Electronic transport of the icosahedral Zn-Mg-Sc quasicrystal and its cubic approximant $Zn_{17}Sc_3$

Jun Hasegawa, Ryuji Tamura, and Shin Takeuchi
Department of Materials Science and Technology, Tokyo University of Science, Noda, Chiba 278-8510, Japan

(Received 4 April 2002; published 4 October 2002)

The electrical resistivity and specific-heat measurements have been performed for the recently discovered *P*-type icosahedral Zn-Mg-Sc of high structural perfection and its crystalline approximant $Zn_{17}Sc_3$. The temperature coefficient of the resistivity is found to be negative with $\rho_{300K} = 330\ \mu\Omega$ cm for the quasicrystal, while it is positive with $\rho_{300K} = 250\ \mu\Omega$ cm for the crystalline approximant. The electronic specific-heat coefficient γ is found to be small and nearly the same for both alloys; 0.55 and 0.65 mJ/(mole K^2) for the quasicrystal and the crystalline approximant, respectively. Such small γ values are consistent with the recent electronic structure calculation [Ishii and Fujiwara, J. Alloys. Compd. **342**, 343 (2002)], and can be taken as an indication of the existence of a pseudogap in the density of states at the Fermi level for the *P*-type *i* phase.

DOI: 10.1103/PhysRevB.66.132201 PACS number(s): 71.23.Ft, 72.15.−v, 71.20.Gj

I. INTRODUCTION

In the field of the quasicrystal research, extensive works on the electrical properties of the icosahedral (*i*) phases have been performed on the stable *F*-type *i* phases, such as *i*-AlPd(Mn,Re),[1] *i*-AlCu(Fe,Ru),[2,3] etc., because of their high structural perfection. As a result, many intrinsic properties of the quasicrystals have been clarified,[4] such as an extremely high resistivity value with a pronounced negative temperature coefficient and a small electronic contribution to the specific heat. For such studies the quality of the *i* phase has played a crucial role. Recent work by Préjean *et al.*[5] is implicative with this respect, which has shown that the conductivity of high-quality Al-Pd-Mn single grains is very sensitive to the minute presence of Mn spins, associated with local defects. On the other hand, most of the *P*-type *i* phases discovered so far contain a large amount of intrinsic disorder, even in the stable *i* phases such as *i*-AlLiCu (Ref. 6) and *i*-ZnMgGa.[7] Therefore, it has been difficult to obtain properties intrinsic to the *P*-type quasicrystals in contrast to the cases of the F-type *i* phases.

Recently, a *P*-type *i* phase of high structural quality was found around the composition $Zn_{80}Mg_5Sc_{15}$.[8] The *i* phase has been reported to exhibit sharp diffraction spots with very small deviations from their ideal positions, indicating high structural perfection of the *i*-phase structure.[9] Therefore it has now become possible to obtain a reliable information on the intrinsic electronic transport of the *P*-type *i* phase. In addition, there exists a cubic crystalline approximant $Zn_{17}Sc_3$, which is regarded as a "1/1" approximant, in the vicinity of the *i*-phase composition. $Zn_{17}Sc_3$ is a body-centered-cubic crystal with space group $Im3$, which is reported to contain 160 atoms in a cubic cell with lattice parameter $a = 13.852$ Å with a large hole at the corner and the body center of the unit cell.[10] Since the compositions of the *i* phase and the approximant are very close (less than 5 at % Zn), one expects that the local atomic configurations are nearly the same between the two compounds except for the presence of Mg atoms in the *i* phase. Therefore it is also of interest to compare the electronic transport between the two closely related compounds in terms of the temperature dependence of the resistivity and the electronic contribution to the specific heat. Until now, comparison of the electrical properties between the *i* phase and approximants of various approximation degrees has been done in a number of alloy systems, e.g., Al-Cu-Fe,[11–13] Al-Cu-Ru,[14] Al-Pd-(Fe, Ru, Os) (Ref. 15) for the Mackay-Icosahedron (MI)-type systems, Al-Li-Cu[16,17], Al-Cu-Mg,[16] Mg-Ga-Al-Zn (Ref. 18) for the Frank-Kasper (FK)-type systems. For the MI-type approximants, it has been conjectured that the electronic transport of quasicrystals is mainly determined by the local atomic environment of a scale less than 20 Å.[13,15]

In this paper, results of the electrical resistivity and specific-heat measurements for *i* ZnMgSc and crystalline $Zn_{17}Sc_3$ are reported and a comparison between the two closely related compounds is made in detail.

II. EXPERIMENT

Pure elements of Zn(6N), Mg(4N) and Sc(3N) with nominal compositions around $Zn_{80}Mg_5Sc_{15}$ and $Zn_{17}Sc_3$ were melted in molybdenum foil sealed in a quartz tube under argon atmosphere. The ingots were subsequently annealed at 973 K for 100 h or 1073 K for 24 h to obtain a homogeneous, equilibrium phase. The samples were confirmed to be a single phase of the icosahedral quasicrystal or the cubic approximant by x-ray diffraction spectroscopy with Cu $K\alpha$ radiation. The electrical resistivity was measured from 14 to 300 K by a four-probe method. The specific-heat measurements were performed by an adiabatic relaxation method between 1.8 and 200 K.

III. RESULTS AND DISCUSSION

Among a variety of the alloy compositions investigated in the present work, the single *i* phase has occurred at the composition of $Zn_{81}Mg_6Sc_{13}$ with high reproducibility. Figure 1 presents x-ray diffraction patterns of the $Zn_{81}Sc_{13}Mg_6$ and $Zn_{85}Sc_{15}$ alloys annealed at 973 K for 100 h and 1073 K for 24 h, respectively, together with the pattern calculated using the structural model[10] for cubic $Zn_{17}Sc_3$ for comparison. For the $Zn_{81}Mg_6Sc_{13}$ alloy, the widths of the diffraction peaks

0163-1829/2002/66(13)/132201(4)/$20.00

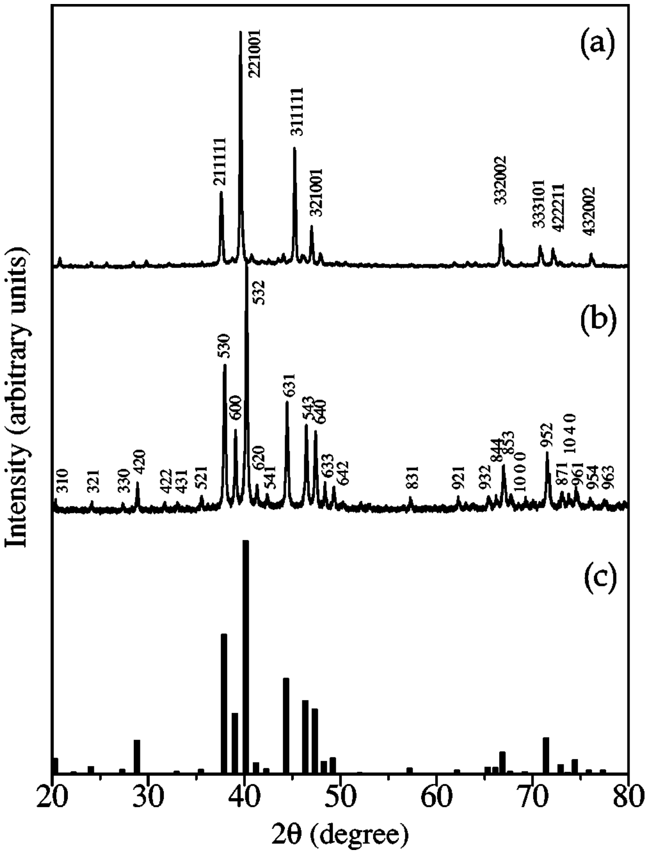

FIG. 1. X-ray diffraction patterns of $Zn_{81}Mg_6Sc_{13}$ (a) and $Zn_{85}Sc_{15}$ (b) alloys annealed at 973 K for 100 h and at 1073 K for 24 h, respectively. A pattern (c) calculated from the structural model (Ref. 10) for the cubic $Zn_{17}Sc_3$ is also shown for a comparison.

are very narrow and all the peaks can be assigned to those of the *P*-type *i* phase using the Elser's indexing method,[19] indicating that a single *i* phase of high structural perfection is obtained for the composition. For the $Zn_{85}Sc_{15}$ alloy, both peak position and intensity of the observed pattern show an excellent agreement with the calculated one, thus confirming that the alloy is composed of a single $Zn_{17}Sc_3$ phase.

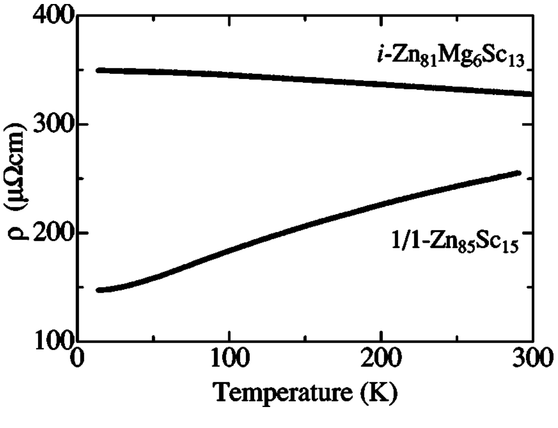

FIG. 2. Resistivity ρ as a function of temperature for i-$Zn_{81}Mg_6Sc_{13}$ and 1/1-$Zn_{85}Sc_{15}$.

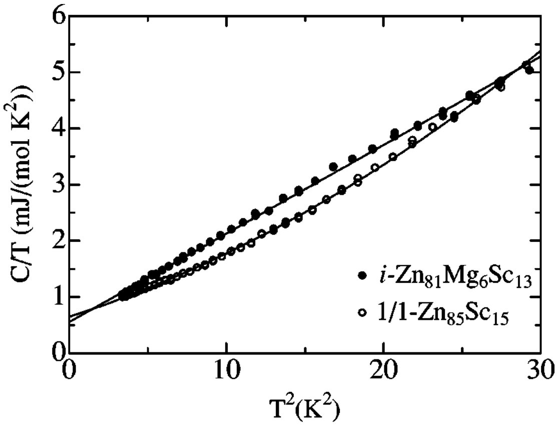

FIG. 3. Low-temperature specific heat for i-$Zn_{81}Mg_6Sc_{13}$ and 1/1-$Zn_{85}Sc_{15}$ plotted in the form of C/T vs T^2.

Figure 2 presents the temperature dependence of the resistivity ρ from 14 to 300 K for i-$Zn_{81}Mg_6Sc_{13}$ and 1/1-$Zn_{85}Sc_{15}$. The magnitude of ρ_{300K} is 330 $\mu\Omega$ cm for the *i* phase and 250 $\mu\Omega$ cm for the approximant. These values are considerably smaller than those of Al-TM (transition metal)-based *i* phases and are comparable to those of ternary rare-earth-containing *i*-phases, such as *i*-ZnMgRE(RE=Tb, Dy, Ho and Er) (Ref. 20) and the binary *i*-CdYb.[21] $\rho(T)$ of *i*-ZnMgSc is found to exhibit a negative temperature coefficient in the whole temperature region with $\rho_{14K}/\rho_{300K} = 1.07$, which also falls in the range of the values observed in *i*-ZnMgRE.[20] On the other hand, $\rho(T)$ of 1/1-ZnSc exhibits a metallic behavior with a positive temperature coefficient. The temperature variation of the resistivity is found to be almost linear with a small convex curvature at high temperatures and the resistivity was found to converge to a residual value at low temperatures, which is reminiscent of the behavior of normal metals. Such a metallic behavior has been also seen in FK-type approximants such as 1/1-MgZn(Ga,Al) (Refs. 18,22) and 1/1-AlLiCu,[17] and is dissimilar to what was observed in MI-type approximants such as 1/1-AlMnSi,[23] 1/1-AlCuFeSi,[24] and 1/1-AlReSi.[25] Considering that the local atomic configurations are nearly the same for the *i* phase and the 1/1 approximant except for the presence of Mg atoms in the *i* phase, the significant difference in the transport behavior is attributed either to their different long-range orders or to the influence of the substituted Mg atoms on the electronic states.

Figure 3 presents the result of the specific-heat measurement for i-$Zn_{81}Mg_6Sc_{13}$ and 1/1-$Zn_{85}Sc_{15}$ in the C/T vs T^2 plot. In the case of the *i* phase, the data are fairly well described by a linear line ($C=\gamma T+\beta T^3$), whereas a higher-order term ($C=\gamma T+\beta T^3+\delta T^5$) needs to be included in order to fit the data for the 1/1 approximant. The electronic specific-heat coefficient γ is determined to be 0.55 and 0.65 mJ/(mole K^2) for the *i* phase and the 1/1 approximant, respectively. These γ values are substantially small considering that the γ values for the simple metals are generally larger than unity in terms of the same unit. Recently, Ishii and Fujiwara performed an electronic structure calculation on the cubic $Zn_{17}Sc_3$ and found that there exists a pseudogap near the Fermi level, which is formed as a result of splitting

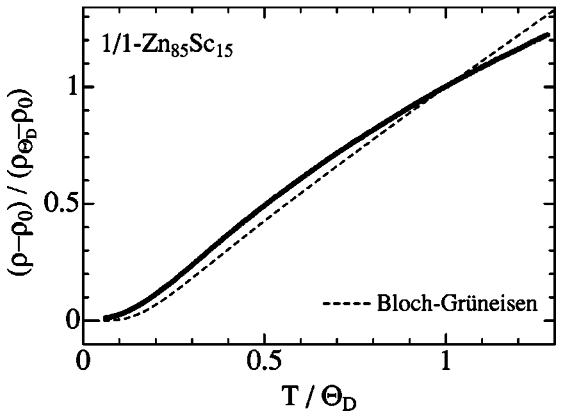

FIG. 4. Comparison of the temperature dependence of the resistivity normalized by the value at $T=\Theta_D$ between the observed resistivity (a solid line) for the 1/1-$Zn_{85}Sc_{15}$ and the one (a dotted line) expected from the Bloch-Grüneisen theory.

of the *p*- and *d*-symmetric components due to a sp-d hybridization effect.[26] From the calculation, they obtained 0.69 mJ/(mole K^2) for the γ value.[27] The observed small γ value for the 1/1-$Zn_{17}Sc_3$ is in quantitatively good agreement with the theoretical γ value, indicating the presence of the pseudogap at the Fermi level. Furthermore, the γ value of the *i* phase is found to be smaller than that of the approximant by a factor $\sim$15%, which implies that the dip in the density of states at the Fermi level is deeper in the *i* phase than in the crystalline analog, and that a more energetical gain of the conduction electrons is responsible for the stability of the quasicrystal with respect to its approximant. On the other hand, the Debye temperature Θ_D is estimated to be 240 K and 227 K for the *i* phase and the 1/1 approximant, respectively, and the almost identical Θ_D values mean similar force constants for both compounds. These Θ_D are considerably small compared with those seen in the other ternary *i* phases, where, for instance, Θ_D is 500$\sim$600 K (Refs. 11 and 28) and about 300 K (Ref. 29) for stable Al-TM-based and Zn-Mg-based *i* phases, respectively. In fact, Θ_D of *i*-ZnMgSc and 1/1-ZnSc is even smaller than those of the constituent elements; Zn (327 K), Sc (360 K), and Mg (400 K). We note that Θ_D is slightly larger for the *i*-phase, possibly due to the larger Θ_D of Mg metal.

According to the Bloch-Grüneisen theory, the temperature-dependent resistivity $\rho(T)$ of normal metals can be expressed by the formula,

$$\rho(T)=BT^5\int_0^{\Theta_D/T}\frac{x^5}{(1-e^{-x})(e^x-1)}dx,$$

where B is a constant that depends on the alloy system. As is well known, the ratio $\rho(T)/\rho(\Theta_D)$ plotted vs T/Θ_D does not depend on the alloy system and is thus universal for all the normal metals that obey the theory. Therefore, in order to assess the validity of the theory in 1/1-$Zn_{85}Sc_{15}$, we plot the reduced resistivity values normalized by the value at $T=\Theta_D$ against T/Θ_D in Fig. 4, together with the one expected from the Bloch-Grüneisen theory. Here the reduced resistivity values were obtained by subtracting the estimated residual resistivity ρ_0 ($\rho_0\sim 150\ \mu\Omega$ cm) from the observed resistivity. As seen from the figure, the temperature dependence of the resistivity of 1/1-$Zn_{85}Sc_{15}$ is found to agree fairly well with the theory, indicating that the electronic transport of 1/1-$Zn_{85}Sc_{15}$ is essentially the same as that of normal metals. At higher temperatures, some deviation from the theory was observed. Here we note that although the temperature dependence of the 1/1-$Zn_{85}Sc_{15}$ is close to that of simple metals the residual resistivity is still high ($\rho_0 \sim 150\ \mu\Omega$ cm). Hence, the observed saturation trend at higher temperatures may be attributed to the temperature variation of the Debye-Waller factor as in the case of amorphous metals of similar resistivity values. Finally, the observed agreement with the Bloch-Grüneisen theory for 1/1-$Zn_{85}Sc_{15}$ clearly manifests that the 1/1 approximant to the *P*-type *i* phase possesses a metallic nature in contrast with the cases of the MI-type 1/1 approximants ‘‘and the local atomic environment of the 1/1 approximant is not responsible for the quasicrystalline properties in this case.’’

IV. CONCLUSIONS

The electrical resistivity and specific-heat measurements have been performed for the recently discovered *P*-type icosahedral Zn-Mg-Sc of high structural perfection and its crystalline approximant $Zn_{17}Sc_3$. As a result, different transport behaviors were observed between the two closely related compounds: The resistivity of the *i* phase shows a negative temperature coefficient with $\rho_{300K}=330\ \mu\Omega$ cm, while it possesses a positive temperature coefficient with $\rho_{300K}=250\ \mu\Omega$ cm for the approximant. The transport of the 1/1-$Zn_{85}Sc_{15}$ is found to be fairly well described by the Bloch-Grüneisen theory, which clearly shows that the transport of the 1/1 approximant is essentially the same as that of normal metals ‘‘and there exist well-extended electronic states at the Fermi level despite its large unit cell ($a=13.852$ Å). The electronic specific heat coefficient γ is found to be small and almost the same for both alloys; 0.55 and 0.65 mJ/(mole K^2) for the quasicrystal and the approximant, respectively. Hence the marked difference in the resistivity behavior between them is mainly attributed to the difference in the electronic diffusivity, which is due either to their different long-range orders or to the influence of substituted Mg atoms on the electronic states. Furthermore, the small γ values are found to be in quantitative agreement with the result of the electronic structure calculation, indicating the presence of a dip in the density of states at the Fermi level for the *P*-type *i* phase as well as its crystalline approximant.

ACKNOWLEDGMENTS

We thank Dr. K. Motoya for help in the experiments, and Dr. Y. Ishii for providing us results of his calculations. This work was supported in part by a Grant-in-Aid for Scientific Research (13750616) from the Japan Society for Promotion of Science and also by Core Research in Environmental Science and Technology (CREST), Japan Science and Technology Corporation.

[1] A.P. Tsai, Y. Yokoyama, A. Inoue, and T. Masumoto, Mater. Trans., JIM **31**, 98 (1990).

[2] A.P. Tsai, A. Inoue, and T. Masumoto, Jpn. J. Appl. Phys., Part 2 **26**, L1505 (1987).

[3] A.P. Tsai, A. Inoue, and T. Masumoto, Jpn. J. Appl. Phys., Part 2 **27**, L1587 (1988).

[4] For a review, see Ö. Rapp, in *Physical Properties of Quasicrystals*, edited by Z.M. Stadnik. (Springer-Verlag, Berlin, 1999), p. 127, and references therein.

[5] J.J. Préjean, C. Berger, A. Sulpice, and Y. Calvayrac, Phys. Rev. B **65**, 140203 (2002).

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

[7] W. Ohashi and F. Spaepen, Nature (London) **330**, 555 (1987).

[8] Y. Kaneko, Y. Arichika, and T. Ishimasa, Philos. Mag. Lett. **81**, 777 (2001).

[9] Y. Kaneko and T. Ishimasa, in *Proceedings of the Fourth Pacific Rim International Conference on Advanced Materials and Processing*, edited by S. Hanada, Z. Zhong, S.W. Nam, and R.W. Wright (Japan Institute of Metals, Sendai, 2001), p. 2523.

[10] P. Villars and L.D. Calvert, *Pearson's Handbook of Crystallographic Data*, 2nd ed. (ASM International, Ohio, 1996).

[11] B.D. Biggs, Y. Li, and S.J. Poon, Phys. Rev. B **43**, 8747 (1991).

[12] D. Mayou, C. Berger, F. Cyrot-Lackmann, T. Klein, and P. Lanco, Phys. Rev. Lett. **70**, 3915 (1993).

[13] C. Berger, D. Mayou, and F. Cyrot-Lackmann, in *Quasicrystals*, edited by C. Janot and R. Mosseri (World Scientific, Singapore, 1995), p. 423.

[14] R. Tamura, K. Kirihara, K. Kimura, and H. Ino, in *Quasicrystals*, (Ref. 13), p. 539.

[15] R. Tamura, T. Asao, and S. Takeuchi, Mater. Trans. **42**, 928 (2001).

[16] P.A. Bruhwiler, J.L. Wagner, B.D. Biggs, Y. Shen, K.M. Wong, S.E. Schnatterly, and S.J. Poon, Phys. Rev. B **37**, 6529 (1988).

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

[18] K. Edagawa, N. Naito, and S. Takeuchi, Philos. Mag. B **65**, 1011 (1992).

[19] V. Elser, Phys. Rev. B **32**, 4892 (1985).

[20] I.R. Fisher, K.O. Cheon, A.F. Panchula, P.C. Canfield, M. Chernikov, H.R. Ott, and K. Dennis, Phys. Rev. B **59**, 308 (1999).

[21] R. Tamura, Y. Murao, S. Takeuchi, K. Tokiwa, T. Watanabe, T.J. Sato, and A.P. Tsai, Jpn. J. Appl. Phys., Part 2 **40**, L912 (2001).

[22] U. Mizutani, A. Kamiya, T. Fukunaga, and T. Matsuda, in *Proceedings of the China-Japan Seminar on Quasicrystals*, edited by K.H. Kuo and T. Ninomiya (World Scientific, Singapore, 1997), p. 700.

[23] B.D. Biggs, F.S. Pierce, and S.J. Poon, Europhys. Lett. **19**, 415 (1992).

[24] A. Quivy, M. Quiquandon, Y. Calvayrac, F. Faudot, D. Gratias, C. Berger, R.A. Brand, V. Shimomet, and F. Hippert, J. Phys.: Condens. Matter **8**, 4223 (1996).

[25] R. Tamura, T. Asao, and S. Takeuchi, Phys. Rev. Lett. **86**, 3104 (2001).

[26] Y. Ishii and T. Fujiwara, J. Alloys. Compd. **342**, 343 (2002).

[27] Y. Ishii (private communication).

[28] B.D. Biggs, S.J. Poon, and N.R. Munirathnam, Phys. Rev. Lett. **65**, 2700 (1990).

[29] A. Inaba, H. Takakura, A.P. Tsai, I.R. Fisher, and P.C. Canfield, Mater. Sci. Eng., A **294-296**, 723 (2000).