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LETTER TO THE EDITOR

Precipitation of an icosahedral phase in amorphous $Al_{90}Fe_5Ce_5$ alloy

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Abstract
Isothermal and non-isothermal differential scanning calorimetry experiments were carried out to study rapidly solidified $Al_{90}Fe_5Ce_5$ alloy. Microstructural analysis suggests that icosahedral nanoparticles are homogeneously distributed in the matrix of annealed amorphous $Al_{90}Fe_5Ce_5$ alloy. The presence and homogeneous distribution of icosahedral structure units and icosahedral short-range domains appear to be critical for the formation and stability of the amorphous phase.

Since the discovery of the icosahedral phase (I-phase) in a rapidly quenched $Al_{86}Mn_{14}$ alloy, there have been several studies on transformation of alloys from an amorphous phase to the I-phase [1–4]. Chen and Spaepen showed a transformation from an amorphous to an I-phase without a nucleation step [1]. On the basis of their calorimetric analysis, Chen and Spaepen propose that the glass is actually 'microquasicrystalline'. By contrast, Shen *et al* found that the transformation from an amorphous to an I-phase in $Pd_{5.8}U_{20.6}Si_{20.6}$ is a polymorphic nucleation and growth process [2]. Recently, it has been reported that an I-phase could also be formed as a metastable phase in a primary crystallization stage in Zr-based amorphous alloys of the Zr–Al–Cu (–O) and Zr–Al–Ni–Cu (–O) systems [3, 4]. However, most of these studies have focused on the kinetics of and mechanism for the transformation from the amorphous to the I-phase.

The amorphous $Al_{90}Fe_5Ce_5$ alloy shows a high strength-to-weight ratio. The excellent mechanical properties of amorphous $Al_{90}Fe_5Ce_5$ alloy have attracted increasing attention [5–9]. The atomic structure of amorphous $Al_{90}Fe_5Ce_5$ alloy has been studied by means of pulsed x-ray scattering [5] and neutron scattering [6]. Recently, the atomic structures of liquid and amorphous $Al_{90}Fe_5Ce_5$ alloys were studied and their differences assessed [8].

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The results from the above studies are consistent. Based on their studies, some researchers propose that some icosahedral short-range orders produced by packing of Al–Fe clusters exist in these amorphous alloys. In fact, the I-phase has been found in rapidly cooled Al–Fe–Ce alloys [10]. However, there is no direct evidence of the existence of an I-phase in amorphous $Al_{90}Fe_5Ce_5$ alloys. Neither is there evidence that icosahedral short-range order is present in liquid Al–Fe–Ce alloys.

In the studies presented in this letter, we discovered that icosahedral structure units surrounded by fcc Al phase are homogeneously distributed in the matrix of amorphous $Al_{90}Fe_5Ce_5$ alloy. Our results shed light on the understanding of the correlation between the disordered amorphous structure and the icosahedral atomic configuration in the amorphous Al–Fe–Ce alloy with high glass formability. The high glass formability of the Al–Fe–Ce system is probably due to the homogeneous distribution of icosahedral short-range domains in the matrix.

Ingots of $Al_{90}Fe_5Ce_5$ alloy were prepared from the pure elements by arc melting under an argon atmosphere. Melt spinning was carried out in a partial helium atmosphere using a copper wheel (35 cm in diameter) with a typical circumferential velocity of 40 m s^{-1}. The ribbons were $\sim$2 mm in width and $\sim$25 μm in thickness. The structure of the ribbon samples was examined by means of x-ray diffraction (XRD) using monochromatic Cu Kα radiation. Both isothermal and non-isothermal differential scanning calorimetry (DSC) experiments were carried out in a Perkin-Elmer DSC II system under a pure argon atmosphere. The microstructural changes in the amorphous $Al_{90}Fe_5Ce_5$ ribbons upon annealing were observed by means of XRD as well as transmission electron microscopy (TEM).

The continuous-heating curve of the amorphous $Al_{90}Fe_5Ce_5$ alloy derived from the DSC analysis is shown in figure 1. The continuous-heating trace does not show the characteristic patterns of glass transformation. Instead, two exothermic peaks are seen with temperature intervals of $\sim$150 °C for $Al_{90}Fe_5Ce_5$. These two exothermic peaks indicate that the $Al_{90}Fe_5Ce_5$ alloy crystallizes through two stages. The XRD pattern of the $Al_{90}Fe_5Ce_5$ as-quenched alloy is shown in figure 2. The emergence of the shoulder (marked by the downward-pointing arrow) in the first main peak of the $Al_{90}Fe_5Ce_5$ alloy indicates the presence of strong

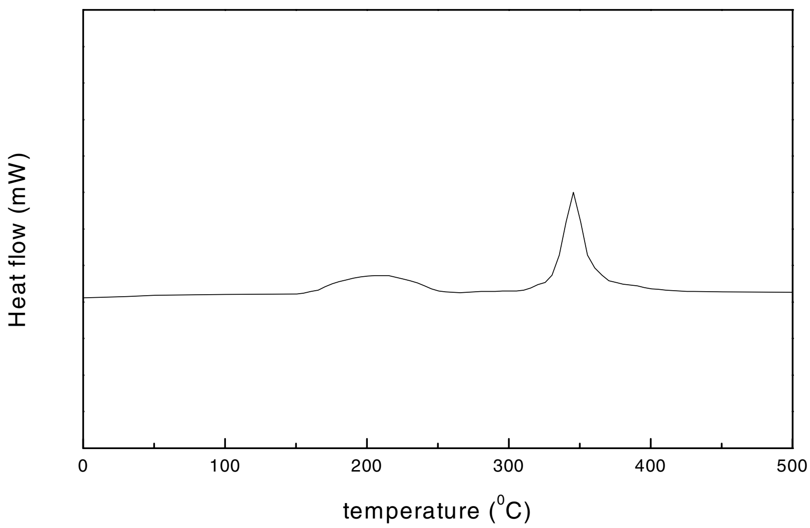

Figure 1. The DSC curve of amorphous $Al_{90}Fe_5Ce_5$.

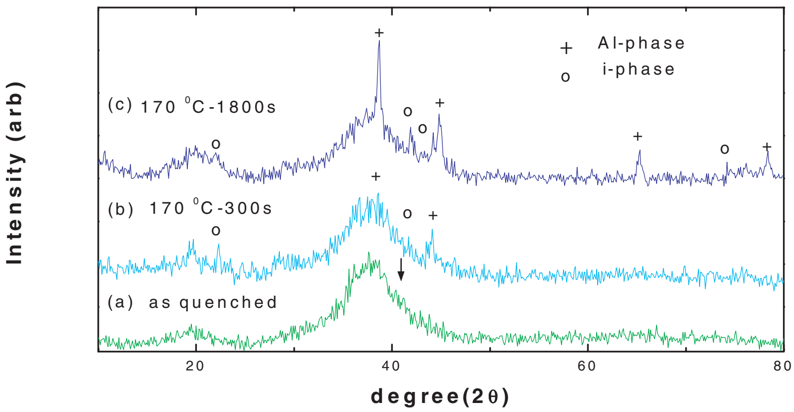

Figure 2. X-ray diffraction patterns of $Al_{90}Fe_5Ce_5$ as quenched (a), annealed for 300 s at 170 °C (b), annealed for 1800 s at 170 °C.

Al–Fe interaction [5, 6]. We then carried out the exothermic reaction with the $Al_{90}Fe_5Ce_5$ alloy at 170 °C, a temperature that is below the onset temperature of the first exothermic peak in figure 1. The changes in the first exothermic reaction of the $Al_{90}Fe_5Ce_5$ alloy with annealing time at different annealing temperatures are shown in figure 3. The exothermic reaction can be divided into two stages. It provides evidence not only for grain growth, but also for nucleation. The XRD patterns of the sample annealed for 300 s and 1800 s at 170 °C are shown in figure 2. An I-phase is observed in the annealed alloy. The icosahedral peaks were indexed using the Elser method [11]. Bright-field micrographs and selected-area diffraction patterns of the amorphous $Al_{90}Fe_5Ce_5$ alloy annealed for 30 min at 170 °C are shown in figure 4. The precipitates have near-spherical morphology and are homogeneously distributed. The diffraction pattern corresponding to the icosahedral nanoparticles consists of distinct reflection rings with appreciable diffuseness, while the pattern corresponding to the fcc Al phase consists of some reflection spots. It appears that the icosahedral nanoparticles are distributed in a surrounding state with a thin Al layer. The ring pattern of the I-phase indicates that the icosahedral grains are very fine. In figure 5, we show bright-field micrographs and the selected-area diffraction pattern of the primary icosahedral phase in $Al_{90}Fe_5Ce_5$ alloy annealed at 175 °C for 30 min. The electron diffraction pattern strongly suggests fivefold symmetry of the I-phase, although the pattern also contains some reflection spots of the fcc Al phase. It seems that the matrix is still amorphous in the $Al_{90}Fe_5Ce_5$ ribbon annealed for 1800 s at 170 °C (figure 2(c), figures 4(c) and 4(d)). The data on the microstructures, together with the first exothermic reaction with annealing time, indicate that the icosahedral structural units grow prior to the growth of Al nuclei and therefore suppress the growth of the Al phase. Thus, the grain growth stage in the annealing time is the growth of icosahedral structure units, followed by the growth of the fcc Al phase. The nucleation stage is the nucleation of fcc Al in the remaining amorphous zones.

The understanding of the short- and medium-range atomic configurations of the Ce-containing amorphous alloys is expected to shed light on the mechanisms of the precipitation of the I-phase of Al–Fe-based amorphous alloy. The most interesting feature is the presence of a prepeak. The prepeak corresponds to the strong interaction between unlike atoms [12] and reflects the medium-range order of amorphous materials [13]. The prepeak has also been found in the structure factor of liquid $Al_{90}Fe_{10}$ and $Al_{90}Fe_5Ce_5$ alloys [8]. The results support the

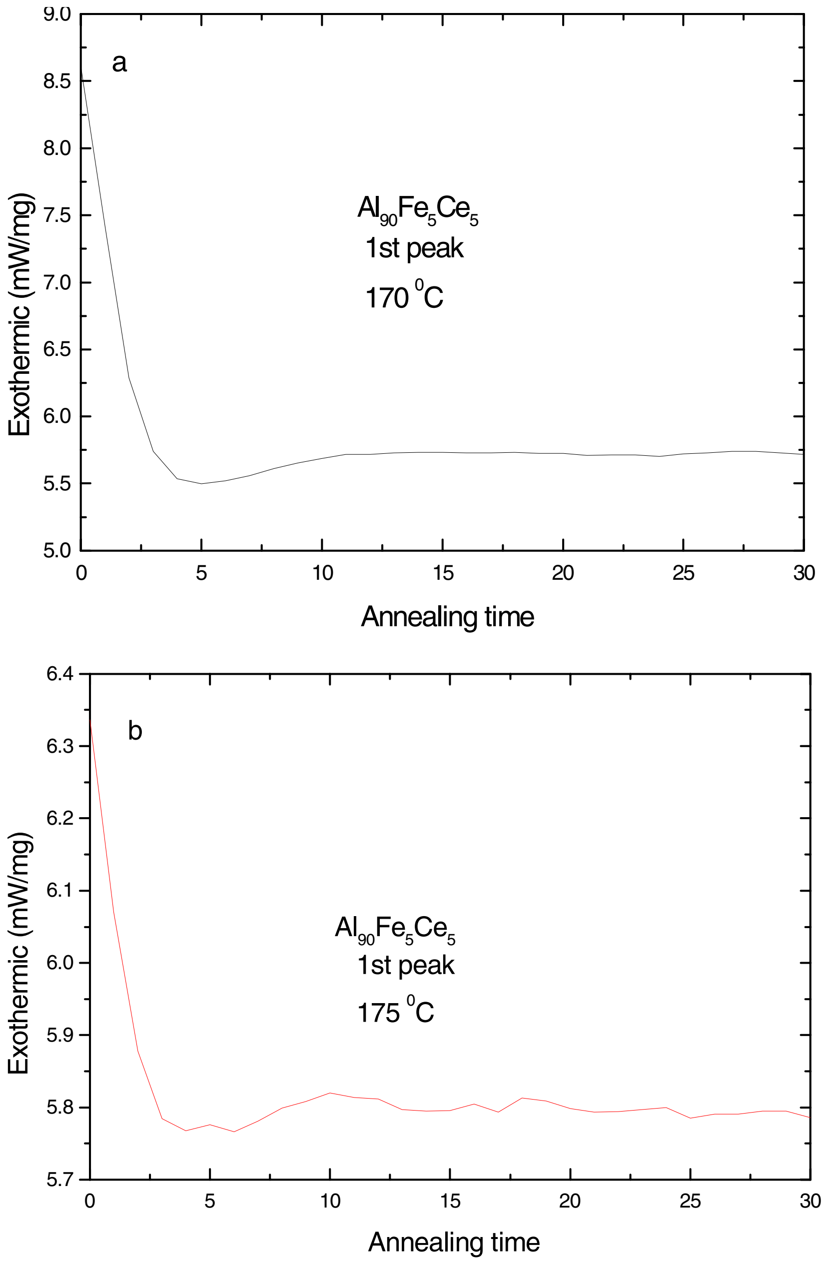

Figure 3. DSC isothermal traces from (a) $Al_{90}Fe_5Ce_5$ annealed at 170 °C for 30 min and (b) $Al_{90}Fe_5Ce_5$ annealed at 175 °C for 30 min.

idea that the chemical short-range order formed in the melts changes with the temperature. It has been proposed that the appearance of a shoulder in the structure is the result of certain kind of short-range order of Fe in the $Al_{90}Fe_5Ce_5$ alloy glass [5]. Wales and Berry have pointed out that the microstructure of superheated melt is not always homogeneous [14]. Thus short-range atomic configurations similar to those of some intermetallic binary compounds can exist in the

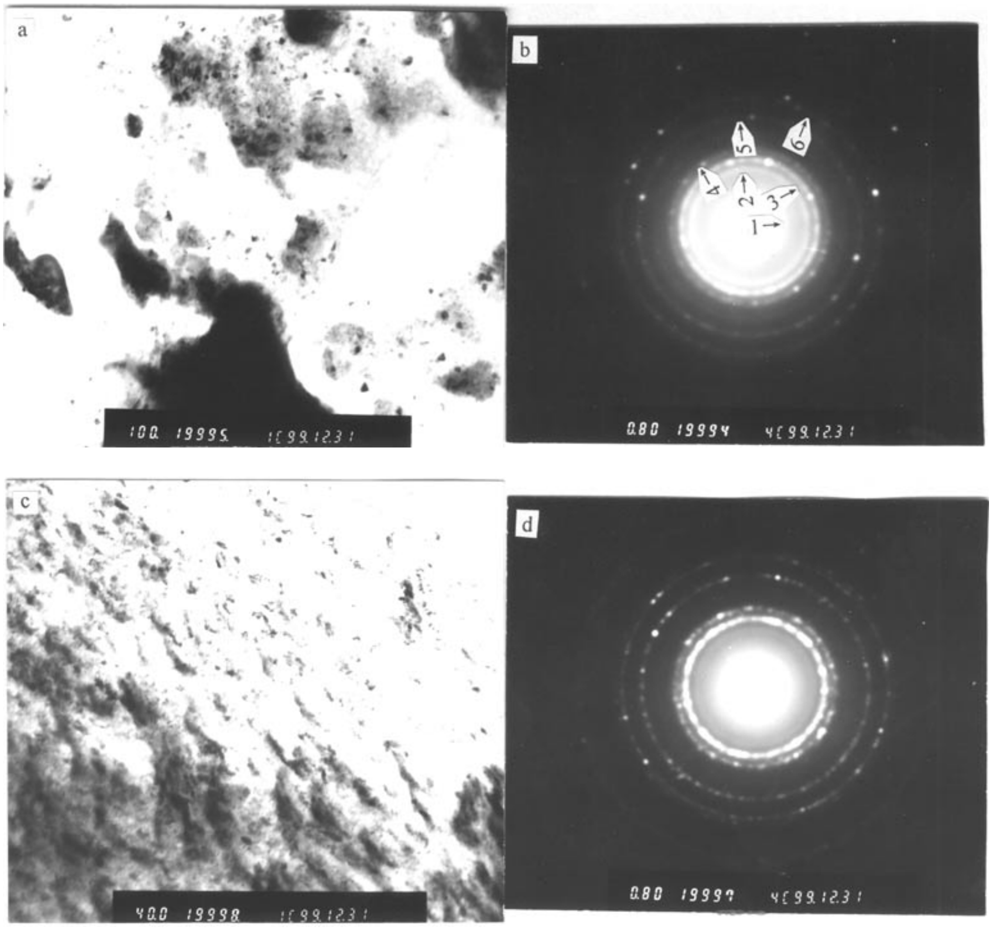

Figure 4. Bright-field electron micrographs and selected-area diffraction patterns of $Al_{90}Fe_5Ce_5$ annealed at 170 °C for 30 min. The reflection rings 1, 2, 3, 4, 5 and 6 are identified to be $(111000)_i$, $(211100_i$, $(221111)_i$, $(221001)_i$, $(322101)_I$ and $(332002)_i$. respectively.

structure of liquid $Al_{90}Fe_{10}$. Unlike in the Al–TM system, in the Al–TM–Ce system adding an appropriate amount of Ce changes the interaction between different atoms and enhances the supercooling tendency. Addition of Ce is expected to enhance the icosahedral short-range order; this is similar to the effect of Si in the Al–Mn system [10]. It has been proposed that the short-range atomic configuration in the amorphous structure is very similar to that in the icosahedral structure. Consequently, upon rapid quenching, these icosahedral structural units are easy to form in the supercooled melt.

The breakthrough of producing rapidly solidified, Al-based metallic glasses has attracted great interest in both the scientific and technological fields [5, 6]. Over the past decade, a number of such glass alloys containing up to 90 at.% Al have been developed [15]. Several studies have addressed the glass-forming ability of Al-based alloys. He *et al* pointed out that glass can be formed while the composition is still away from the eutectic in the equilibrium phase diagram [5]. On the other hand, Inoue *et al* interpreted the ease of glass formation in these alloys as being a result of strong binding (large negative heat of mixing) [16]. Alternatively, the glass-forming ability for such high aluminium concentration might be due to the alterations in

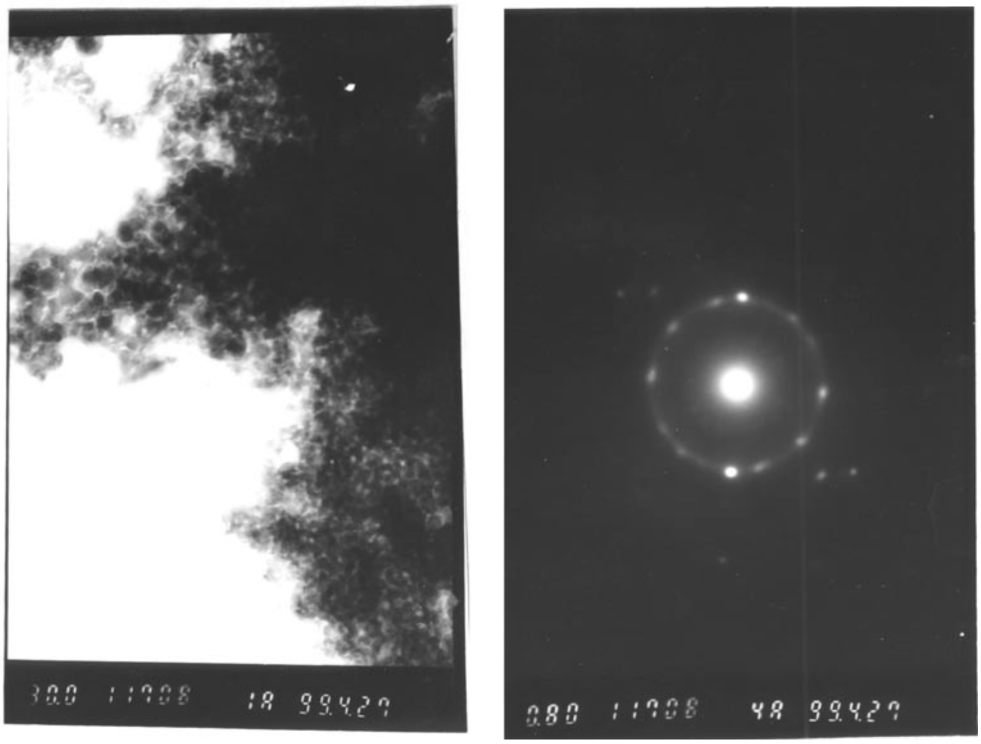

Figure 5. Bright-field electron micrographs and selected-area diffraction patterns of $Al_{90}Fe_5Ce_5$ annealed at 175 °C for 30 min.

atom size caused by strong s–d hybridization [6, 9]. As regards the unusual glass formability of this class of metallic glass, the presence and homogeneous distribution of the icosahedral structure units should be considered critical for the formation of the metallic glass phase. As mentioned above, these icosahedral structure units are easy to produce in the supercooled melt. The units can form clusters via plane or point sharing. These clusters can be regarded as icosahedral short-range domains. The size of these domains is much bigger than that of any single atom. Strong chemical bonding makes the cluster behave like a 'mega-atom'. These 'mega-atoms' can cause great size effects in the matrix, prevent the Al matrix from crystallizing, and improve the formability and stability of the amorphous matrix.

In summary, we observed that icosahedral structure units are homogeneously distributed in the matrix of amorphous $Al_{90}Fe_5Ce_5$ alloy. These structural units can be identified by the characteristic isothermal calorimetric signal associated with their transformation to fine icosahedral quasicrystalline grains. Both the isothermal experiment and the microstructures described in this report indicate that the icosahedral phases reject excess Al as they grow, causing Al to precipitate at the periphery of the icosahedral grain. The presence and homogeneous distribution of icosahedral structure units or icosahedral short-range domains are attributed to the enhanced formability and stability of the amorphous phase.

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References

[1] Chen L C and Spaepen F 1988 *Nature* **336** 366
[2] Shen Y, Poon S J and Shiflet G J 1986 *Phys. Rev.* B **34** 3516
[3] Koster U, Meinhardt J, Roos R and Liebertz H 1996 *Appl. Phys. Lett.* **69** 179
[4] Xing L O, Ecker J, Loser W and Schultz L 1999 *Appl. Phys. Lett.* **74** 2110
[5] He Y, Poon S J and Shiflet G J 1988 *Science* **241** 1640
[6] Hsieh H Y, Toby B H, Egami T, He Y, Poon S J and Shiflet G J 1990 *J. Mater. Res.* **5** 2807
[7] Inoue A, Ohtera K, Zhang T and Masumoto T 1988 *Japan. J. Appl. Phys.* **27** L1583
[8] Zhang L, Wu Y, Bian X, Li H, Wang W and Wu S 2000 *J. Non-Cryst. Solids* **262** 169
[9] Egami T 1996 *J. Non-Cryst. Solids* **205–207** 575
[10] Yang L Y, Zhao J G, Zhan W S, Yang C Y, Zhou Y Q and Fung K K 1987 *J. Phys. F: Met. Phys.* **17** L97
[11] Elser V 1986 *Acta Crystallogr.* A **42** 36
[12] Hoyer W and Jodicke R 1995 *J. Non-Cryst. Solids* **192+193** 102
[13] Elliot S R 1991 *Phys. Rev. Lett.* **67** T11
[14] Wales D J and Berry R S 1990 *J. Chem. Phys.* **92** 4473
[15] Inoue A 1998 *Prog. Mater. Sci.* **43** 365
[16] Inoue A, Ohtera K and Masumoto T 1990 *Sci. Rep. Res. Inst. Tohoku Univ.* A **35** 115
[17] Holzer J C and Kelton K F 1991 *Acta. Metall. Mater.* **39** 1833
[18] Inoue A 1995 *Mater. Trans. JIM* **36** 866
[19] Foley J C and Perepezko J H 1996 *J. Non-Cryst. Solids* **205–207** 102
[20] Kawase D, Tsai A P, Inoue A and Masumoto T 1993 *Appl. Phys. Lett.* **62** 137
[21] Christian J W 1975 *The Theory of Transformation in Metals and Alloys* 2nd edn (New York: Pergamon)
[22] Sokolov A P, Kisliuk A, Soltwisch M and Quitmann D 1992 *Phys. Rev. Lett.* **69** 1540
[23] Lu K and Wang J T 1990 *J. Non-Cryst. Solids* **117/118** 716
[24] Crespo D and Pradell T 1996 *Phys. Rev. Lett.* **54** 3101