

## Universal Symmetry Property of Point Defects in Crystals

Xiaobing Ren and Kazuhiro Otsuka

*Institute of Materials Science, University of Tsukuba, Tsukuba 305-8573, Japan*

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Point defects (vacancies, solute atoms, and disorder) are ubiquitous in crystalline solids. With *in situ* transmission electron microscopy we find clear evidence for the existence of a universal symmetry property of point defects; i.e., the symmetry of short-range order of point defects follows the crystal symmetry when in equilibrium. We further show that this symmetry-conforming property can lead to various interesting effects including “aging-induced microstructure memory” and the associated “time-dependent two-way shape memory.”

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Crystalline solids invariably contain some lattice defects such as vacancies, solute atoms, or some extent of disorder. These point defects strongly affect almost all properties of materials [1,2]. On the other hand, the most prominent property of any crystalline solid lies in its symmetry. Then comes an interesting and basic question: Do these two general properties of crystal correlate to each other?

Recent understanding on a long-standing puzzle of a curious “rubberlike behavior” in alloys [3] implied the existence of a simple but universal correlation between the symmetry of short-range order (SRO) distribution of point defects and crystal symmetry. However, there is no direct evidence for the existence of this symmetry property.

With *in situ* transmission electron microscopy (TEM) we show clear evidence for the existence of the symmetry property of point defects. This universal property leads to the prediction of two new effects, “microstructure memory” and “aging-induced two-way shape memory.” Both are experimentally verified in the present study. This symmetry property of point defects may also provide a unified understanding to a rich spectrum of phenomena related to symmetry change.

Even from a pure geometrical argument it is natural to consider that the SRO distribution of point defects has a simple symmetry property. For simplicity, we consider two-dimensional structures as schematically shown in Fig. 1, but the argument is applicable to any three-dimensional structure because only symmetry is of relevance. Consider a given defect  $B$  (which can be a solute atom or a vacancy or a wrong atom in ordered compounds) in a high-symmetry (square) lattice [Fig. 1(a)]. Because of the fourfold crystal symmetry, the four nearest-neighbor sites 1, 2, 3, and 4 are equivalent to defect  $B$ . Thus it is natural to expect that when in equilibrium the probability of finding another defect  $B$  around the defect at site 0 has the same fourfold symmetry as the crystal symmetry, i.e.,  $P_1^B = P_2^B = P_3^B = P_4^B$ . On the other hand, if the crystal is of lower symmetry (rectangular) [Fig. 1(b)], the environment around  $B$  becomes less symmetrical, and it is natural to expect that  $P_1^B = P_2^B \neq P_3^B = P_4^B$  when in equilibrium, following the twofold crystal symmetry. Apparently, this symmetry consideration also applies to sites farther from

$B$ , but the effect becomes weaker due to the weakening of the influence of  $B$  on farther sites. This means that this is a SRO effect. Therefore, Fig. 1 suggests that there may exist a universal symmetry property for the SRO distribution of point defects. That is, when in equilibrium, the probability of finding another point defect around a given point defect (this conditional probability uniquely defines the SRO parameter [4]) possesses the same symmetry as the crystal symmetry. This can be considered as a symmetry-conforming SRO (SC-SRO) property of point defects.

Though being intuitively reasonable as shown above, it is not easy to prove this “apparent” principle. Here we notice an important feature of SRO symmetry: SRO symmetry cannot be changed abruptly, because such a change involves atomic rearrangement (diffusion). By contrast, crystal symmetry can be changed abruptly, if lattice

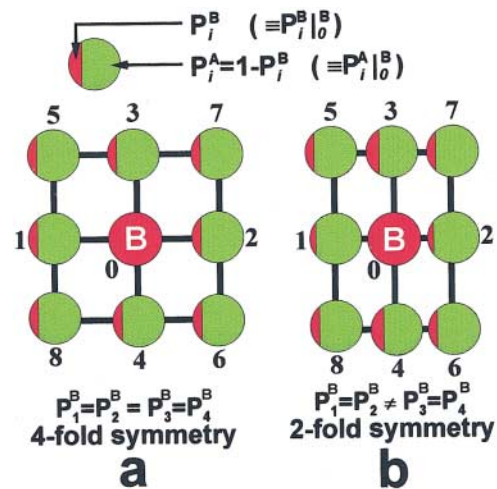


FIG. 1 (color). Symmetry-conforming property of the short-range order of point defects in crystals. When in equilibrium, the probability of finding another defect  $B$  around a given defect  $B$  possesses (a) fourfold symmetry for the square lattice (with fourfold symmetry), and (b) twofold symmetry for the rectangular lattice.  $P_i^B$  (or  $P_i^A$ ) is the conditional probability of defect  $B$  (or an atom  $A$ ) occupying site  $i$  ( $i = 1, 2, 3, 4, \dots$ ) if a defect  $B$  is at site 0. The values of  $P_i^B$  and  $P_i^A$  are represented by red and green areas, respectively. They are uniquely related to SRO parameters [4].

distortion occurs without diffusion, e.g., by diffusionless (or martensitic) structural transformation [2,5], or by deformation. Therefore, if crystal symmetry undergoes a sudden (diffusionless) change, SRO symmetry will show a “time lag” to follow the new symmetry. This important feature allows us to prove the SC-SRO principle by utilizing diffusionless ferroelastic/martensitic transformation, which changes crystal symmetry between a cubic parent phase and a low-symmetry martensite (hereafter abbreviated as P and M, respectively).

Suppose the SC-SRO principle is correct, then let us predict what should happen when crystal symmetry changes diffusionlessly from an equilibrium M (in the sense that SRO conforms to the M symmetry) to the cubic P, as shown schematically (in two dimensions) in Fig. 2. The low-symmetry M is usually composed of many twin-related domains [Fig. 2(a)]. The low-symmetry SRO configurations in different M domains are thus oriented differently [Fig. 2(a), left side] following their corresponding crystallographic orientation. When the equilibrium M [Fig. 2(a)] transforms into cubic P [Fig. 2(b)] by reverse transformation, the crystal symmetry becomes cubic everywhere. However, because of the diffusionless nature of the transformation, the low SRO symmetry of M is inherited to the cubic P. This SRO with M symmetry can slightly distort the nominal cubic lattice toward the M symmetry. Consequently, there exists a slight lattice difference in P between previously different M domains due to the SRO orientation difference [Fig. 2(b), left side]. Such a lattice difference, together with the orientation difference in SRO, will produce a “SRO-induced domain” pattern in the cubic phase [Fig. 2(b)], which is identical to the M domain pattern shown in Fig. 2(a). It is possible to use structure-sensitive imaging technique (such as TEM) to detect this orientation difference and to image the SRO-induced domain pattern.

Of course, the M symmetry of SRO in the cubic P [Fig. 2(b)] is an “incorrect” symmetry for the cubic P, according to the SC-SRO principle. It will change into the cubic symmetry [Fig. 2(c)] when atomic rearrangement (diffusion) is allowed. Then the distinction between different SRO-induced domains disappears, and the “martensitelike distortion” in the cubic phase also disappears after aging in P for some time [Fig. 2(c)].

We performed an *in situ* TEM observation on a M alloy  $\text{Au}_{51.7}\text{Cd}_{48.3}$  to verify the above predictions. This alloy undergoes a diffusionless (martensitic) transformation between an orthorhombic M ( $\gamma_2'$  structure) and a cubic P ( $B2$  structure). The M was aged at 25 °C for two months in order to make the SRO symmetry to conform to the M symmetry. It completely transforms into the cubic P at 50 °C. The results of the *in situ* TEM observation are shown in Figs. 3(a), 3(b), and 3(c).

Figure 3(a) shows a typical domain pattern of aged M. When heated up and transformed into the cubic P, a martensitelike “residual contrast” remains in the cubic P [Fig. 3(b)], which is identical to the M domain pattern [Fig. 3(a)] but has much weaker contrast. Careful examination of the associated diffraction pattern in Fig. 3(b) clearly shows that the specimen is really in P, because the “extra spots” associated with M [as indicated by the arrows in Fig. 3(a)] have disappeared. We confirmed that when the M is not aged, no residual contrast appears. The residual contrast strongly suggests that the different “domains” in the cubic P have some internal differences, as predicted in Fig. 2(b). Besides, from the splitting in the 330 diffraction spot of the P in Fig. 3(b), which has the same split direction as that of the low symmetry M [see the 200 spot of M in Fig. 3(a)], we can conclude that the P in Fig. 3(b) is not strictly cubic, but slightly distorted towards M symmetry. This is a strong indication that the SRO symmetry of martensite is inherited into P by the diffusionless

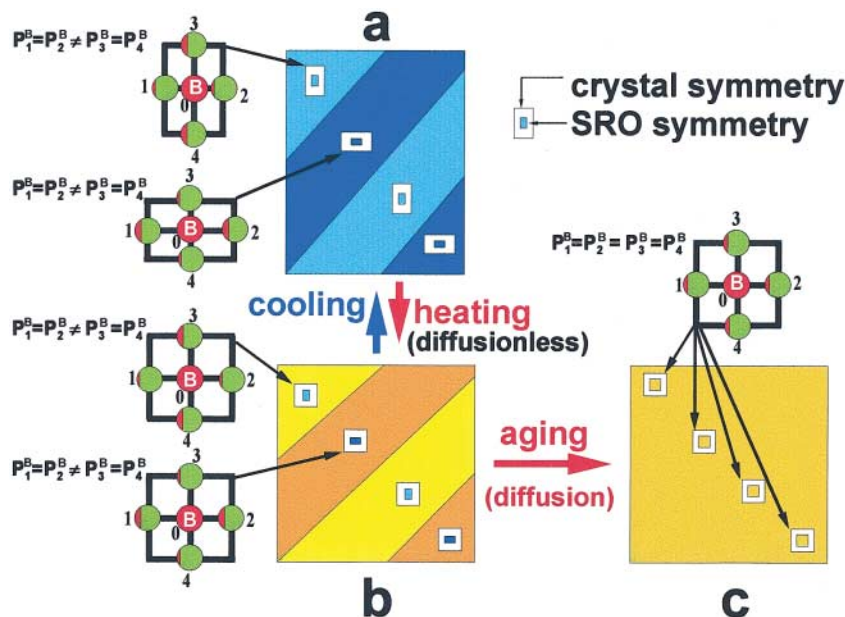


FIG. 2 (color). Predicted microstructure and SRO changes during reverse martensitic transformation from symmetry-conforming SRO principle. (a) Aged martensite (low-symmetry phase) in which SRO symmetry conforms to the crystal symmetry of martensite. (b) Parent phase (cubic) immediately after diffusionless transformation from (a). (c) Parent phase after aging to allow SRO symmetry to conform to the cubic symmetry of parent phase.

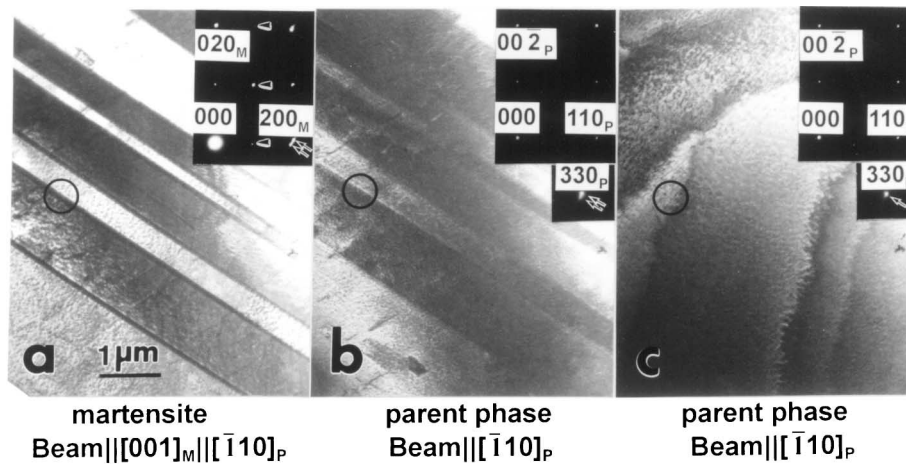


FIG. 3. Evidence for symmetry-conforming SRO principle of point defects by transmission electron microscopy. (a) Well-aged  $\text{Au}_{51.7}\text{Cd}_{48.3}$  martensite (low crystal symmetry) at 23 °C; the split (double-arrow) diffraction spots are due to twin. (b) Parent phase (high crystal symmetry) immediately after the diffusionless reverse martensitic transformation (at 50 °C). (c) Parent phase after aging at 130 °C for 10 min. Diffraction patterns are taken from the circled area containing two domains. The subscripts  $M$  and  $P$  of the diffraction indices designate martensite and parent phase, respectively. The  $330_P$  spot in (b) and (c) is enlarged by 2 times.

transformation, as predicted in Fig. 2(b). Therefore, Fig. 3(b) also proved that the equilibrium SRO symmetry in the aged M also follows the M symmetry, as required by the SC-SRO principle.

The “martensitelike contrast” and the “splitting” in the diffraction spot shown in Fig. 3(b), which indicate the existence of an incorrect (i.e., M) SRO symmetry in the cubic P, disappeared after the P was aged for some time [Fig. 3(c)], as predicted in Fig. 2(c). This is strong evidence for the SRO symmetry to conform to the crystal symmetry when in equilibrium. Therefore, Fig. 3 clearly demonstrates that the equilibrium SRO in M follows the M crystal symmetry, and that in the P follows the parent symmetry; more importantly, any incorrect SRO symmetry will be corrected when diffusion is allowed. These results provide a strong proof for the SC-SRO principle.

The SC-SRO principle, as a universal property of crystals, may lead to various interesting effects in metal alloys, ceramics, and many other materials. Here we show only one example in alloys: It leads to a microstructure memory and the associated aging-induced two-way shape memory (TWSM) in alloys with diffusionless (martensitic) structural transformation. Usually, M alloys possess only “one-way shape memory” [6]; that is, only the macroscopic shape of P can be reproduced, but a predefined M shape (the cold shape) cannot be reproduced because the formation of M domains is rather arbitrary and there is no reason for M to adopt the same domain pattern as before (i.e., no microstructure memory [6]). However, for an aged M shown in Fig. 2(a), the situation becomes different. One can easily deduce that when the aged M, which adopts M SRO symmetry [Fig. 2(a)] is heated up and transformed into P, the P will inherit exactly the same SRO distribution as M due to the diffusionless nature of the transformation [Fig. 2(b)]. Now let this “nonequilibrium” P [Fig. 2(b)] cool down and transform into M again, it is apparent that

M will adopt the previous M domain pattern [Fig. 2(a)] so as to make the SRO orientation conform to the M crystallographic orientation everywhere, as a consequence of the SC-SRO principle. This is a kind of microstructure memory, induced by M aging. The macroscopic manifestation of this microstructure memory is the memory of the previous M shape (the cold shape). Therefore, we can predict that aged M may exhibit microstructure memory and the associated macroscopic TWSM.

Figure 4 is the experimental verification of the microstructure memory for an aged AuCd martensite. It is clear that the domain pattern of the aged M [Fig. 4(a)] is memorized [Fig. 4(c)] if the sample does not stay in P [Fig. 4(b)] for a long time. This is exactly what is predicted above. Moreover, this microstructure memory disappears [Fig. 4(e)] after the sample is aged in P [Fig. 4(d)]. This can also be easily understood from Fig. 2 by considering that the SRO symmetry of P after aging has cubic symmetry [Fig. 2(c)].

Figure 5 is an experimental verification of the “martensite-aging-induced TWSM.” It shows that an aged AuCd M can undergo a reversible shape change between a “hot shape” (P) and a “cold shape” (M) when alternatively heated and cooled around its M start temperature ( $M_s = 30$  °C). This aging-induced TWSM effect is also expected from the SC-SRO principle, as discussed above. We further confirmed that if M is not aged, this effect does not appear. This corresponds to the loss of microstructure memory for “fresh” M [Fig. 4(e)], which transforms from the aged P [Fig. 4(d)]. The aging-induced TWSM may find applications as time-sensitive actuators because the size of the effect is dependent on aging time. Very recently, there is an interesting report on similar TWSM due to M aging in Cu-based alloys [7]. These results, obtained in completely different systems, can be viewed as a nice verification of the generality of the

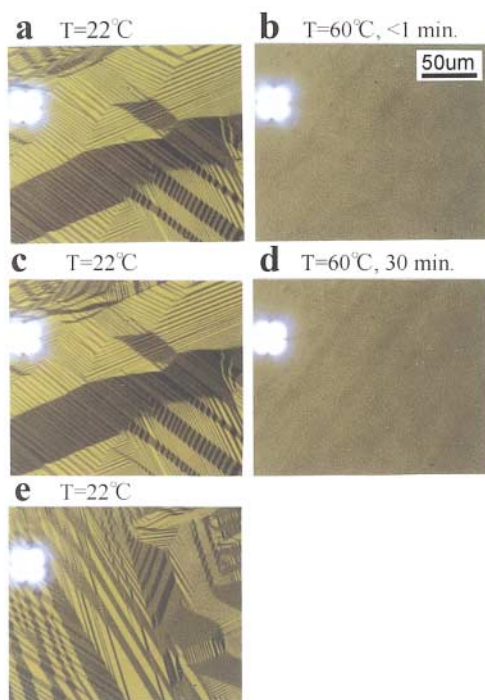


FIG. 4 (color). Optical microscopy verification of the predicted microstructure memory for an aged  $\text{Au}_{51}\text{Cd}_{49}$  martensite and its disappearance after aging in the parent phase. (a) Domain pattern of the aged martensite (aged at room temperature for six months). The sample is heated up to (b) parent phase ( $60^\circ\text{C}$ ), and immediately cooled down to (c) martensite. Then the sample is heated up again to (d) parent phase ( $60^\circ\text{C}$ ) and aged for 30 minutes, followed by cooling down to (e) martensite.

SC-SRO principle. It should be mentioned here that the TWSM discussed above is different in nature from another kind of TWSM produced by a complicated thermomechanical training process [8], where the formation of favorably orientated dislocations is considered to be responsible.

Throughout this paper we can clearly see that whenever crystal symmetry undergoes a sudden change, there will be a time lag for the SRO symmetry of point defects to follow it, because the change in SRO symmetry requires some time for atomic diffusion. This time lag may create a rich spectrum of relaxation phenomena in various materials that undergo abrupt symmetry change. The microstructure memory (Fig. 4), the aging-induced two-way shape memory (Fig. 5), rubberlike behavior [3,9], as well as the stabilization of martensite [3], are just a few examples of this common origin. Zener relaxation [10], directional anisotropy in cubic [11] or in amorphous materials [12] induced by stress or magnetic annealing may also be due to the same reason although the way of changing crystal symmetry is different (i.e., by elastic distortion or magnetostriction). We also expect that ferroelectrics, another large class of material that undergoes abrupt symmetry change, may also exhibit a certain “aging effect,” which is possibly accompanied

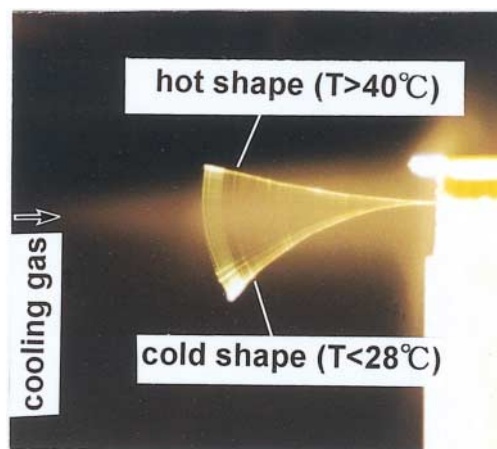


FIG. 5 (color). Aging-induced two-way shape memory effect in a  $\text{Au}_{50.5}\text{Cd}_{49.5}$  alloy after aged in martensite state. The sample was cooled from the well-aged parent phase ( $100^\circ\text{C}$ ) to martensite, then was lightly bent into the “cold shape,” followed by stress-free aging for two days at room temperature ( $25^\circ\text{C}$ ) before testing for two-way shape memory effect.

with some electrical effect due to the interplay between lattice distortion and electric polarization [13].

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