Icosahedral Short-Range Order in Deeply Undercooled Metallic Melts

T. Schenk,[1] D. Holland-Moritz,[1] V. Simonet,[2] R. Bellissent,[3] and D. M. Herlach[1]
[1]*Institut für Raumsimulation, DLR, D-51170 Köln, Germany*
[2]*Laboratoire de Physique des Solides (UMR CNRS/UPS), Batiment 510, Université de Paris-Sud, F-91405 Orsay Cedex, France*
[3]*Centre d'Etudes Nucléaires de Grenoble, DRFMC/SPSMS/MDN, F-38054 Grenoble Cedex, France*
(Received 2 January 2002; published 30 July 2002)

Experimental evidence of icosahedral short-range order in stable and deeply undercooled melts of pure metallic elements is obtained using the combination of electromagnetic levitation with neutron scattering. This icosahedral short-range order is shown to occur in the bulk metallic melt independently of the system investigated. It strongly increases with the degree of undercooling.

DOI: 10.1103/PhysRevLett.89.075507 PACS numbers: 61.20.–p, 61.25.Mv

Since the pioneering work by Turnbull in 1950 [1] it is well established that metallic liquids can be deeply undercooled below their freezing temperatures provided heterogeneous nucleation on container walls and/or impurity sites is reduced or even avoided. Undercoolings as large as approximately 20% of the melting temperatures, T_L, were observed for a great variety of different metals. Such large undercoolings are indicative of a correspondingly high activation barrier to form crystal nuclei of critical size. Frank postulated an icosahedral short-range order (ISRO) in the melt to explain the experimentally observed large undercoolings of pure metals [2].

Icosahedral clusters, consisting of compact arrangements of 13 atoms, possess an energy being 8.4% smaller than that of clusters with dense packed fcc or hcp structure of the same number of atoms, if atomic interactions according to a Lennard-Jones potential are considered [2]. While Frank's arguments were derived from the topological analysis of the energy of small clusters, for larger systems the concept of ISRO is confirmed by several molecular dynamic computer calculations on monoatomic [3,4] and binary [5] Lennard-Jones liquids, which show a growing degree of ISRO with increasing undercooling of the melt. However, no direct experimental proof of ISRO in bulk undercooled melts has been reported until now.

Hints of the existence of ISRO in undercooled liquids were inferred from the evaluation of the degree of undercooling as a function of the nucleated solid structure. The solid-liquid interfacial energy should be the smaller the more similar the short-range order (SRO) of the melt is to that of the solid nucleus [6]. Containerless undercooling experiments have shown that the maximum undercoolability of melts forming quasicrystals and polytetrahedral phases is significantly lower than that of nonpolytetraheral crystalline phases [7,8]. This is related to the fact that quasicrystals [9] show a SRO similar to the ISRO assumed in undercooled metallic melts.

The SRO in metallic liquids of Al-based alloys forming quasicrystalline phases has been investigated by a series of neutron diffraction studies in the stable liquid regime [10–12]. The analysis of experimentally determined atomic pair distribution functions combined with simulations of structure factors and molecular dynamic studies confirm the existence of icosahedral clusters centered on the transition metal atoms in these stable melts of quasicrystal-forming alloys.

On the other hand, the SRO of nonmetallic melts was studied both in the stable regime $T > T_L$ and in the metastable regime of the undercooled melt using x-ray or neutron diffraction in combination with containerless processing techniques [13–17]. None of them gave indications for ISRO in the liquid, since in these nonmetallic compounds and elements their strongly directional bonds control the SRO in the liquid. According to the hypothesis of Frank [2] and the computer simulations on Lennard-Jones liquids [3–5], ISRO should be present in pure metallic melts with compact local order and isotropic bonding. Very recent experiments using synchrotron radiation on liquid Pb at $T > T_L$ adjacent to a solid (001) Si interface gave evidence of fivefold symmetry of Pb clusters captured onto the Si substrate [18]. These studies prove the local icosahedral symmetry of Pb clusters but only in the direct neighborhood of the Si (001) surface. They do not allow investigating the SRO in the bulk melt, or in the undercooled melt which is essential for a study of nucleation of the solid phase in the parent liquid state.

In the present work, neutron scattering experiments on bulk melts of several pure transition metals both in the stable liquid and in the undercooled melt are presented. The SRO of pure metals was studied directly with the benefit that chemical influences on the SRO as present in alloys are excluded and exclusively topological effects are probed. The metallic elements were chosen such that they form bcc (Fe, Zr) and fcc (Ni) structures in the solid state in order to test whether the structure of the crystalline solid might influence the SRO in the liquid.

Electromagnetic levitation under high purity environmental conditions was applied to deeply undercool liquids for extended periods of time necessary to perform diffraction investigations. This method produces a freely

0031-9007/02/89(7)/075507(4)$20.00

suspended liquid drop, undercooled owing to the avoidance of heterogeneous nucleation on container walls with the extra benefit that it is directly accessible for diffraction experiments [19]. Despite the fact that an undercooled melt is a metastable state of limited lifetime, we were able to record diffraction spectra on deeply undercooled melts of quality comparable with those obtained in good experiments on stable liquids. The temperature of the specimen is measured by a two-color pyrometer with an absolute accuracy of ±5 K. Neutron diffraction experiments were performed at the high-intensity two-axis diffractometer D20 [20] of the Institut Laue-Langevin (ILL) in Grenoble, France, in a new levitation device specially designed for neutron diffraction using wavelengths of 0.94 Å (Ni) and 0.88 Å (Fe and Zr). At a given temperature T\hbox{,} the differential scattering cross section was obtained by subtracting the measured spectrum of the empty levitation furnace (without sample) from the measured spectrum of the specimen inside the furnace. Conventional self-absorption correction, inelastic scattering, and standard multiple scattering corrections [21] were carried out. The spectrum was normalized using a vanadium sample so that its asymptotic value at large Q coincides with the total scattering cross section. The structure factor, $S(Q)$, was then obtained after subtraction of the incoherent scattering and the magnetic contribution (the latter is negligible for Zr).

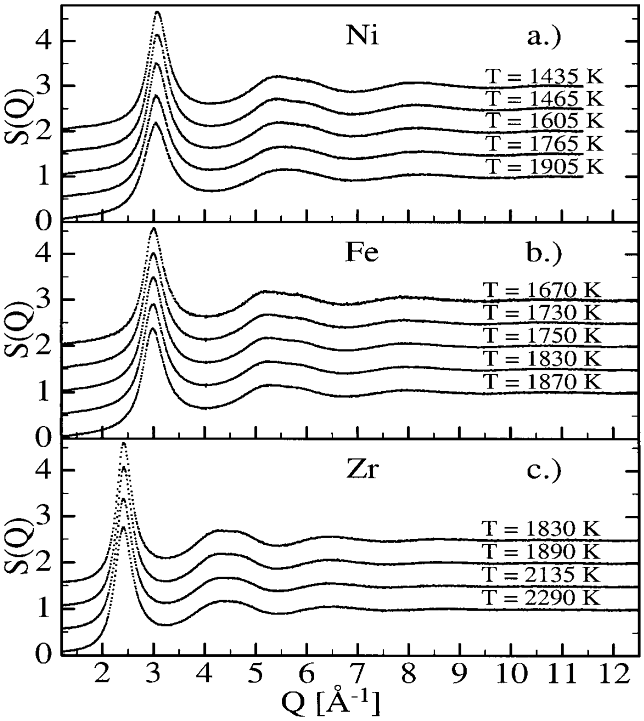

FIG. 1. Structure factors $S(Q)$ inferred from neutron diffraction experiments on Ni melts (a), Fe liquids (b), and Zr melts (c) at different temperatures.

TABLE I. Nearest (R_1) and second (R_2) neighbor distances and coordination numbers, Z, inferred from the diffraction experiments on the different melts as a function of the temperature T. [T_L(Ni) = 1726 K, T_L(Fe) = 1811 K, T_L(Zr) = 2125 K].

Element	T (K)	R_1 (Å)	R_2 (Å)	Z
Ni	1905	2.48 ± 0.02	4.53 ± 0.05	11.2 ± 0.5
Ni	1765	2.48 ± 0.02	4.50 ± 0.05	11.5 ± 0.5
Ni	1605	2.49 ± 0.02	4.46 ± 0.05	11.9 ± 0.5
Ni	1465	2.49 ± 0.02	4.43 ± 0.05	12.1 ± 0.5
Ni	1435	2.49 ± 0.02	4.43 ± 0.05	12.3 ± 0.5
Fe	1870	2.55 ± 0.02	4.55 ± 0.05	12.3 ± 0.5
Fe	1830	2.55 ± 0.02	4.54 ± 0.05	12.3 ± 0.5
Fe	1750	2.55 ± 0.02	4.53 ± 0.05	12.4 ± 0.5
Fe	1730	2.55 ± 0.02	4.52 ± 0.05	12.5 ± 0.5
Fe	1670	2.55 ± 0.02	4.52 ± 0.05	12.6 ± 0.5
Zr	2290	3.12 ± 0.02	5.74 ± 0.05	11.9 ± 0.5
Zr	2135	3.12 ± 0.02	5.73 ± 0.05	12.0 ± 0.5
Zr	1890	3.12 ± 0.02	5.72 ± 0.05	12.2 ± 0.5
Zr	1830	3.13 ± 0.02	5.71 ± 0.05	12.2 ± 0.5

The structure factors for the different melts were measured at several temperatures (Table I) above T_L in the stable regime and below T_L at undercoolings up to 140 K for Fe and even to 290 K for Ni and Zr. This corresponds to high relative undercoolings ($\Delta T/T_L$) especially in the case of Ni (17%). Such a large temperature range should allow one to evidence significantly the structural changes occurring in the liquid. $S(Q)$ and corresponding pair correlation functions $g(R)$ are presented in Fig. 1 and in Fig. 2, respectively.

A shoulder on the right-hand side of the second oscillation is observed for all measured $S(Q)$ of Ni, Fe, and Zr melts. This is the first time such a clear shoulder is observed in structure factors of monoatomic liquids. This shoulder is therefore characteristic of a particular SRO. Such a feature has been identified as a signature of ISRO from the theoretical work of Sachdev and Nelson [22] and was recently evidenced in quasicrystal forming alloy melts [12]. It should be noticed that this feature becomes more pronounced as T is lowered.

Interatomic distances and coordination numbers are simple quantitative parameters of SRO straightly obtained from the $g(R)$ (Table I). For the three liquids, the nearest neighbor distance, R_1, remains essentially unchanged while the second neighbor distance, R_2, slightly decreases with decreasing T. The nearest neighbor coordination number, Z, is of ~12 for all three liquids. Z is obtained by the area under the first maximum of $4\pi\rho R^2 g(R)$ (ρ denotes the density). In the present work, it was determined by integration over the whole area between first and second minima limiting this first oscillation. There are other ways to obtain Z leading to a spreading of Z values in a 10% range of Z [23] (not included in Table I). This does not affect the relative variations of Z. The value of Z increases slightly with decreasing T. This temperature evolution of Z is mainly responsible for the thermal expansion of the

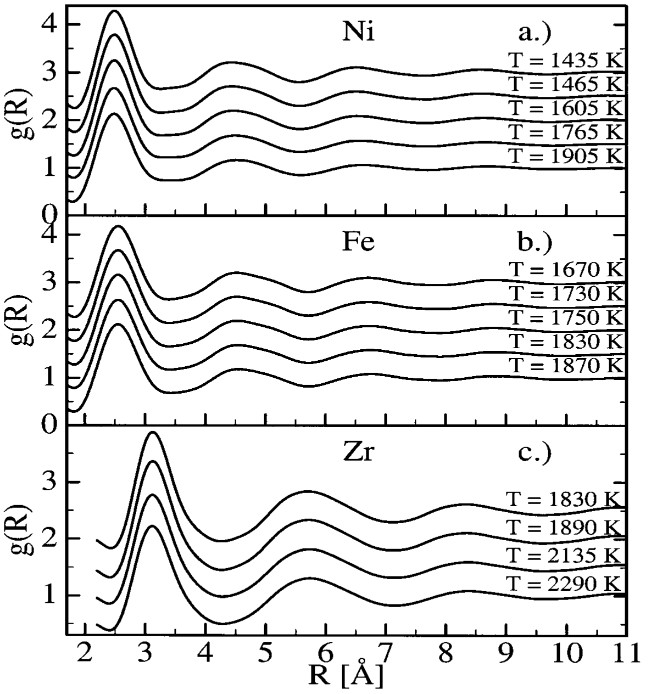

FIG. 2. Pair correlation functions $g(R)$ of Ni (a), Fe (b), and Zr (c) melts at different temperatures inferred from the $S(Q)$ shown in Fig. 1.

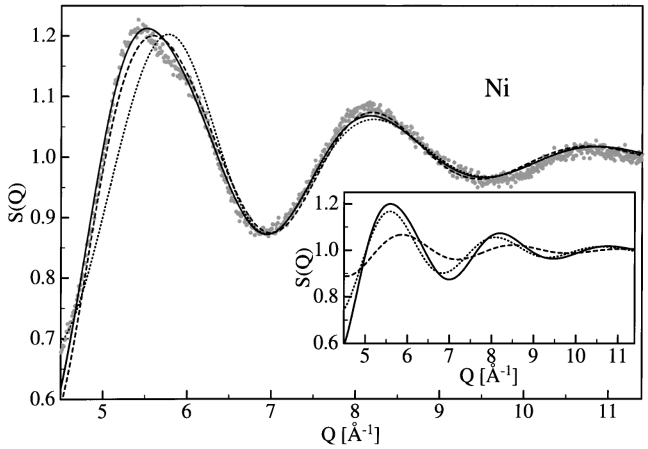

FIG. 3. Measured structure factor $S(Q)$ of a Ni melt at $T = 1435$ K in the range 4.5 Å^{-1} $< Q <$ 11.4 Å^{-1} (dots), and simulated $S(Q)$ by assuming clusters with different symmetries prevailing in the melt: icosahedra (dashed line, $\langle r_0 \rangle = 2.38$ Å, $\langle \delta r_0^2 \rangle = 0.029$ Å^2, $X = 0.99$), dodecahedra (solid line, $\langle r_0 \rangle = 2.42$ Å, $\langle \delta r_0^2 \rangle = 0.026$ Å^2, $X = 0.95$), fcc clusters (dotted line, $\langle r_0 \rangle = 2.45$ Å, $\langle \delta r_0^2 \rangle = 0.032$ Å^2, $X = 0.99$). The inset shows the results of the simulation under assumption of icosahedral clusters (solid line) together with the contributions of the two shortest interatomic distances within these clusters: distance of the central atom to the atoms on the shell $\langle r_0 \rangle$ (dashed line) and next neighbor distance of atoms on the shell $\langle r_1 \rangle$ (dotted line).

liquids while the interatomic distances remain almost unchanged as a function of T. The Z values ($Z \sim 12$) obtained are characteristic of several types of densely packed SRO, e.g., icosahedral, fcc, and hcp.

To obtain further information concerning the SRO in the melt, simulations of $S(Q)$ were carried out. Molecular dynamic computer calculations [3,4] on simple liquid models reveal an ISRO. In the present work, however, a simple approach of large Q simulation of $S(Q)$ based on isolated clusters was used. Indeed it implies only three fitted variables to discriminate between the different geometries of clusters: bcc, fcc, hcp, icosahedral, and dodecahedral. The simulation method is outlined in detail in [12]. The parameters of the simulation are the shortest mean distance, $\langle r_0 \rangle$, of cluster atoms (all larger mean distances of atoms inside the cluster, $\langle r_i \rangle$, are related), its mean thermal variation $\langle \delta r_0^2 \rangle$ that determines the Debye-Waller factor, $\exp(-\langle \delta r_i^2 \rangle/3)$, and the concentration, X, of cluster atoms in the liquid. The mean thermal variations of the other intracluster distances, $\langle r_i \rangle$, are estimated by $\langle \delta r_i^2 \rangle = \langle \delta r_0^2 \rangle \langle r_i^2 \rangle / \langle r_0^2 \rangle$ [12]. The parameters are adjusted such that a good fit of the experimentally determined $S(Q)$ is obtained especially at high Q values. Note that the large Q part of $S(Q)$ is determined by the SRO only as far as the contribution of larger distances is damped by thermal motions [12]. The results for liquid Ni in the undercooled regime at $T = 1435$ K are presented in Fig. 3. First for a SRO of bcc- and hcp-like structure it is not possible to achieve a reasonable fit of the measured $S(Q)$. The best fits obtained for icosahedral- ($\langle r_0 \rangle = 2.38$ Å, $\langle \delta r_0^2 \rangle = 0.029$ Å^2, $X = 0.99$) and fcc- ($\langle r_0 \rangle = 2.45$ Å, $\langle \delta r_0^2 \rangle = 0.032$ Å^2, $X = 0.99$) type SRO are shown in Fig. 3 together with the measured $S(Q)$ at large Q. If a SRO with fcc-like structure is assumed, neither the position nor the shape of the second oscillation of $S(Q)$ are described, while for the icosahedral clusters a significantly better agreement is achieved. The better agreement of the simulation of ISRO compared to that of fcc-type SRO can be understood by examining the individual contributions of each interatomic distance within these clusters to $S(Q)$ [cf. the inset in Fig. 3]. Let us recall that for an icosahedron the distance of the central atom to the atoms on the shell ($\langle r_0 \rangle$) and the next neighbor distance of atoms on the shell ($\langle r_1 \rangle$) differ by $\sim$5%, while for fcc clusters all distances of next neighbors are identical. As the contributions from the distances of nearest neighbors are the major ones to the total simulation, this explains the better fit obtained with the icosahedral cluster. In particular, the assumption of ISRO can better reproduce the large oscillation at about 5.5 Å (Fig. 3) and the presence of the characteristic shoulder as an asymmetry on the right-hand side of this oscillation. Furthermore, it has to be noticed that the first interatomic mean distances $\langle r_0 \rangle$ and $\langle r_1 \rangle = 1.0515 \langle r_0 \rangle$ obtained by the simulations for icosahedral clusters are quite consistent with the intermediate value of R_1, the position of the maximum of the first oscillation of $g(R)$ which includes both r_0 and r_1.

We have been dealing up to now with isolated 13 atom clusters, but we may wonder about the nature of SRO at larger distances. For this purpose, a simulation based on a larger cluster, the dodecahedron, was also performed (Fig. 3, $\langle r_0 \rangle = 2.42$ Å, $\langle \delta r_0^2 \rangle = 0.026$ Å^2, $X = 0.95$). The dodecahedron is an icosahedral cluster of higher order consisting of 33 atoms, which can be constructed from the icosahedron by placing atoms densely on all its 20 triangular faces. When comparing the results obtained for the two clusters with icosahedral symmetry it is obvious that the assumption of dodecahedral clusters leads to a better description of the measured $S(Q)$. This may indicate that a SRO order consisting of larger polytetrahedral aggregates (such as dodecahedra) prevails in the liquid. Moreover, at higher T, a larger $\langle \delta r_0^2 \rangle$ and a smaller X must be assumed in order to obtain a good fit of the experimental data, with dodecahedral clusters ($\langle \delta r_0^2 \rangle = 0.026$ Å^2, $X = 0.95$ at $T = 1435$ K compared to $\langle \delta r_0^2 \rangle = 0.033$ Å^2, $X = 0.80$ for a Ni melt at $T = 1905$ K). The increase of $\langle \delta r_0^2 \rangle$ reflects the T dependence of the Debye-Waller factor, while the decrease of X indicates a less pronounced ISRO at high T. The same conclusions were inferred from simulations of the $S(Q)$ of stable and undercooled Fe and Zr melts.

In summarizing the results of the present work, the SRO of Ni, Zr, and Fe metallic melts was investigated by neutron scattering in a large temperature range from well above T_L to the deeply undercooled metastable state at $T < T_L$. From the radial distribution function analysis and the simulation of the measured structure factor, ISRO is evidenced in all bulk metallic liquids and independently of the structure of the nucleating solid phases. Moreover, ISRO is revealed already above T_L and becomes more pronounced in the undercooled state with decreasing T. The present work gives an unambiguous experimental proof of the early hypothesis of Frank [2] that was based on arguments of topological ordering only.

The authors are grateful to Professor Dr. K. Urban, Professor Dr. F. Spaepen, Professor Dr. H. Ruppersberg, and Professor Dr. K. F. Kelton for fruitful discussions, to Dr. P. Convert, Dr. T. Hansen, Dr. T. Volkmann, Dr. L. Keller, and Dr. K.-R. Bauchspieß for experimental support, and to Professor Dr. B. Feuerbacher and Dr. H. Bach for continuous support. We thank the Institut Laue-Langevin (ILL) for making the instrument D20 available for these experiments. Financial support from Deutsche Forschungsgemeinschaft (DFG) under Contracts No. HO 1942/1 and No. HO 1942/2 and from ILL is gratefully acknowledged.

[1] D. Turnbull, J. Appl. Phys. **21**, 1022 (1950).
[2] F. C. Frank, Proc. R. Soc. London A **215**, 43 (1952).
[3] P. J. Steinhardt, D. R. Nelson, and M. Ronchetti, Phys. Rev. B **28**, 784 (1983).
[4] S. Nosé and F. Yonezawa, J. Chem. Phys. **84**, 1803 (1986).
[5] H. Jónsson and H. C. Andersen, Phys. Rev. Lett. **60**, 2295 (1988).
[6] D. R. Nelson and F. Spaepen, *Solid State Physics*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1989), Vol. 42, p. 1.
[7] D. Holland-Moritz, D. M. Herlach, and K. Urban, Phys. Rev. Lett. **71**, 1196 (1993).
[8] D. Holland-Moritz, Int. J. Non-Equilib. Process. **11**, 169 (1998).
[9] D. Shechtman, I. Blech, D. Gratias, and J. W. Cahn, Phys. Rev. Lett. **53**, 1951 (1984).
[10] M. Maret, A. Pasturel, C. Senillou, J. M. Dubois, and P. Chieux, J. Phys. (Paris) **50**, 295 (1989).
[11] M. Maret, F. Lançon, and L. Billard, J. Phys. I (France) **3**, 1873 (1993).
[12] V. Simonet, F. Hippert, H. Klein, M. Audier, R. Bellissent, H. Fischer, A. P. Murani, and D. Boursier, Phys. Rev. B **58**, 6273 (1998); V. Simonet, F. Hippert, M. Audier, and R. Bellissent, Phys. Rev. B **65**, 024203 (2002).
[13] S. Ansell, S. Krishnan, J. K. R. Weber, J. J. Felten, P. C. Nordine, M. A. Beno, M.-L. Saboungi, and D. L. Price, Phys. Rev. Lett. **78**, 464 (1997).
[14] C. Landron, L. Hennet, T. E. Jenkins, G. N. Greaves, J. P. Coutures, and A. K. Soper, Phys. Rev. Lett. **86**, 4839 (2001).
[15] S. Ansell, S. Krishnan, J. J. Felten, and D. L. Price, J. Phys. Condens. Matter **10**, L73 (1998).
[16] H. Kimura, M. Watanabe, K. Izumi, T. Hibiya, D. Holland-Moritz, T. Schenk, K. R. Bauchspieß, S. Schneider, I. Egry, K. Funakoshi, and M. Hanfland, Appl. Phys. Lett. **78**, 604 (2001).
[17] S. Krishnan, S. Ansell, J. J. Felten, K. J. Volin, and D. L. Price, Phys. Rev. Lett. **81**, 586 (1998).
[18] H. Reichert, O. Klein, H. Dosch, M. Denk, V. Honkimaki, T. Lippmann, and G. Reiter, Nature (London) **408**, 839 (2000).
[19] C. Notthoff, H. Franz, M. Hanfland, D. M. Herlach, D. Holland-Moritz, and W. Petry, Rev. Sci. Instrum. **71**, 3791 (2000).
[20] Yellow Book, http://www.ill.fr
[21] H. H. Paalman and C. J. Pings, J. Appl. Phys. **33**, 2635 (1962); J. L. Yarnell, M. J. Katz, R. G. Wenzel, and S. H. Koenig, Phys. Rev. A **7**, 2130 (1973); I. A. Blech and B. E. Averbach, Phys. Rev. 137, A1113 (1965).
[22] S. Sachdev and D. R. Nelson, Phys. Rev. Lett. **53**, 1947 (1984).
[23] Y. Waseda, *The Structure of Non-Crystalline Materials* (McGraw-Hill, New York, 1980).