations and the narrow superconducting transitions indicate homogenous samples of well-controlled composition with small structural differences between samples of different cooling rates.

The magnetic susceptibility was found to be somewhat field dependent which we ascribe to minor ferromagnetic inclusions. For the true magnetic susceptibility χ one can write

$$\chi=\chi_A-\frac{\omega\sigma}{B}\ , \tag{1}$$

where χ_A is the measured apparent susceptibility at field strength B and ω is the weight fraction of ferromagnetic inclusions of saturated magnetization σ. One obtains χ by measuring χ_A at various sufficiently high fields and extrapolating linearly to $1/B=0$ according to Eq. (1). Such a field dependence is often observed in amorphous Zr-Co and Zr-Fe alloys.[7,10,11]

The temperature dependence of χ is shown in Fig. 2 and the temperature dependence of the field dependence, $\omega\sigma$, is shown in Fig. 3. At room temperature χ is within 19.7 ± 0.2 mJ/T^{2}kg for all samples and therefore, within measurement error, almost independent of cooling rate over the range of cooling rates employed. Our result for χ at room temperature is in good agreement with 19.65 mJ/T^{2}kg given by Babić *et al.*[6] and higher than that obtained by Altounian and Strom-Olsen[7] who report 18.7 mJ/T^{2}kg for the valence susceptibility of amorphous $Zr_{65}Co_{35}$, from which a core contribution of the order of a few mJ/T^{2}kg should be subtracted to obtain the measured susceptibility.

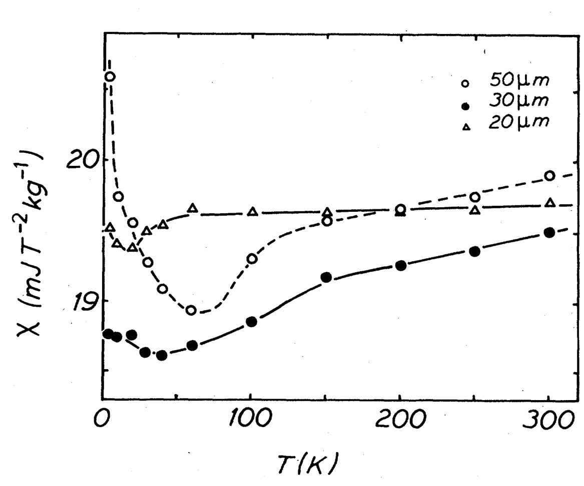

FIG. 2. Temperature dependence of χ for three $Zr_{65}Co_{35}$ samples of different thickness.

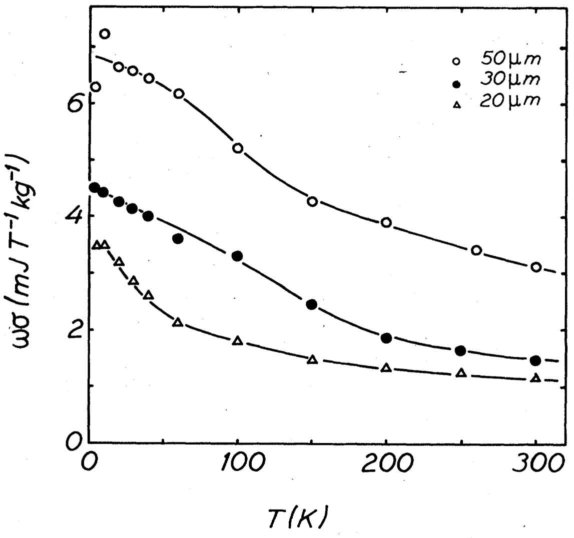

FIG. 3. Temperature dependence of $\omega\sigma$, defined in Eq. (1), for the same samples as in Fig. 2.

The prominent features of Figs. 2 and 3 are the following: With decreasing temperature χ decreases for intermediate temperatures and increases at low temperatures. There is thus a minimum in χ at a temperature $T_{\min}$ which increases with decreasing cooling rate. The field dependence, $\omega\sigma$, decreases monotonically with increasing temperature. It increases at all temperatures with decreasing cooling rate.

As discussed previously,[11] the temperature dependence of $\omega\sigma$ may be due to one or several of the following mechanisms. With decreasing temperature (i) the apparent sizes of ferromagnetic clusters increase, (ii) successively more such clusters may become saturated, and (iii) the saturation moment of the clusters may increase.

These clusters are presumably a small fraction of the matrix. A lower limit is obtained if it is assumed that σ of Eq. (1) is due to saturated Co with $\sigma=160$ A m^2/kg. The range of values of $\omega\sigma$ spanned in Fig. 3 would then correspond to cluster fractions in the range 6—40 ppm. Real cluster fractions may be significantly larger. In amorphous ZrCo alloys the Co moment decreases gradually with increasing Zr concentration. A moment of $\sim0.2\mu_B$/Co atom was observed[12] at 4.2 K in amorphous $Zr_{38}Co_{62}$ and clusters of this composition would therefore correspond to weight fractions up to 40 times $1.7/0.2\approx350$ ppm (where 1.7 is the ferromagnetic Bohr magneton number of pure Co). Even somewhat larger fractions could be imagined. The Co moment disappears rapidly above 40 at. % Zr, however.[12] It is interesting to note that T_c is not appreciably affected by the different cluster arrangements. T_c is strongly depressed in many superconductors with paramagnetic impurities already at the level below 100 ppm.[13] In the present case we may expect[14] the size of the clusters to be at most of the order of a coherence length ξ_0. In $Zr_{65}Co_{35}$ ξ_0 was found to be[8] about 70 Å.

These qualitative estimates serve to set a rough scale for these clusters. In reality a distribution of clusters of different sizes and Co concentrations is expected. In particular, the Co-rich clusters will decrease in number and average size when the cooling rate increases.

This simple physical picture provides a consistent interpretation of the main features of Figs. 2 and 3. $\omega\sigma$ increases with decreasing cooling rate because the number

TABLE I. Representative results for amorphous $Zr_{65}Co_{35}$ alloys.

Sample thickness (μm)	Nominal composition (at. % Zr)	k_p [a] (Å^{-1})	Δk_p [a] (Å^{-1})	T_c (K)	ΔT_c [b] (mK)	χ at 300 K (mJ/T^2 kg)	$T_{\min}$ [c] (K)	$\omega\sigma$ at 300 K (mJ/T kg)
20	64.62	2.60±0.01[d]	0.50±0.01	2.67±0.05[d]	13,20	19.7±0.2[d]	20	1.15
30	64.58		0.50±0.01		6,7,10		40	1.47
50	64.62		0.49±0.01		7		60	3.12

[a] k_p and Δk_p are the position and width at half maximum of the first peak in the structure factor.

[b] ΔT_c is the width of the superconducting transition. In some cases T_c was measured on different pieces from the same ingot.

[c] $T_{\min}$ is the temperature where χ has a minimum.

[d] Results for all samples within limits given.

and average size of clusters increase. Thereby the probability increases that clusters of larger Co concentration are formed which carry a larger moment. Hence both ω and σ increase. The Curie temperature also increases with increasing cluster size. Therefore, more clusters contribute to $\omega\sigma$ already at higher temperatures in the more slowly cooled samples and the temperature dependence of $\omega\sigma$ is stronger and displaced towards higher temperatures in these samples.

Above 100 K χ and its temperature dependence are similar for the different samples of Fig. 2 although the correction to the measured susceptibility has a different magnitude and temperature dependence for each sample as seen in Fig. 3. This result supports our view that a magnetic field of 1.3 T is sufficient to saturate most of the ferromagnetic clusters at these temperatures and that Fig. 2 thus, in contrast to a recent contention by Kaul,[15] displays the true magnetic susceptibility for our samples at these temperatures. Furthermore, the positive temperature dependence of χ at higher temperatures is similar to that of polycrystalline Zr.[16] This observation and a number of different results[17–20] all suggest Zr-like Fermi-surface properties of amorphous Zr-based alloys.

The rise in χ at decreasing low temperatures may be due to superparamagnetic clusters and (or) ferromagnetic clusters which are unsaturated at our measuring fields. More such clusters may be expected in the more slowly cooled samples and the temperature dependence is then stronger.

The minimum in χ which develops from the combination of these two mechanisms is therefore displaced towards higher temperatures with decreasing cooling rate. A few aspects of Fig. 2 are not accounted for by this simple model. Specifically we do not understand why $d\chi/dT$ at high temperatures is so small for the 20-μm sample, nor why $d\chi/dT$ is significantly higher than the high-temperature value for all samples in the temperature region just above the minima. The experimental results are summarized in Table I.

IV. SUMMARY AND NEW PROBLEMS

Structural changes have been introduced in an amorphous ZrCo alloy by cooling with different rates from the melt. We have found that the magnetic susceptibility is a sensitive probe to these small structural changes, more sensitive than the otherwise structure-sensitive superconducting T_c and certainly more sensitive also than the rather structure-insensitive x-ray results. To describe these results we assume that there are small regions in the samples which are rich in Co and ferromagnetic. The size and weight fraction of these clusters depend on cooling rate and temperature. This model accounts for all of the main features of the influence of varying cooling rates on χ. We thus obtain a simple physical picture of a relation between structure and property for an amorphous metal.

In this paper we have not further pursued the study of the small differences in x-ray and T_c results, but rather used these results as an indication that the structural changes involved are small and as an additional check on our sample quality. The present method, however, shows promising potential in the further study of the interesting and difficult problem of the relation between structure and physical properties in disordered systems. For the present alloys other interesting physical properties include the resistivity and its temperature dependence and various superconducting properties such as T_c and its field dependence and the excess conductivity above T_c.

It is of particular interest that the present alloys are superconducting and contain a large fraction of a magnetic element, the distribution of which can be monitored to some extent by the cooling rate. This would suggest the possibility for one to study the problem of how superconductivity vanishes with decreasing Zr concentration and how ferromagnetism eventually emerges. For instance, it has been argued[6,21–23] that spin fluctuations depress T_c in ZrCo and ZrFe alloys already at smaller Co concentrations than that presently studied. If there were spin fluctuations in this alloy, however, they would presumably be enhanced by the presence of ferromagnetic inclusions. Since the fraction of these clusters can be varied by more than a factor of 2 by varying the cooling rate, without any corresponding important change in T_c, we find it likely that spin fluctuations are not significant in depressing T_c in ZrCo alloys up to 35 at. % Co. We also note that the magnitude of χ in this and similar alloys supports the view that spin fluctuations are small or negligible at these concentrations of a late transition metal.[11,24] This and related problems would merit further studies by attempting to obtain a larger range of different cooling rates and by increasing the magnetic component somewhat while remaining in the superconducting phase.

ACKNOWLEDGMENTS

We are grateful to Å. Östlund for preparing the samples, to P. -E. Werner and K. E. Johansson for putting the x-ray equipment at our disposal and kindly advising us about it, to L. Khlaif for his technical assistance, to G. Grimvall for his comments on the manuscript, and to Dr. J. O. Strom-Olsen for communicating the results of Ref. 24 prior to publication.

---

[1] H. H. Liebermann and C. D. Graham, Jr., IEEE Trans. Magn. **MAG-12**, 921 (1976).

[2] K. H. J. Buschow and N. M. Beekmans, Phys. Rev. B **19**, 3843 (1979).

[3] K. H. J. Buschow, J. Phys. F **14**, 593 (1984).

[4] P. Garoche, Y. Calvayrac, W. Cheng, and J. J. Veyssié, J. Phys. F **12**, 2783 (1982).

[5] Ö. Rapp, M. Flodin, Å. Östlund, and H. Fredriksson, Phys. Scr. **25**, 804 (1982).

[6] E. Babić, R. Ristic, M. Miljak, and M. G. Scott, in *Proceedings of the 4th International Conference on Rapidly Quenched Metals, Sendai, 1981,* edited by T. Masumoto and K. Suzuki (Institute of Metals, Sendai, 1982), p. 1079.

[7] Z. Altounian and J. O. Strom-Olsen, Phys. Rev. B **27**, 4149 (1983).

[8] M. G. Karkut and R. R. Hake, Phys. Rev. B **28**, 1396 (1983).

[9] A. J. Drehman and W. L. Johnson, Phys. Status Solidi A **52**, 499 (1979).

[10] Ö. Rapp, M. Flodin, and L. Hedman, in *Superconductivity in d- and f-Band Metals—1982,* edited by W. Buckel and W. Weber (Kernforschungszentrum, Karlsruhe, 1982), p. 351.

[11] L. Hedman and Ö. Rapp, Phys. Lett. **100A**, 251 (1984).

[12] N. Heiman and N. Kazama, Phys. Rev. B **17**, 2215 (1978).

[13] M. B. Maple, in *Magnetism,* edited by H. Suhl (Academic, New York, 1973), Vol. 5, p. 289.

[14] P. W. Anderson and H. Suhl, Phys. Rev. **116**, 898 (1959).

[15] S. N. Kaul, Phys. Lett. **100A**, 254 (1984).

[16] E. W. Collings and J. C. Ho, Phys. Rev. B **4**, 349 (1971).

[17] P. Oelhafen, E. Hauser, H-J. Güntherodt, and K. H. Benneman, Phys. Rev. Lett. **43**, 1134 (1979).

[18] Ö. Rapp, J. Jäckle, and K. Froböse, J. Phys. F **11**, 2359 (1981).

[19] R. H. Fairlie, W. H. Temmerman, and B. L. Gyorffy, J. Phys. F **12**, 1641 (1982).

[20] V. L. Moruzzi, P. Oelhafen, A. R. Williams, R. Lapka, H-J. Güntherodt, and J. Kübler, Phys. Rev. B **27**, 2049 (1983).

[21] M. Tenhover and W. L. Johnson, Physica **108B**, 1221 (1981).

[22] J. Willer, G. Fritsch, and E. Lüscher, J. Less-Common Met. **77**, 191 (1981).

[23] M. Tenhover and W. L. Johnson, Phys. Rev. B **27**, 1610 (1983).

[24] E. Batalla, Z. Altounian, and J. O. Strom-Olsen, Phys. Rev. B (to be published).