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# Tunneling states in Al-Li-Cu quasicrystals

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We report on measurements of the velocity of sound at low temperature in three samples of the alloy Al-Li-Cu: a single crystal of the cubic approximant phase $R$ and two samples of the imperfect icosahedral phase $T2$, one of them after annealing to improve its structural quality. All samples exhibit glasslike properties. We analyze our results within the tunneling state model and show that the tunneling strength increases with the degree of the quasicrystalline order in the sample.

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The low-temperature ($T \leq 1$ K) properties of amorphous materials differ drastically from those of simple crystals. In the phenomenological tunneling state model, these specific properties are explained by the presence in disordered matter of two-level systems, arising from the tunneling of atoms between nearly degenerate configurations.[1,2] However, a microscopic description of these *tunneling states* (TS's), which could account for their presence in all amorphous materials and with almost the same density of states, is still missing. To address this long-standing question, it is interesting to study materials with an intermediate order between crystals and amorphous solids. Thus, one can hope to find out the necessary conditions for the existence of TS's.

In 1984, the discovery by Shechtman *et al.*[3] of quasicrystals, a new class of materials, long-range ordered but without any periodicity, gave a new opportunity to fulfill this program. Several recent acoustic studies of high-quality quasicrystals *i*-AlPdMn,[4,5] *i*-AlCuFe,[6] and *i*-ZnMgY (Ref. 7) showed the presence of TS's with a density of states similar to what is found in amorphous metals, and it is now generally accepted that the low-temperature lattice vibrations of perfect quasicrystals are amorphouslike. Therefore, a disordered network is not necessary for TS's to exist.

However, some former experimental results on the first discovered low-quality quasicrystals do not match this recent picture. Low-frequency measurements of the acoustic velocity and damping of several samples had revealed either a very small density of state of TS's or no TS's at all.[8,9] So, surprisingly, one is tempted to conclude that the presence of defects in quasicrystals reduces the number of TS's.[6] On the contrary the introduction of defects in crystals, by ion implantation[10] or neutron irradiation,[11] leads to a glasslike behavior. At this point it seems important to reinvestigate in detail the occurrence of TS's in relation with structural defects in quasicrystals. The breakdown of the universality of the tunneling state model in the case of defective quasicrystals is indeed an opportunity to enlighten our understanding of the link between disorder and TS's, and more generally to clear up the microscopic nature of the TS's.

The icosahedral $T2$-phase $Al_6CuLi_3$ was the first stable quasicrystal to be discovered. Contrary to more recent quasicrystalline alloys (e.g., *i*-AlPdMn or *i*-AlCuFe), it does not show a perfect icosahedral symmetry and it is described as a phason-strained quasicrystal. Phason strains are long-range, static defects specific to the quasicrystalline structure, which are responsible for a discrepancy with the perfect quasicrystalline order. When annealed, the amplitude of the phason strain is reduced and the quasicrystalline order significantly increases, even though a perfect icosahedral symmetry is not reached even after long heat treatments.[12] It is therefore a good candidate for our purpose and we have studied three samples of the ternary alloy Al-Li-Cu. Sample (a) is a centimeter-sized single grain of the cubic-approximant phase $R$-$Al_5CuLi_3$. This phase is crystalline, with a large cubic unit cell ($a = 1.39$ nm) and a local order resembling that of the related icosahedral $T2$ phase.[13] Sample (b) is a polycrystal of the $T2$ icosahedral phase. Samples (a) and (b) were prepared by slow solidification following the method described by Dubost *et al.*[14] Sample (c) was extracted from the same ingot as sample (b) in order to avoid any possible effect of a different preparation or composition. It was then annealed for several days under helium pressure (about 50 bars) to prevent lithium evaporation. X-ray powder-diffraction patterns of samples (b) and (c) revealed that both samples consist mainly of the $T2$ icosahedral phase with a small contribution of a residual fcc aluminum phase.

All samples were slab shaped with a length of 5 mm, 9 mm, and 7 mm for samples (a), (b), and (c), respectively. A great care was taken to obtain two parallel faces that were polished, and two piezoelectric transducers were glued on these faces. Longitudinal acoustic waves were produced by $LiNbO_3$ transducers and shear waves by AC-cut quartz transducers. The working frequencies were chosen for each sample to get the best experimental accuracy. They finally ranged from 90 MHz to 420 MHz. The acoustic velocity and the attenuation variations were measured with a phase-sensitive method. A $^3$He-$^4$He dilution refrigerator permitted to cool the samples down to 20 mK.

Figure 1 shows the acoustic velocity variation of longitudinal waves in the three samples between 20 mK and 4 K. Figure 2 focuses on the results obtained, in the same temperature range, in the approximant phase for shear waves at 204 MHz and for longitudinal waves at two frequencies 222 MHz and 420 MHz. All samples exhibit a similar behavior. The acoustic velocity increases from the lowest temperatures and is proportional to the logarithm of the temperature. It reaches a maximum at about 0.9 K for sample (a) and about 2 K for both samples (b) and (c). Then, it decreases linearly with temperature until about 10 K as shown in Fig. 3. Above 10 K, the acoustic velocity decreases more rapidly.

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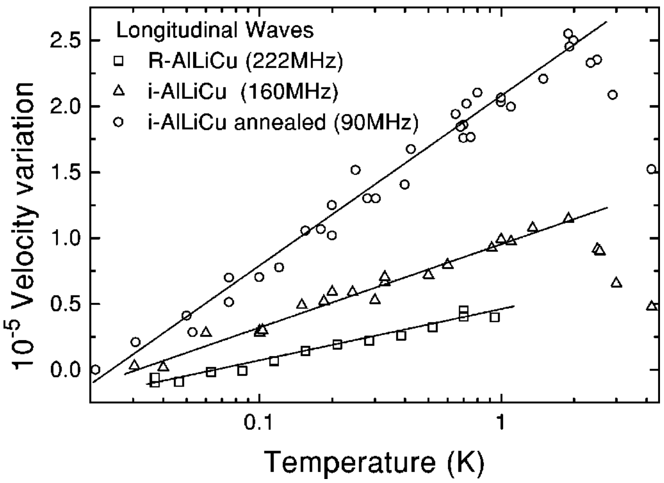

FIG. 1. Low-temperature acoustic velocity variation of longitudinal waves in $R$-$Al_5CuLi_3$ [sample (a)] at 222 MHz (□), $i$-$Al_6CuLi_3$ [sample (b)] at 160 MHz (△), and annealed $i$-$Al_6CuLi_3$ [sample (c)] at 90 MHz (○). The curves have been shifted arbitrarily for clarity. The solid lines are the best logarithmic fits with the low-temperature data.

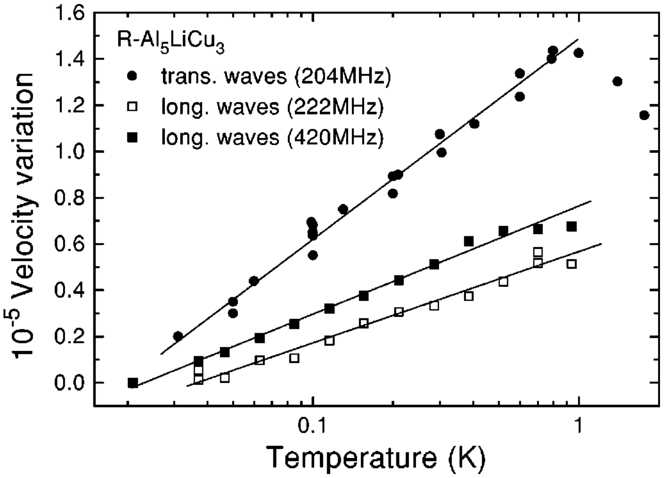

FIG. 2. Low-temperature acoustic velocity variation in $R$-$Al_5CuLi_3$ [sample (a)] for longitudinal waves at 222 MHz (□) and 420 MHz (■), and for shear waves at 204 MHz (●). The curves have been shifted arbitrarily for clarity. The solid lines are the best logarithmic fits for the low-temperature data.

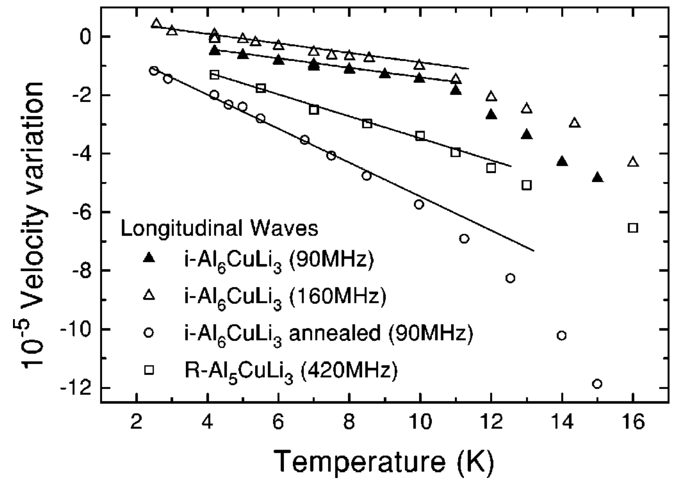

FIG. 3. High-temperature acoustic velocity variation of longitudinal waves in $R$-$Al_5CuLi_3$ [sample (a)] at 420 MHz (□), $i$-$Al_6CuLi_3$ [sample (b)] at 90 MHz (▲) and 160 MHz (△), and annealed $i$-$Al_6CuLi_3$ [sample (c)] at 90 MHz (○). The curves are shifted arbitrarily. The solid lines are the best linear fits for the data below 10 K.

These behaviors are characteristic of amorphous materials and differ strongly from simple crystals where the acoustic velocity is constant at low temperatures, and decreases as a power law of the temperature at higher temperatures. Thus, we will analyze our results in the framework of the tunneling state model, which was first introduced to explain the anomalous low-energy excitations of glasses. In this model, TS's interact with the incident acoustic wave via a resonant process that leads to the characteristic acoustic velocity variation,[15]

$$\left.\frac{v_i(T)-v_i(T_0)}{v_i}\right|_{res}=C_i\ln\left(\frac{T}{T_0}\right), \tag{1}$$

where the subscript $i$ stands for the polarization ($t$ for transverse and $l$ for longitudinal) of the acoustic wave and $T_0$ is a reference temperature. The slope $C_i$ in Eq. (1), called the tunneling strength, is directly proportional to the TS's density of states $\overline{P}$ and is equal to

$$C_i=\frac{\overline{P}\gamma_i^2}{\rho v_i^2}, \tag{2}$$

where $\gamma_i$ is the average deformation potential of the TS's, which describes the coupling of the TS's with the acoustic wave and $\rho$ is the density of the material. In the tunneling state model, $\overline{P}$ is assumed to be constant. In dielectric materials and for ultrasonic waves, the resonant processes are dominant below about 1 K. In addition, in metallic glasses, conduction electrons provide an effective channel for the relaxation of the TS's even at the lowest temperature. These relaxation processes are responsible for a logarithmic decrease of the acoustic velocity with a slope equal to half the tunneling strength. In metallic glasses, the total velocity variation is therefore[16]

$$\left.\frac{v_i(T)-v_i(T_0)}{v_i}\right|_{tot}^{metal}=C_i\ln\left(\frac{T}{T_0}\right)-\frac{C_i}{2}\ln\left(\frac{T}{T_0}\right)=\frac{C_i}{2}\ln\left(\frac{T}{T_0}\right). \tag{3}$$

In quasicrystals, the resistivity can be much higher than in metallic glasses[17] and it is not obvious whether we should use Eq. (3) rather than Eq. (1). If the relaxation by electrons is efficient there should be no shift of the maximum of the acoustic velocity with frequency and the acoustic attenuation should be constant.[18] In i-AlPdMn (Ref. 5) those conditions were fulfilled and Eq. (3) was used, whereas in $i$-AlCuFe (Ref. 6) the acoustic-attenuation measurements were in favor of a relaxation by phonons and Eq. (1) was used. Unfortunately, in our samples the results on the acoustic attenuation

TABLE I. Numerical values of the tunneling strengths $C_i$, coupling parameters $\overline{P}\gamma_i$, and linear slopes $\beta_i$, as deduced from Figs. 1, 2, and 3.

| Sample | $R$-$Al_5CuLi_3$ (a) | $i$-$Al_6CuLi_3$ (b) | Annealed $i$-$Al_6CuLi_3$ (c) |
|---|---|---|---|
| $C_t$ $(\times 10^{-6})$ | 7.5 | | |
| $\overline{P}\gamma_t^2$ $(\times 10^5$ J m$^{-3})$ | 3.1 | | |
| $C_l$ $(\times 10^{-6})$ | 3.6 | 5.5 | 11.2 |
| $\overline{P}\gamma_l^2$ $(\times 10^5$ J m$^{-3})$ | 3.8 | 5.5 | 11.3 |
| $\beta_t$ $(\times 10^{-6}$ K$^{-1})$ | −5.5 | | |
| $\beta_l$ $(\times 10^{-6}$ K$^{-1})$ | −3.8 | −1.7 | −5.6 |

are too imprecise to draw any conclusion. The comparaison of Fig. 1 with a former low-frequency study[8] indicates that there is a shift of the maximum velocity with frequency, but it is much smaller than what is expected for a phonon-assisted relaxation and depends too much on the sample to be conclusive. Moreover, in Ref. 8 the authors claim that the acoustic attenuation in their samples is dominated by a relaxation process involving conduction electrons. On this basis, and according to the small resistivity of low-quality $i$-AlLiCu quasicrystals,[19] we will use Eq. (3) to analyze our results.

The tunneling strengths deduced from the low-temperature measurements shown in Fig. 1 and Fig. 2 are summarized in Table I. The density of the $R$-$Al_5CuLi_3$ crystal is $\rho = 2.464$ g cm$^{-3}$ according to Ref. 13. Due to the small difference in composition between the approximant and the quasicrystalline phase, we also take this value for the quasicrystal. The absolute acoustic velocities in the icosahedral phase[20] are $v_l = 6400$ m s$^{-1}$ and $v_t = 3800$ m s$^{-1}$. In the cubic-phase $R$-AlLiCu we have measured $v_l = 6600$ m s$^{-1}$ and $v_t = 4090$ m s$^{-1}$. With these values and the measured tunneling strengths, we have calculated in Table I the coupling parameters $\overline{P}\gamma_i^2$. For comparison, with the same experimental method, in a typical amorphous metal $a$-PdSi,[21] $\overline{P}\gamma_l^2 = 6.4\times 10^6$ J m$^{-3}$ and $\overline{P}\gamma_t^2 = 3.8\times 10^6$ J m$^{-3}$ and in high-quality quasicrystal $i$-AlPdMn,[4] $\overline{P}\gamma_t^2 = 3.2\times 10^6$ J m$^{-3}$. The coupling parameters in all samples are much smaller than those typical values. This is in agreement with a former study on the same alloy Al-Li-Cu at low frequency.[8] In Ref. 8, the damping and the Young-modulus sound velocity $v_E$ were measured with a vibrating-reed technique. A quantitative comparison with our results is not straightforward. Indeed, $v_E$ is related to the longitudinal and transverse velocities by

$$v_E = v_l \left( \frac{3v_t^2 v_l^2 - 4v_t^4}{v_l^4 - v_t^2 v_l^2} \right)^{1/2}. \tag{4}$$

From our measurements we deduce $\gamma_l^2/\gamma_t^2 = 1.25$ for sample (a). Since the local order is similar in the approximant and the quasicrystalline phase we can assume this ratio to be roughly equal in the quasicrystal. With this assumption and Eq. (4), the results of Ref. 8 would lead to a longitudinal tunneling strength $C_l = 1.2\times 10^{-6}$ (from sound velocity) or $C_l = 3.1\times 10^{-6}$ (from damping) for a single crystal of $R$-AlLiCu, and $C_l = 3.8\times 10^{-6}$ (velocity) or $C_l = 6.5\times 10^{-6}$ (damping) for a quasicrystalline ribbon $i$-AlLiCu. These values agree well with our measurements on samples (a) and (b).

The new point appearing in our study is the strong increase of the tunneling strength after annealing [sample (c)]. From our study, it is not possible to attribute this behavior to a change in $\overline{P}$ or $\gamma_l$ separately. A measure of $\overline{P}$ alone is, in principle, achievable through low-temperature specific-heat measurements. TS's are indeed responsible for a linear increase of the specific heat with temperature, the slope being proportional to $\overline{P}$. The annealing treatment was found to have no influence on the linear term of the specific heat of an icosahedral quasicrystal Al-Li-Cu.[22] However, the lowest temperature in this experiment was 1.5 K, which is too high to study precisely the influence of TS's. Moreover, in metals, conduction electrons also lead to a linear term and both contributions can not be separated. This difficulty is all the more emphasized in quasicrystals since the electronic contribution is unclear.

Table I also summarizes the slopes $\beta_i$ of the linear decrease of the velocity above the maximum. In Fig. 3 the acoustic velocity for sample (b) is represented at two working frequencies, 90 MHz and 160 MHz, and shows that the slope of the linear variation does not depend on frequency. Such a linear variation, independent of the working frequency, is a common feature of glasses[23] and of quasicrystals.[4,6,9] However, it is here much smaller than usually observed and it also extends on a reduced temperature range. For comparison, in $i$-AlPdMn the velocity variation is linear until at least 25 K and the slope is $\beta_t = -1.7\times 10^{-5}$ K$^{-1}$.[4] This linear variation probably arises from thermally activated processes, but it is not yet fully understood. Our results on samples (b) and (c) show that the increase of the tunneling strength after annealing comes with an increase of the linear slope. This is in favor of a connection between the TS's and the processes responsible for the high-temperature behavior.[23] However, this link is not straightforward since in sample (a) (the sample with the smallest tunneling strength), the slope $\beta_l$ falls in between that of sample (b) and (c).

Our results shed a new light on our understanding of the TS's. First, the presence of TS's in sample (a), a single crystal, confirms a former experimental study on single mineral crystals, which presented an increase of the density of states of TS's with the size of the unit cell.[24] The conclusion of this work was that if the unit cell of a crystal is large enough, one can find within the cell some neighboring configurations for tunneling. Our results on $R$-AlLiCu, a crystal with a complex local order and a large unit cell, extend this observation to the case of metallic compounds.

The second point to be noticed is *the strong enhancement of the tunneling strength in the icosahedral phase after annealing*. This contrasts clearly with the behavior of amorphous materials. Indeed, among other studies, thermal-conductivity measurements in amorphous $Zr_xCu_{1-x}$ (Ref.

25) and ultrasonic-attenuation measurements in neutron-irradiated quartz[26] show a strong decrease of the coupling parameter $\overline{P}\gamma^2$ after annealing below the glass transition temperature. In glasses this was attributed to a structural relaxation induced by the annealing treatment.[25] The effect of annealing on Al-Li-Cu quasicrystals has been investigated in detail in Ref. 12. The first effect is the growth of the quasicrystalline grains through a coalescence process. In the slow-cooled samples, the grain size is roughly below 0.1 mm whereas in the annealed samples it can reach 0.5 mm.[27] This grain growth may, *a priori*, lead to a change in the observed density of states of TS's. Indeed, let $x$ be the volume fraction of the quasicrystalline grains and $\overline{P}^*$ the intrinsic density of states of TS's of the $i$-AlLiCu phase. Then, the observed density of states in a polygrain sample, if there is no contribution of the grain boundaries, is $\overline{P}=x\overline{P}^*$. The grain-growth process modifies $x$ and therefore $\overline{P}$. However, even in the slow-cooled sample, the grain boundaries are much smaller than the typical size of a grain[27] and thus $x$ is already close to unity in sample (b). Therefore, the change of $x$ upon annealing cannot reach the factor 2 needed to explain the changes in the coupling parameters between sample (b) and sample (c), and the grain-growth effect alone cannot account for our results. The second effect is a general reduction of structural defects as seen by the enhanced number and sharpness of Bragg peaks in electron-diffraction patterns.[12] The third effect is specific to quasicrystals; electron-diffraction patterns of $i$-AlLiCu samples show small misalignments of the spots with respect to real icosahedral symmetry. After annealing treatment, these deviations are clearly reduced.[12] Such distorted diffraction patterns were explained by the introduction of a linear phason strain in the six-dimension description of imperfect quasicrystals.[28] By tuning the amplitude of this linear phason strain one can induce a structural transformation from the idealized icosahedral quasicrystal to imperfect quasicrystals, and finally the corresponding approximant crystalline structure. This has been shown experimentally in the system Al-Li-Cu (Ref. 29) and theoretically.[30] In Ref. 12, it is concluded that the annealing treatment in Al-Li-Cu quasicrystal reduces the amplitude of the phason strain through thermal activation. Thus, we get a coherent picture of our results. The progressive decrease of the amplitude of the linear phason strain from sample (a) to sample (b) and to sample (c) comes with an increase of the observed tunneling strength. In the extreme case of phason-free quasicrystals such as $i$-AlCuFe or $i$-AlPdMn, the tunneling strength reaches the value usually observed in amorphous metals. This explanation disagrees with Ref. 8 in which TS's were attributed to phason strains. We think that the difference between the tunneling strengths measured in Ref. 8 in a quasicrystalline ribbon and a single crystal of $i$-AlLiCu are mainly due to a different sample preparation or composition. Our results emphasize the role of symmetry in relation with the occurrence of TS's. Indeed, the presence of a symmetry of higher order than the cubic symmetry seems to be favorable for the existence of TS's.

In conclusion, we have measured the acoustic velocity variation in a single crystal of the approximant $R$-AlLiCu phase and two samples of the related icosahedral $T2$ phase. One of them was annealed to improve its structural quality. All samples show a glasslike behavior. The tunneling strength increases with the perfection of the quasicrystalline order in the sample. Our results point out the importance of the presence of a symmetry of higher order than the cubic symmetry for the occurrence of TS's.

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[1] P.W. Anderson, B.I. Halperin, and C.M. Varma, Philos. Mag. **25**, 1 (1972).

[2] W.A. Phillips, J. Low Temp. Phys. **7**, 351 (1972).

[3] D. Shechtman, I. Blech, D. Gratias, and J.W. Cahn, Phys. Rev. Lett. **53**, 1951 (1984).

[4] N. Vernier, G. Bellessa, B. Perrin, A. Zarembowitch, and M. de Boissieu, Europhys. Lett. **22**, 187 (1993).

[5] E.J. Thompson, P.D. Vu, and R.O. Pohl, Phys. Rev. B **62**, 11 437 (2000).

[6] F. Bert, G. Bellessa, A. Quivy, and Y. Calvayrac, Phys. Rev. B **61**, 32 (2000).

[7] R. Sterzel, C. Hinkel, A. Haas, A. Langsdorf, G. Bruls, and W. Assmus, Europhys. Lett. **49**, 742 (2000).

[8] N.O. Birge, B. Golding, W.H. Haemmerle, H.S. Chen, and J.M. Parsey, Jr., Phys. Rev. B **36**, 7685 (1987).

[9] J.E. VanCleve, N.A. Gershenfeld, K. Knorr, and P.A. Bancel, Phys. Rev. B **41**, 980 (1990).

[10] X. Liu, P.D. Vu, R.O. Pohl, F. Schiettekatte, and S. Roorda, Phys. Rev. Lett. **81**, 3171 (1998).

[11] J. Classen, I. Rohr, C. Enss, S. Hunklinger, and C. Laermans, Eur. Phys. J. B **10**, 623 (1999).

[12] K. Wang, P. Donnadieu, and P. Garoche, Eur. Phys. J. B **13**, 279 (2000).

[13] M. Audier, J. Pannetier, M. Leblanc, C. Janot, J.M. Lang, and B. Dubost, Physica B **153**, 136 (1988).

[14] B. Dubost, J.M. Lang, M. Tanaka, P. Stainfort, and M. Audier, Nature (London) **324**, 48 (1986).

[15] L. Pich, R. Maynard, S. Hunklinger, and J. Jäckle J, Phys. Rev. Lett. **32**, 1426 (1974).

[16] J.L. Black, in *Glassy Metals I*, edited by H.J. Güntherodt and H. Beck (Springer, Berlin, 1981), Vol. 46.

[17] T. Klein, C. Berger, D. Mayou, and F. Cyrot-Lackmann, Phys. Rev. Lett. **66**, 2907 (1991).

[18] A.K. Raychaudhuri and S. Hunklinger, Z. Phys. B: Condens. Matter **57**, 113 (1984).

[19] K. Kimura, H. Iwahashi, T. Hashimoto, S. Takeuchi, U. Mizutani, S. Ohashi, and G. Itoh, J. Phys. Soc. Jpn. **58**, 2472 (1989).

[20] G.A.M. Reynolds, B. Golding, A.R. Kortan, and J.M. Parsey, Jr., Phys. Rev. B **41**, 1194 (1990).
[21] G. Bellessa and O. Bethoux, Phys. Lett. **62A**, 125 (1977).
[22] K. Wang and P. Garoche, Phys. Rev. B **55**, 250 (1997).
[23] B.E. White, Jr., and R.O. Pohl, Z. Phys. B: Condens. Matter **100**, 401 (1996).
[24] F. Bert and G. Bellessa, Europhys. Lett. **52**, 647 (2000).
[25] S. Grondey, H.v. Löhneysen, and H.J. Schink, Z. Phys. B: Condens. Matter **51**, 287 (1983).
[26] V. Keppens, A. Vanelstraete, and C. Laermans, Physica B **165&166**, 899 (1990).
[27] K. Wang, P. Garoche, and L. Dumoulin, J. Phys.: Condens. Matter **10**, 3479 (1998).
[28] Z. Mai, S. Tao, L. Zeng, and B. Zhang, Phys. Rev. B **38**, 12 913 (1988).
[29] F.H. Li, G.Z. Pan, S.Z. Tao, M.J. Hui, Z.H. Mai, X.S. Chen, and L.Y. Cai, Philos. Mag. B **59**, 535 (1989).
[30] Y. Ishii, Phys. Rev. B **39**, 11 862 (1989).