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Brief Reports

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Universality of the Hall-effect anisotropy in decagonal quasicrystals

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Careful studies on single decagonal quasicrystals show that the anisotropy of the Hall coefficient R_H is quite universal for these structures. R_H changes sign when the magnetic field rotates by 90° from the tenfold axis. In both cases, R_H depends weakly on the temperature T between 80–330 K. All the single quasicrystals (Al-Ni-Co, Al-Cu-Co, and Al-Si-Cu-Co) have actual compositions which lead to a definite average valence-electron number, in spite of the nominal compositions, indicating the formation of the decagonal phase confined in a narrow composition range by the strong interaction of the Fermi surface with the quasi-Brillouin zone.

Since the discovery of quasicrystals, there have been continuous efforts in an attempt to uncover the influence of the new symmetry on the electronic properties of the materials. However, progress was made only after the stable single phase samples[1] were available. The barely metallic behavior of icosahedral (*i*) Al-Cu-Ru (Ref. 2) and Al-Cu-Fe (Ref. 3) alloys, which are based on good metals, strongly suggests the interaction of the Fermi surface with a quasi-Brillouin zone (QBZ) boundary. For the decagonal (*D*) phase, samples in the single crystalline form have been obtained for several Al-based systems,[4,5] which opens the possibility for investigating the intrinsic properties of the phase. Up to now, anisotropy has been observed in the Hall effect,[6] electrical resistivity,[7,8] thermopower,[7] and thermal conductivity.[9] In this paper we present our careful measurements on the Hall effect for all the *D*-phase single quasicrystals available. We find that the anisotropy discovered in Al-Si-Cu-Co (Ref. 6) is a universal property for the materials with decagonal symmetry. This universality can be understood in the framework of the interaction of the Fermi surface with the QBZ boundaries which are determined by the structural symmetry, and that are not so sensitive to the properties of special atoms.

Hall coefficients R_H were measured by a double-ac method in the van der Pauw configuration.[10] An ac current with amplitude 10–80 mA and frequency 88 Hz was fed to the sample, and an ac magnetic field of ~ 0.1 T in amplitude and 55 Hz in frequency was applied perpendicularly to the sample plane. The Hall signal was picked up at the difference frequency by a lock-in amplifier and its sign was determined by comparing its phase with that of a Cu film connected in series with the sample. This method greatly improves the signal-to-noise ratio, avoids the error from off balance, and allows us to trace continuously the T dependence.

Four kinds of decagonal quasicrystals, Al-Si-Cu-Co, Al-Ni-Co, Al-Cu-Co No. 1, and Al-Cu-Co No. 2, were measured in our experiments. The details of the growth of Al-Si-Cu-Co and Al-Cu-Co No. 1 single quasicrystals were reported in Ref. 5. The Al-Ni-Co single quasicrystals were grown by a method similar to that reported in Ref. 4 and the Al-Cu-Co No. 2 single quasicrystals were grown by the directional solidification method.[11] The quasicrystals of all these materials were well-formed columnar prisms with tenfold rotation symmetry and proved to be single-domained over the whole sample which was usually a few tenths mm in diameter and several mm in length. The x-ray diffraction studies on all these materials showed diffraction peaks only slightly broader than those for good crystals, indicating the good quality of the quasicrystals. Convergent beam diffraction patterns along the columnar axis display Kikuchi lines with a regular intensity distribution revealing the tenfold rotational symmetry and no appreciable distortion.

The quasicrystals were cut and polished to thin slices of 2–10 μm in thickness and 100–200 μm in length as measured by scanning electron microscopy. Two configurations were made: one had its main plane perpendicular to the crystalline direction (QC sample); another included the crystalline direction in its main plane (CQC sample). The alignment of the tenfold axis with respect to the sample plane plays a key role in obtaining reliable results of the amplitude as well as its T

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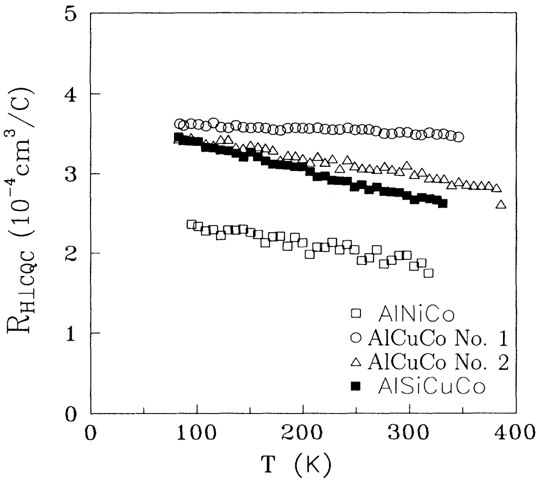

FIG. 1. The Hall coefficients $R_{H\perp CQC}$ of the decagonal quasicrystals with the magnetic field perpendicular to the crystalline direction.

dependence of R_H. The correct alignment is not difficult to realize for CQC samples but great care has been taken for QC samples because of the very small cross section of the quasicrystals. The good alignments of QC samples were checked by the resistivity isotropy in the plane, which gave a misalignment of less than 10°.

Figures 1 and 2 show typical results of $R_{H\perp CQC}$ (measured on QC samples) and $R_{H\perp QC}$ (measured on CQC samples) for the four kinds of single quasicrystals. The sign anisotropy for Al-Si-Cu-Co shown in these figures is consistent with previous measurements,[6] but T dependence of $R_{H\perp QC}$ is quite different. We think that our present results are more reliable because in the earlier measurements the misalignment of electrodes could give rise to some parasite T dependence. From Figs. 1 and 2 several features immediately emerge: (a) For all the four kinds of quasicrystals, $R_{H\perp CQC}$ is positive and $R_{H\perp QC}$ is negative. This is indicative of that the sign anisotropy is closely related to the structural symmetry and relatively immune to the properties of specific atoms; (b) in both directions R_H is only weakly T dependent between 80–330 K with the amplitudes slightly higher at low temperature. The results seem more consistent with a single-band picture than with a two-band model, which is supported by the simple behavior of thermopower;[7] (c) In spite of the sign reversal of R_H between the two directions, the absolute values of $R_{H\perp CQC}$ and $R_{H\perp QC}$ are not far from each other for each kind of quasicrystal. The room temperature values are $(1.85\pm0.05)\times10^{-3}$ cm^3/C (Al-Ni-Co), $(2.7\pm0.3)\times10^{-4}$ cm^3/C (Al-Cu-Co No. 2), $(2.9\pm0.2)\times10^{-4}$ cm^3/C (Al-Si-Cu-Co), and $(4.2\pm0.8)\times10^{-4}$ cm^3/C (Al-Cu-Co No. 1), respectively. These features seem not to be only a fortuity and may imply that the dynamical properties of the carriers on the same areas of the Fermi surface are quite different along different directions.

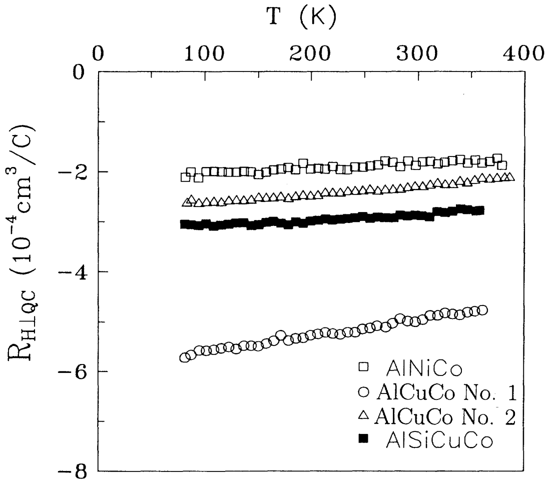

FIG. 2. The Hall coefficients $R_{H\perp QC}$ of the decagonal quasicrystals with the magnetic field perpendicular to the quasicrystal plane.

The universal behavior of Hall coefficients for decagonal quasicrystals encouraged us to investigate more carefully the compositions of the alloys. The compositions were first checked by x-ray energy dispersive spectrometry (EDS) and then analyzed in detail by plasma direct reading spectroscopy (PDRS). Fourteen samples have been investigated in which five were checked by EDS and nine were analyzed by PDRS. An advantage of EDS is that we can check the composition homogeneity of the quasicrystal. The results for Al-Si-Cu-Co and Al-Cu-Co No. 2 show that the local composition fluctuation is within ±1%, far below the accuracy of the method. PDRS has a much higher accuracy (1%). A comparison of the results gives a consistency within the accuracies of the two methods. The most striking result of the analyses is that, in spite of the nominal composition of the starting materials, the resulting compositions for a given kind of quasicrystals have converged in a narrow range. The composition discrepancies from sample to sample for three Al-Ni-Co quasicrystals, two Al-Cu-Co No. 1, two Al-Cu-Co No. 2, and two Al-Si-Cu-Co quasicrystals are shown in Table I. Again, the discrepancies are within the accuracy of the method.

It has been recognized that the stable high-quality i-phase samples are highly resistive,[12] and their average valence electron number Z being close to fully occupy the QBZ.[13] The close relation of structural stability with Z is indicative of a Hume-Rothery stabilization.[14] Generally, it is difficult to evaluate Z for alloys containing transition metals because of their unknown valencies. Fortunately, for Al-Ni-Co and Al-Cu-Co the measurements of susceptibility[15] and other previous work on Al-Tm alloys[16] proved that the d band is fully occupied in Al-rich samples. Therefore, a simple way is to assume the numbers of effective valence electrons of $+3$ for Al, $+4$ for Si, 0 for Ni, -1 for Co, and $+1$ for Cu. This yields the average Z values as shown in Table I (denoted as Z_A). In the Table we have also listed the Z estimated according to Raynor[17] (denoted as Z_B) in which the numbers of effective valence electrons were taken as -0.62 for Ni and -1.71 for Co. An interesting result is that although the Al content spans more than 20% change between the

TABLE I. The compositions and average valence electron numbers of decagonal quasicrystals. The measured composition of Al-Si-Cu-Co quasicrystal is from EDS and those of the other quasicrystals are from PDRS.

	Nominal composition	Measured composition	Z_A (*e*/at.)	Z_B (*e*/at.)
Al-Ni-Co	$Al_{65}Ni_{20}Co_{15}$	$Al_{73.1\pm0.3}Ni_{16.6\pm0.3}Co_{10.3\pm0.1}$	2.09±0.01	1.91±0.01
Al-Cu-Co No. 1	$Al_{65}Cu_{20}Co_{15}$	$Al_{67.6\pm0.1}Cu_{14.6\pm0.2}Co_{17.8\pm0.2}$	2.00±0.01	1.87±0.01
Al-Cu-Co No. 2	$Al_{62}Ge_3Cu_{20}Co_{15}$	$Al_{66.4\pm0.3}Cu_{14.7\pm0.0}Co_{18.9\pm0.3}$	1.95±0.01	1.82±0.01
Al-Si-Cu-Co	$Al_{62}Si_3Cu_{20}Co_{15}$	$Al_{60.2\pm0.7}Si_{4.3\pm0.3}Cu_{19.0\pm1.1}Co_{16.5\pm0.9}$	2.00±0.05	1.89±0.06

four kinds of quasicrystals, the compositions adjust themselves to give a Z fluctuated within only $\pm3\%$ and $\pm2.4\%$ for the two methods of estimation. The result clearly demonstrates the electronic nature in stabilizing the D-phase quasicrystals. Additional uncertainty is introduced when the carrier density n is calculated because no experimental atomic density (N) data are available. According to some models[18,19] and the data on some approximants[20] we may take N as 0.068 Å^{-3} for the four quasicrystals.[18] This gives $n=1.36\times10^{23}$ cm^{-3} for Z_A and 1.27×10^{23} cm^{-3} for Z_B. The effective n deduced from Hall measurements are greatly lower than the above estimation, proving that the Fermi surface is seriously distorted by the interaction of electrons with a QBZ boundary.

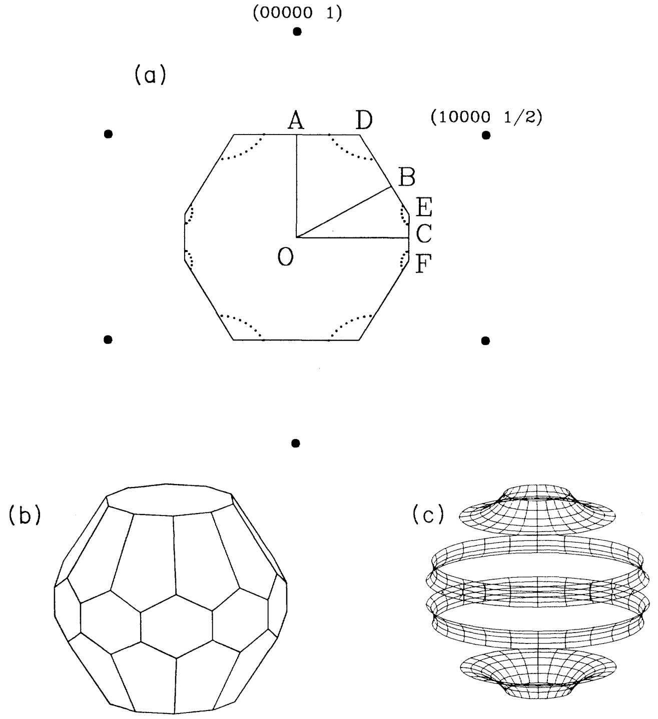

FIG. 3. The quasi-Brillouin zone (QBZ) and the Fermi surface of the decagonal quasicrystal. (a) The QBZ and the Fermi surface in the decagonal D pattern (Ref. 24). The spots are (00000 1) and (10000 $\frac{1}{2}$) diffraction peaks; the octagon is the QBZ; the dotted lines are the Fermi surface; according to Ref. 11, $OA\approx OB\approx1.54$ Å^{-1}, $OC\approx1.58$ Å^{-1}, $OD\approx1.78$ Å^{-1}, $OE=OF\approx1.62$ Å^{-1}; the side EF is determined by (01$\bar{1}$00 0) diffraction peaks which are not in this plane. (b) The three-dimensional QBZ. (c) The three-dimensional Fermi surface.

The QBZ can be built in the following way. Electron diffraction and x-ray diffraction on the four decagonal phases show[4,5,11] that their reciprocal lattices are identical and their quasilattice constants are almost equal. According to x-ray powder diffraction intensity data,[4,11] and taking the effect of the angle factor into account, we find the structure factor of the (00000 1)/(10000 $\frac{1}{2}$) peaks (using the index notations of Ref. 21) is the largest, followed by the (01$\bar{1}$00 0) peak, and the others are much smaller. Following the procedures as for a crystal a QBZ from (00000 1)/(10000 $\frac{1}{2}$) and (01$\bar{1}$00 0) reciprocal lattice points can be defined as shown in Figs. 3(a) and 3(b). The QBZ in three dimensions is a tenfold rotational body around the crystalline axis [Fig. 3(b)]. The volume of the QBZ (V) is 17.7 Å^{-3} as calculated. The electron density for the QBZ fully filled by electrons is 1.43×10^{23} cm^{-3} $[N_{\text{full}}=V/(4\pi^3)]$. When the Fermi surface on the basis of free electron model just touches the position A and B in Fig. 3(a), the electron density N_{touch} is given to be 1.23×10^{23} cm^{-3}. We can see, for all four decagonal quasicrystals, the electron densities estimated by both methods are larger than N_{touch} and less than N_{full}. This again proves the strong interaction between the Fermi surface and the QBZ, reminding us of Hume-Rothery-type stabilization in the formation of stable decagonal quasicrystals.

However, the Hume-Rothery law is well known and successfully used to explain the structural transformations in many alloys. The applicability of the law to quasicrystals is quite understandable because, as shown above, the QBZ, which plays a key role in the formation of quasicrystals, is determined only by the local structural symmetry and has nothing to do with the long-range quasicrystalline order. Therefore, we have reason to expect great similarity in their electronic properties between quasicrystals and their high-order approximants. In fact, similar anisotropy of the Hall effect was reported for the hexagonal Be crystal,[22] which has a very anisotropic Brillouin zone.

The sign anisotropy of R_H can be understood as follows. If the QBZ was a complete rotational body of which any sections perpendicular to its rotational axis are circles, the Fermi surface in it would be the surface of a complete rotational body. In this case, the R_H would be negative regardless of the anisotropy of electron scattering when the magnetic field was along the rotational axis.[23] The QBZ of a decagonal quasicrystal is much like a rotational body thanks to the tenfold symmetry, so the negative value of $R_{H\perp\mathrm{QC}}$ is easy to understand. However the nearly full single-band structure results in great distortion of the Fermi surface cross section perpendicular to the quasiperiodic direction [Figs. 3(a) and 3(c)], which give rise to a positive $R_{H\perp\mathrm{CQC}}$.

In summary, we have made careful investigations on the anisotropic R_H of four kinds of decagonal quasicrystals. All materials show electronlike R_H in quasicrystalline plane and holelike R_H in the plane including the crystalline direction. Based on the results of the composition analysis and Hall measurement, it is suggested that nearly full single-band structures exist in decagonal quasicrystals and Hume-Rothery-type stabilization play a key role in the formation of decagonal quasicrystals. The electronlike and holelike R_H are the consequences of the tenfold symmetry and the nearly full single-band structure.

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