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A New Disordering Mechanism in A15 Type Compounds Submitted to Low Temperature Irradiation or to Quenching from High Temperatures

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Abstract

A new diffusion mechanism describing the changes of the long range order parameter in A15 type compounds after both quenching from high temperatures or low temperature irradiation with high energy particles is presented. It is based on the occupation of nonequilibrium or "virtual" sites centered halfway between two neighbouring A atoms on 6c sites, arising from the instability of a single 6c vacancy recently found by Welch and coworkers by pair potential calculations. After low temperature irradiation, the occupation of this interstitial site creates the necessary conditions for A↔B site exchanges over several interatomic distances by focused replacement collision sequences.

Due to the occupation of a certain concentration of virtual sites, atomic "overlapping" is not only possible between A atoms on the chains or between A and B atoms (due to deviations from perfect ordering), but also between B atoms on BBB sequences. The latter are retained after low temperature irradiation only and are responsible for the observed lattice expansion and static displacement.

Ein neuer Entordnungsmechanismus in A15 Verbindungen bei Tieftemperaturbestrahlung oder Abschrecken aus hohen Temperaturen

Zusammenfassung

Ein neuer Diffusionsmechanismus zur Beschreibung der Änderungen des Fernordnungsparameters in A15 Verbindungen bei Tieftemperaturbestrahlung oder Abschrecken aus hohen Temperaturen wird vorgeschlagen. Wesentlich ist dabei die Besetzung von Nichtgleichgewichtsgitterplätzen ("virtuellen Gitterplätzen) auf halbem Wege zwischen zwei benachbarten A Kettenatomen als Folge der Instabilität von isolierten 6c Gitterfehlstellen, die kürzlich von Welch und Mitarbeitern mittels Paarpotentialberechnungen gefunden wurde. Nach Tieftemperaturbestrahlung schafft die partielle Besetzung dieses interstitiellen Gitterplatzes die notwendigen Bedingungen für A↔B Platzwechsel über mehrere Gitterabstände durch fokussierte Ersetzungsstoßfolgen.

Durch die Besetzung einer kleinen Anzahl virtueller Gitterplätze wird nicht nur "Überlappung" zwischen A Atomen oder zwischen A und B Atomen auf derselben Kette möglich, letzteres wegen der abnehmenden Fernordnung, sondern auch zwischen B Atomen, womit BBB Folgen entstehen. Letztere werden nur nach Tieftemperaturbestrahlung erhalten und sind für die beobachtete Gitteraufweitung und statischen Auslenkungen bei A15 Verbindungen verantwortlich.

INTRODUCTION

The variation of the superconducting transition temperature, T_c, after irradiation with high energy particles has been studied for various A15 type compounds in the last decade[1,2,3]. From the wealth of published data, it follows that in typical A15 type compounds, e.g. V_3Si, Nb_3Ge, Nb_3Sn,.... a strong decrease of T_c is observed after irradiation doses exceeding certain values (10^{18} neutrons/cm^2, 10^{14} sulfur ions/cm^2 or 10^{15} He ions/cm^2) for irradiation temperatures $T_{irr} \leqq 150^{o}C$.

The initial decrease of T_c at low doses (for convenience, this term will here be arbitrarily applied for doses reducing the original value of the superconducting transition temperature, T_{co}, by less than 50%) is generally attributed to a decrease of the long range atomic order parameter, S. The first experimental evidence for the decrease of S in A15 type compounds after irradiation was furnished by Sweedler et al.[4] on the basis of neutron diffraction measurements on neutron irradiated Nb_3Al. More recently, a decrease of S in the same compound has also been reported by Schneider et al.[5] after irradiation with H^+ and Ne^+ ions of several hundreds keV. A competing mechanism to this picture of homogeneous disordering has been advanced by Pande[6], who postulated that the formation of disordered microregions (or depleted zones) of sizes below the coherence length (i.e. ≤ 50 Å) could lead to a decrease of T_c by proximity effects.

Due to the complexity of the problem, involving simultaneously additional effects as lattice expansion[4] and static atomic displacements[7,8], it is, however, difficult to decide whether homogeneous (disordering) or inhomogeneous (depleted zones) effects have a dominant influence on the initial decrease of T_c in irradiated A15 type compounds. In spite of the arguments given in Refs. 4 and 5, which strongly support the hypothesis of a homogeneous decrease of the long range order parameter over the whole sample volume, the mechanism of disordering during irradiation is still unknown. The question arises: How is it possible that a homogeneous decrease of S implying site exchanges over several lattice spacings can occur during irradiations at temperatures $T < 150\ ^{o}C$, where no noticeable thermal diffusion takes place? It is the aim of the present paper to show that disordering in irradiated

A15 type compounds occurs by focused replacement collision sequences, which are possible in the particular configuration of the irradiated A15 structure. A model is proposed on the basis of occupied interstitial (or "virtual") sites, placed midway between two 6c sites. As recently shown by Welch et al.[9], this configuration is energetically more favourable than a 6c vacancy. It will be shown that this picture explains as well the occurrence of the lattice expansion as of static atomic displacements in irradiated A15 type compounds.

1. Arguments in favour of homogeneous disordering

Up to the present day, a decrease of S in irradiated A15 type compounds has been detected by diffraction methods in the following cases: Nb_3Al by Sweedler and Cox[4], Nb_3Ge by Sweedler et al.[3], Nb_3Pt by Moehlecke et al.[10] V_3Si by Cox and Tarvin[11] and Nb_3Al by Schneider et al.[5]. These observations, which in one case include single crystal measurements[11], show without any doubt that the intensity of the A15 superlattice lines decreases with higher doses. In order to show that this decrease is really due to homogeneous disordering rather than to increasing portions of disordered (depleted) zones, a comparison has to be made with cases where such zones cannot occur, i.e. after quenching from high temperatures or after irradiation with high energy electrons. The agreement between the behavior of T_c as a function of S in Nb_3Pt after neutron irradiation [10] and argon jet quenching[12] can be considered as a convincing argument for homogeneous disordering. However, neither lattice expansion nor static atomic displacements are present after quenching. Therefore, besides homogeneous disordering, additional influence of the damage by irradiation cannot be excluded by this experiment.

The most conclusive experiment was later performed by Rullier-Albenque et al.[13] who compared the ratios $\Delta T_c/\Delta\rho$ of the change of superconducting transition temperature and residual resistivity in Nb_3Ge after irradiation with 2.5 MeV electrons and 1 MeV neutrons and found essentially no difference for both projectiles. Since electrons of these energies do not produce displacement cascades (the transmitted energy being nearly a factor 100 below that of neutrons[14]), this means that the inhomogeneous mechanism based on the formation of disordered zones which would lead to a decrease of T_c by proximity effects[6] can definitively be ruled out in the low dose region. At high doses, close to the saturation of T_c, proximity effects become important, but this is not relevant for the topic of interest and will thus not be discussed here.

Once the initial decrease of T_c has been recognized as being due to disordering effects, it is interesting to know the spread (or the distribution) of the order parameter across the irradiated sample. This information is provided by the specific heat data of Cort et al.[15] on Nb_3Al and of Viswanathan and Caton[16] on V_3Si. In both cases, the calorimetric superconducting transition width increases only weakly with dose, e.g. from $\Delta T_c = 0.8K$ to 1.3K for Nb_3Al and from $\Delta T_c = 0.6K$ to 1.2K for V_3Si, after neutron doses corresponding to a lowering to T_c/T_{co} values of 0.51 and 0.40, respectively. Since T_c for various typical A15 type compounds varies at a rate of 1K/1%S[17,18], this means that the order parameter over the whole sample volume after irradiation is still homogeneously distributed, the order parameter gradient remaining essentially unaffected: $\delta S \leq 1$ %.

It is interesting that the very small increase in ΔS after irradiation is comparable to the situation in argon quenched A15 type compounds, where the calorimetric superconducting transition remains unchanged by the quenching procedure, i.e. $\delta S \simeq 0$[19]. The question now arises about the mechanism able to produce at temperatures below T_c such an extraordinary atomic mobility including all the atoms in the irradiated volume, regardless of the irradiation dose.

2.The "Virtual" Lattice Site in the A15 Structure

In the tightly packed A15 structure, the site exchanges required for a change in atomic ordering, as well at high as at low temperature temperature irradiation are ordinarily assumed to occur by a vacancy diffusion mechanism[3]. In a bcc lattice, such a mechanism would be described by an atom jumping into a neighbouring vacancy, thus creating a new vacant site. Atoms and vacancies are expected to undergo a large number of position exchanges, in order that a very small number of vacant lattice sites ($\sim 10^{-3}$) would be sufficient to induce a substantial diffusion by vacancies. In the A15 structure, however, the diffusion mechanism is expected to be considerably more complex than for the simple bcc structure, essentially due to the covalent bonding[20] between two A atoms lying on neighbouring 6c sites (in the perfectly ordered case, the A atoms of the A15 type compound A_3B are at the 6c sites, the B atoms at the cubic 2a sites). This leads to AA interatomic distances being considerably shorter than the sum of two A atomic radii, and thus to highly nonspherical shapes for the atoms lying on the 6c sites.

The question arises whether this "overlapping" (or covalent bonding) between two neighbouring A atoms on the 6c or chain sites still resides if one of the A atoms is next to a 6c vacancy. Welch et al.[9] have recently shown by means of pair potential calculations that such an individual vacancy of an A atom on a 6c site is unstable. They found that the state of lower energy corresponds to a configuration where one of the two A atoms adjacent to the 6c vacancy is shifted towards a new site which is equidistant from the next two A neighbours (see Fig. 1a).

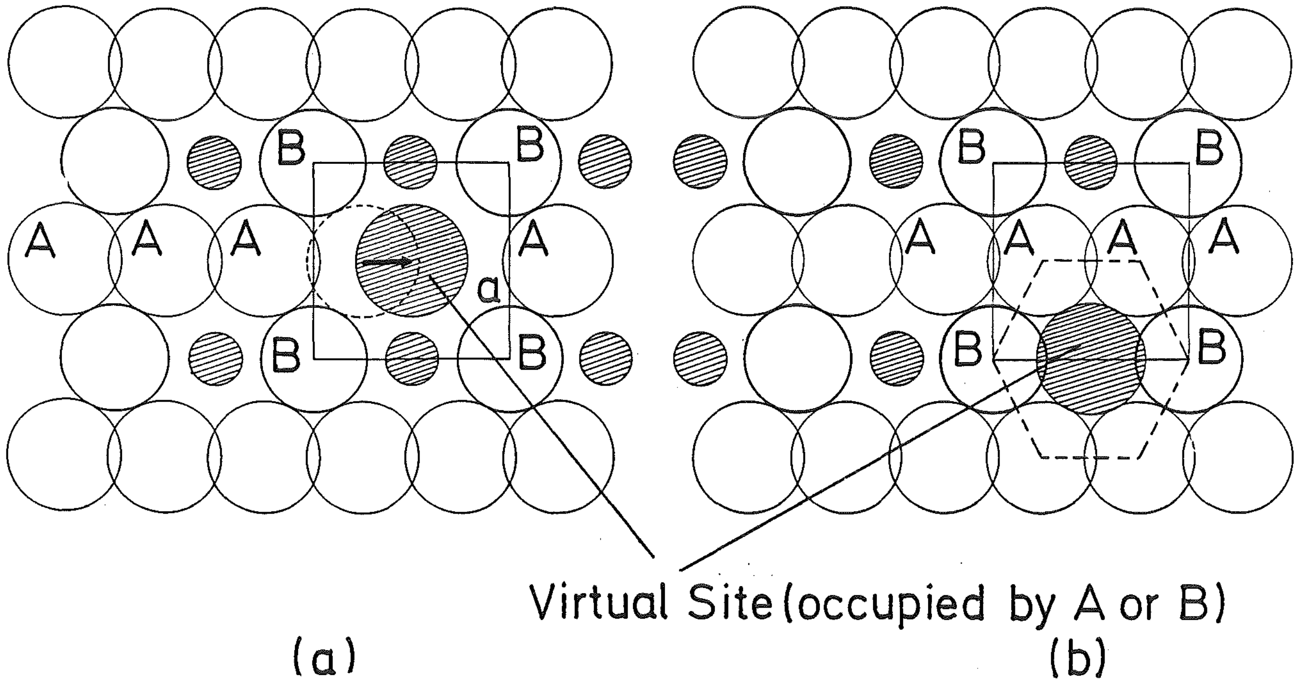

Fig. 1. Occupation of the virtual site in the A15 structure, as a consequence of the instability of single 6c vacancies:

a) in a chain parallel to the image plane.

b) in a chain perpendicular to the image plane, showing the hexagonal arrangement of the complex around this site.

The small circles correspond to the overlapping region between two A atoms belonging to chains perpendicular to the {100} plane.

a is the lattice parameter.

This kind of vacancy can either be called "split vacancy", as proposed by Welch et al.[9] or "negative crowdion", following the terminology of Seeger[21]. It has to be noted that the corresponding new site is not an equilibrium site of the A15 structure, but coincides with the region of overlapping between two neighbouring A atoms on 6c sites and will thus be called "virtual" site in the following.

Two possibilities of site exchange in the A15 structure are illustrated in Fig. 2. In Fig. 2a, the jump of a B atom into a 6c site is shown, which simultaneously requires the motion of an A atom from a virtual site to an equilibrium 6c site. In Fig. 2b, an A atoms jumps into a B vacancy, followed by the motion of an adjacent A atom into the vacant virtual site. In both cases, it appears that the diffusion mechanism in the A15 structure comprises at least two steps, in contrast to the one-step mechanism for bcc structures. As suggested by Welch et al.[9], various multi-step processes can also be imaginated, leading to even more possibilities for site exchanges by diffusion mechanisms in the A15 structure. It can now be recognized that the type of diffusion mechanism for this kind of structure does not correspond to vacancy diffusion, nor it corresponds to the so-called interstitialcy diffusion mechanism, where the atom diffuses from a normal site to an interstitial site. In the present case of the A15 structure, the situation is complicated by the fact that a jump into the virtual site (which is an interstitial site) requires simultaneously a rearrangement of more than one neighbour atom.

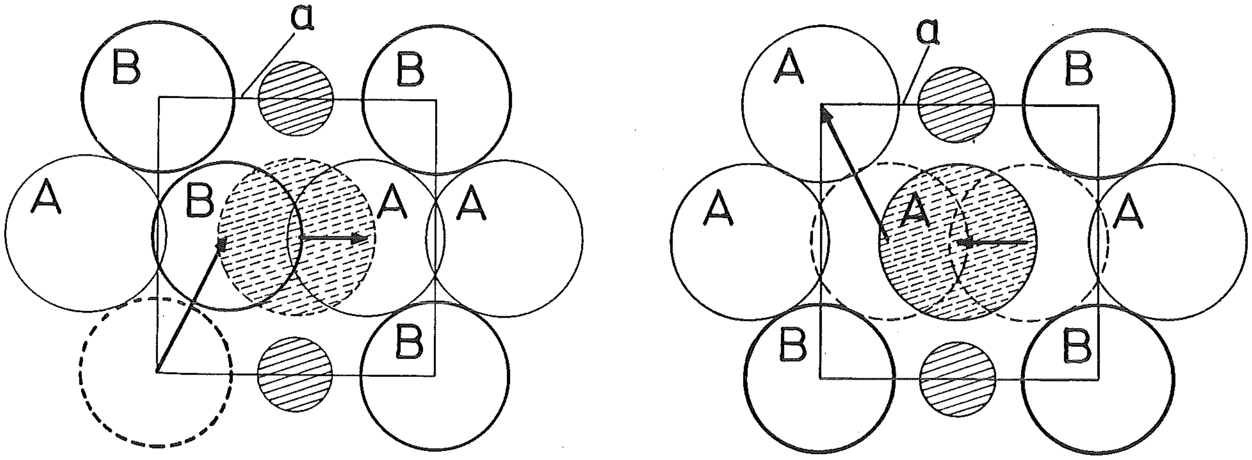

Fig. 2. A↔B site exchanges in the A15 structure.
a) jump of a B atom into a 6c site,
b) jump of an A atom into a 2a vacancy, followed by the occupation of the vacant virtual site by the neighbouring A atom (two-step processes).

3. Focused Replacement Collision Sequences

As first recognized by Seeger[21], the transport energy in an irradiated crystal is focused along certain crystallographical directions of the lattice. The so-called "focused replacement collision sequences" (or dynamic crowdions) can carry both energy and matter, thus transporting the interstitial atoms of Frenkel pairs formed during the primary collision events several interatomic distances away from their associated vacancy. It can be immediately seen that in the A15 structure, replacement collision sequences are possible in the <100> and the <111> direction. However, this does not produce A↔B site exchanges, these directions containing only one type of atom, A or B, respectively. The only focusing direction where collision sequences could in principle produce A↔B site exchanges is the <102> direction. In the unirradiated state, however, the atomic sequence in the <102> direction is ●ABA●ABA● , the space between two ABA sequences being occupied by the region of overlap between two A atoms belonging to perpendicular chains (small circles in Fig. 3). This renders the occurrence of AB site exchanges quite unlikely, as pointed out by Pande[23] and Schulson[14], who thus excluded focused replacement collision sequences as a possible mechanism for the homogeneous decrease of S in irradiated A15 type compounds.

The occupation of the virtual site, however, renders the situation in irradiated A15 crystals quite different from that encountered prior to irradiation. Indeed, the new sequence in the <102> direction including an occupied virtual site is now ●ABA●ABAAABA●ABA● or ●ABA●ABABABA●ABA● , depending on the occupation of this site by an A or a B atom, as shown in Fig. 3. It is obvious that the large amount of lattice vacancies created by irradiation (for example, $\sim$ 0.3% in V_3Si after a dose of 22.2×10^{18} neutrons/cm^2, as reported by Cox and Tarvin[11]) corresponds to a large number of occupied virtual sites. Due to the transport of matter caused by the large number of focusing replacement collisions (each entering particle removes up to 100 atoms), the site exchanges between normal and virtual sites will occur at a rapid sequence, thus leading to a high mobility of the atoms, even at low temperatures. The virtual sites will alternatively be occupied by either A or B atoms, thus constituting a "bridge" between ABA sequences and allowing A↔B exchanges over several interatomic distances. This is the necessary condition for a homogeneous decrease of the degree of ordering over the whole crystal volume after irradiation of an A15 type compound at low temperatures.

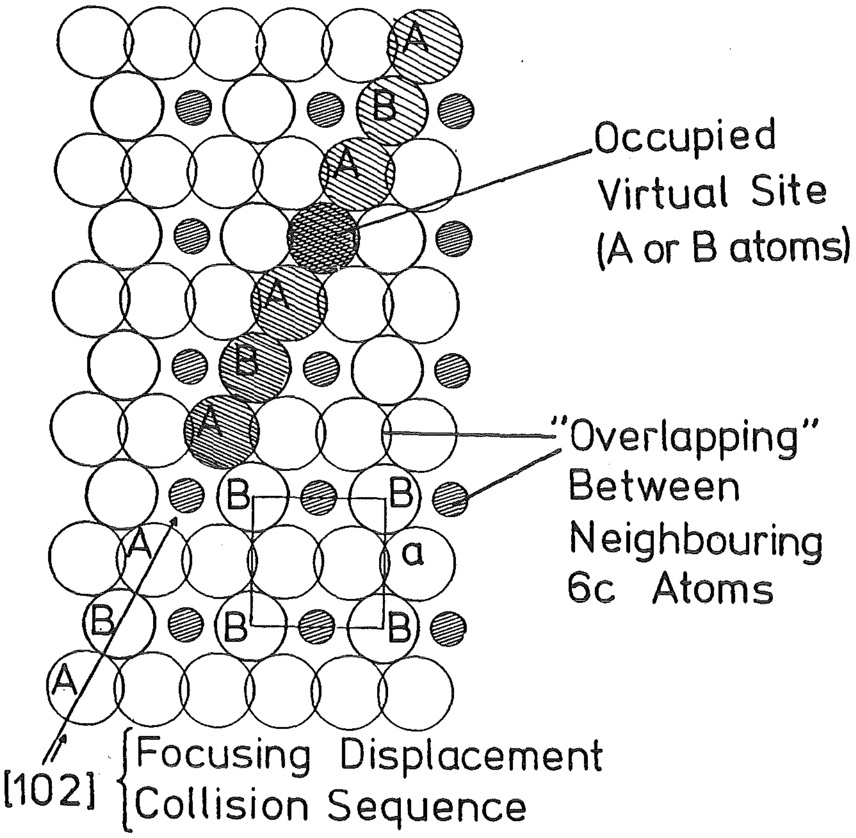

Fig. 3. Representation of the {100} plane of the A15 lattice (the atomic radii are the Pauling radii[22] for Nb_3Al). The small circles correspond to the overlapping region between two A atoms belonging to the chains perpendicular to the {100} plane.The occupation of the virtual site by an atom A or B leads to the sequences ●ABAAABA● or ●ABABABA● , respectively, instead of ●ABA● as in the unirradiated case, thus enabling A↔B site exchanges in the <102> focusing direction. a is the A15 lattice parameter.

4. The Variation of the Lattice Parameter after Irradiation

The lattice expansion after irradiation observed in A15 type compounds seems to be connected with particularities of this crystal structure. Indeed, a comparison shows that the transition elements V, Nb and Mo do not exhibit a lattice expansion after irradiation, except when they contain impurities, as shown by Linker[24,25].

A very important conclusion can be drawn from Fig. 1b showing that the occupation of the virtual site not only leads to very short interatomic distances and thus to overlapping between A and B atoms, but also between B atoms. As will be shown in the following, the occurrence of BBB sequences (retained by low temperature irradiation only) could furnish the key for understanding the causes of the lattice expansion and the static displacements observed in this

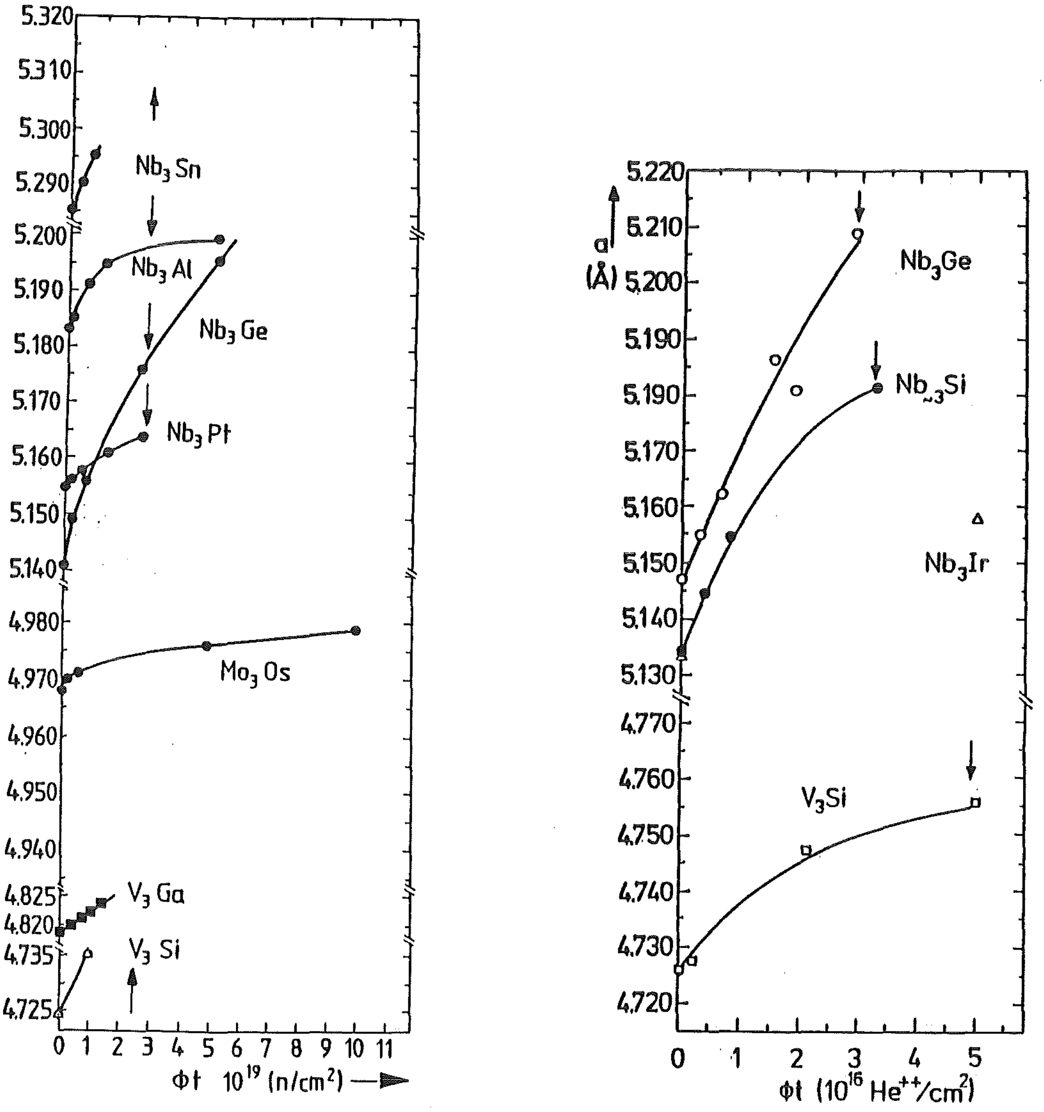

Fig. 4. Lattice parameters of different A15 type compounds after irradiation with high energy particles, a) neutrons (E>1 MeV), ● Sweedler et al.[3], ■ Francavilla et al.[26], Δ Cox and Tarvin[11], and b) Helium ions (E = 300 keV), o Pflüger and Meyer[27], • Haase and Rudzicka[28], □ Meyer and Linker[29], Schneider and Linker[30]. The arrows indicate the approximate dose at which T_c saturates.

class of materials. It is particularly interesting to study the consequence of BBB sequences if B is a nontransition element.

The observed increase of the lattice parameter in several A15 type compounds is represented in Fig. 4a for neutron and in Fig. 4b for He ion irradiation. In spite of the small number of analyzed systems, it can be concluded that for compounds with the same A element the increase Δa is considerably smaller if the B atom is a transition element, e.g. Os, Ir or Pt. The largest lattice expansion is observed on systems containing nontransition B elements, as Ge, Si or Sn, independently on the A element. It is interesting that Nb_3Ge[27] and $Nb_{\sim 3}Si$[28] in Fig. 4b show the same increase Δa with He dose, in spite of the very different atomic radii of Ge and Si. The same conclusion can be drawn from a comparison between Mo_3Ge[31] and Mo_3Si[32] after irradiation with ^{32}S ions, both showing an expansion Δa/a exceeding 1.1% as follows from Table I. This shows convincingly that there is no simple correlation between the lattice expansion rate in irradiated A15 type compounds and the ratio of the radii of the constituents: It is suggested that the value of Δa is primarily due to the electronic charge distribution of the B element, which influences the repulsion between the atoms in the complex around the virtual site, the radius ratio being of secondary importance only.

Spherical Atomic Shapes and their Limitations

In spite of the fact that the shapes of the A atoms in the A15 structure are highly nonspherical, there have been several attempts to calculate the A15 lattice parameters using spherical (geometrical) approximations. Two approaches, the Pauling[22] and the Geller[33] model, are based on spherical shapes of the atoms A and B, while other ones describe the atomic sizes by using atomic volumes[34,35]. It is remarkable that all these geometrical models are able to predict the A15 lattice parameters with an accuracy better than 1% without any consideration of the respective electronic configurations. The present considerations about the lattice parameter changes as a function of increasing damage and disorder, as well as of compositional changes will show the limitations of these geometrical models.

The observed lattice expansion in A15 type compounds after irradiation has been attributed to the effect of increased disorder[4,10], the slope $d(\Delta a)/d(\phi t)$ being assumed to depend on the difference between the atomic radii, characterized by the ratio r_A^G/r_A^G, where r_A^G and r_B^G are the Geller radii of the atoms A and B[3,4,10]. This hypothesis was mainly based on the Geller model[33], which postulates atomic "contact" between spherical A and B atoms, the lattice parameter being obtained by the formula $a = \frac{4}{\sqrt{5}} (r_A^G + r_B^G)$. Taking into account

System	a_o (Å)	$\Delta a/a$(%) at $\phi t = y \cdot 10^{15}$ $^{32}S/cm^2$		r_A^G/r_B^G	r_A^P/r_B^P	Ref.
		y = 1	y = 3			
Nb_3Ge	5.140	0.49	0.91	1.119	1.111	10,49
Nb_3Sn	5.289	0.13	0.37	1.041	0.950	39
Mo_3Ge	4.937	1.11	1.32	1.044	1.066	31
Mo_3Si	4.900	1.16		1.068	1.112	32

System	a_o (Å)	$\Delta a/a$(%) at $\phi t = y \cdot 10^{16}$ He/cm^2				r_A^G/r_B^G	r_A^P/r_B^P	Ref.
		y = 0.5	y = 1	y = 3	y = 5			
Nb_3Ge	5.147	0.23	0.42	1.20		1.119	1.111	27
$Nb_{\sim 3}Si$	5.134	0.27	0.47	0.93		1.144	1.158	28
Nb_3Ir	5.133				0.48	1.110	1.077	30
V_3Si	4.727	0.13	0.21		0.59	0.992	1.057	29

System	a_o (Å)	$\Delta a/a$(%) at $\phi t = y \cdot 10^{19}$ neutrons/cm^2			r_A^G/r_B^G	r_A^P/r_B^P	Ref.
		y = 1	y = 3	y = 5			
Nb_3Ge	5.140	0.38	0.76	1.07	1.119	1.111	3
Nb_3Sn	5.289	0.25			1.041	0.950	3
Nb_3Al	5.183	0.19	0.27	0.31	1.094	1.047	4
Nb_3Pt	5.155	0.08	0.17		1.094	1.051	6
Mo_3Os	4.968	0.10	0.12	0.18	1.037	1.036	3
V_3Ga	4.818	0.10			0.956	0.965	26
V_3Si	4.725	0.21			0.992	1.057	11

Table I. Lattice parameter changes in several A15 type compounds after irradiation with neutrons (E>1 MeV), He ions (E = 300 keV) and ^{32}S ions (E>20 MeV). For comparison, the ratios between the Pauling[22] and the Geller[33] radii of the A and B atoms, respectively, have been added.

site exchanges due to disordering, this formula can be modified to $\Delta a = a(S \neq 1) - a(S = 1) = \frac{8}{\sqrt{5}}(1 - r_a)(r_A^G - r_B^G)$, where r_a is the probability of occupying 6c sites by A atoms. The validity of this formula is, however, seriously limited by the absence of lattice parameter changes in A15 type compounds disordered by quenching form high temperatures, even after the highest quenching rates[17,18,36]. In addition, this formula would predict a contraction of the lattice for A15 systems where $r_A^G < r_B^G$, as for example V_3Ga and V_3Si, which is in contrast to the experimental results (see Fig. 4a).

It is interesting that the invariance of the lattice parameter against order parameter changes, $\Delta a(S) = 0$, is correctly described by the Pauling model[22]. The Geller model[33] also fails in describing the effects of stoichiometry on the lattice parameter. For example, the lattice parameter in the system $Nb_{1-\beta}Sn_{\beta}$ as a function of the Sn content should be minimum at the stoichiometric composition, $\beta = 0.25$, if the Geller radius for Sn, 1.44 A, would be correct. In reality, the lattice parameter is maximum at $\beta = 0.25$, $a = 5.289$ Å[37]. Similarly, stoichiometric V_3Si should exhibit a maximum of a, while in reality, a minimum is observed: $a = 4.724$ Å for $\beta = 0.25$ and $a = 4.736$ Å for $\beta = 0.20$[38]. Again, the Pauling model predicts in all cases a variation Δa in the correct direction. In spite of the spherical approximation, this model[22] describes the situation in A15 type compounds far better than the Geller model.

Deviation from Sphericity and the Electronic Configuration

Based on the proposed virtual site exchange mechanism leading to AB or BB "overlapping", the variation of the lattice parameter in irradiated A15 type compounds can be interpreted as reflecting the electrostatic repulsion between the pairs AB and BB, respectively. In this picture, the repulsion would be smallest between two transition elements, intermediate between a transition and a nontransition element and maximum between nontransition elements.

It is possible to estimate the effect of AB repulsion on the lattice parameter by studying the variation of the latter as a function of composition in A15 systems where the phase field extends to both sides of stoichiometry. This is the case in the four systems Nb - Ir, Nb - Pt, V - Pt and V - Ga, where the A15 phase is stable within the composition ranges $0.22 \leq \beta \leq 0.28$[40], $0.20 \leq \beta \leq 0.30$[41], $0.19 \leq \beta \leq 0.325$[42] and $0.18 \leq \beta \leq 0.32$[18,43], respectively. At compositions $\beta > 0.25$, the number of B atoms exceeds that of disponible 2a sites, and the quantity $(\beta - 0.25)$ of B atoms will thus be located on 6c sites, giving rise to AB "overlapping". The repulsive effect of the presence of B atoms on the chain sites can be visualized by the different slopes $da/d\beta$ at both sides of the stoichiometric composition. It can be seen from Fig. 5 that there is a lattice expansion contribution at $\beta > 0.25$ in the three systems Nb - Pt, V - Pt and V - Ga, regardless of the respective sizes of A and B atoms.

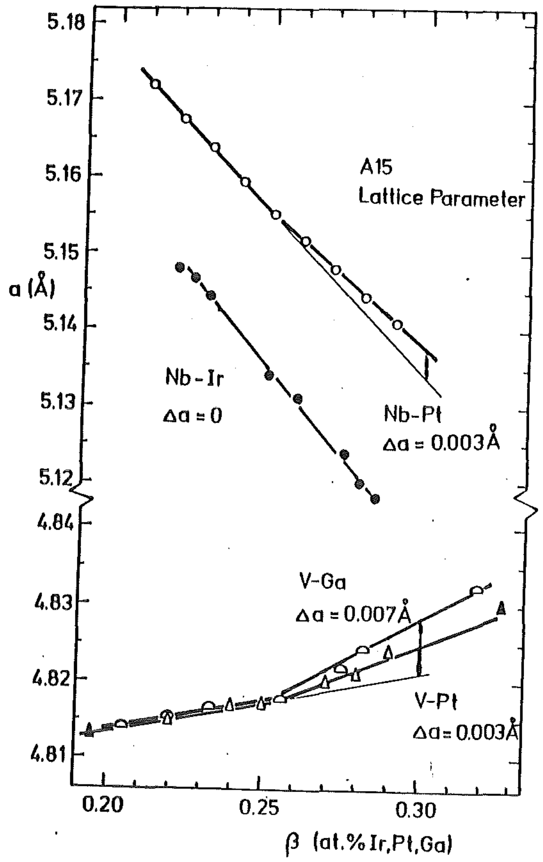

Fig. 5. Lattice parameter vs. composition in the systems Nb - Ir (●, Ref. 17), Nb - Pt (o, Ref. 10), V - Pt (△, Ref. 17, ▲ , Ref. 42) and V - Ga (⌓ , Ref. 43). For comparison, Δa has been indicated for the composition β = 0.30 and is defined as the difference between the measured lattice parameter and the value obtained by extrapolation from the data below β = 0.25.

At β = 0.30, which corresponds to 6.7% of 6c sites occupied by B atoms or to Bragg-Williams long range order parameters S_a = 0.78 and S_b = 1[45], the measured value of a is larger than that obtained by extrapolation from the data below β = 0.25. The positive difference, Δ a, corresponding to a lattice expansion, is 0.003 Å for Nb_3Pt, 0.003 Å for V_3Pt and 0.007 Å for V_3Ga, while no deviation could be observed for Nb_3Ir (see Fig. 5). The positive change of the slope da/dβ for β > 0.25 in Nb-Pt and in V-Pt can also be found by applying the Geller model[33], as pointed out by Moehlecke et al.[44], while no change is predicted by the Pauling model[22]. However, the agreement with the Geller model is accidental, since for V_3Ga, this model would predict a contraction instead of the observed expansion. In reality, no geometrical model is able to explain the additional lattice expansion at β > 0.25 shown in Fig. 5.

The lattice expansion $\Delta a = \Delta a(\beta)$ for V_3Ga in Fig. 5 exceeds the corresponding ones for the Pt based systems by more than a factor two. This can be interpreted as the effect of stronger repulsion due to the presence of the nontransition element Ga on the 6c sites. Indeed, there are now interactions between a nontransition and a transition element (represented by Ga_{6c} and V_{6c}) and between two nontransition elements (Ga_{6c} and Ga_{2a}), the distances V_{6c}-Ga_{6c} (2.409 Å) and Ga_{6c}-Ga_{2a} (2.693 Å) being both shorter than the corresponding sums $r_V^P + r_{Ga}^P = 2.713$ Å and $2 \times r_{Ga}^P = 2.762$ Å, respectively.

From the small deviations of $\Delta a = \Delta a(\beta)$ from linearity in Fig.5, it can be understood why no lattice parameter changes have so far been observed in quench disordered A15 type compounds. Indeed, the variations of the order parameter after quenching are limited to $\Delta S \leq 0.10$[17,36] (or $\Delta S_a \leq 0.10$[17,36]), while the values for Δa in Fig. 5 have been taken for $\Delta S_a = 0.22$. For V_3Ga, a change $\Delta S = 0.02$ has been observed[18], which would correspond to a variation $\Delta a = 0.0007$ Å, when assuming the same lattice expansion as in Fig. 5. The corresponding change for Nb_3Pt is $\Delta S = 0.06$[36], which would lead to the expansion $\Delta a = 0.0008$ Å. In both cases, V_3Ga and Nb_3Pt, the value of Δa is just below the accuracy of ordinary lattice parameter determination, of the order of ± 0.001 Å.

5. Static Displacements of the Atoms from their Equilibrium Positions

The occurrence of static displacements of the atoms from their equilibrium positions observed in several A15 type compounds after irradiation[5,7,8] is also related to the proposed virtual site exchange mechanism. As illustrated in Fig. 1b, an occupied virtual site causes a perturbation of the potential in the surrounding hexagonal complex, which not only leads to an increase of the lattice parameter, but also to displacements from the equilibrium atomic positions for this group of atoms. A comparison between the known static displacement data shows that the lattice parameter expansion, Δa, as well as the static displacements, $\langle u^2 \rangle$, are enhanced when heavier incident particles are chosen. For example, irradiation of Nb_3Al up to saturation of T_c (Ref. 5) yielded for 300 keV H^+ ions a value $\langle u^2 \rangle = 0.05$ Å^2, while 700 keV N^+ ions yielded $\langle u^2 \rangle = 0.1$ Å^2. For both systems V_3Si and Nb_3Al, neutron irradiation causes considerably smaller static displacements than irradiation with heavier particles[4,5,11,29]. This could be explained by the fact

that the heavier incident particles would cause an increased number of Frenkel pairs, i.e. an increased number of 6c vacancies during the primary collision events. In the light of the proposed virtual site exchange mechanism, this would also lead to an enhanced number of occupied virtual sites, which would in turn cause a larger lattice expansion Δa as well as larger $<u^2>$ values.
No static displacements have so far been determined on A15 type compounds containing a transition B element. It would be interesting to compare the static displacements in such a system with the known cases where B = Si[8], Al[5] or Sn[46] is a nontransition element.

6. Comparison Between Irradiated and Quenched A15 Type Compounds

It is interesting to compare the disordering phenomena in both cases, quenching from high temperatures and low temperature irradiation. It appears that both processes are influenced by the number of occupied virtual sites, the time of occupation being very different in both cases.

At high temperature, the occupation of the virtual site is dynamic, having the character of an intermediate state in the course of two-step or multi-step processes connected with the particular diffusion mechanism in A15 type compounds. The time of occupation of a virtual site is expected to be very short, depending on temperature and varying from compound to compound. In order to retain a significant amount of occupied virtual sites, the total cooling time during the quenching process should be shorter than the occupation time. From quenching experiments on V_3Si, where a lowering of T_c is only observed at cooling rates well above 10^5 °C/s[47], the occupation time at high temperature can be estimated to be less than 10^{-3} s, the probability of retaining occupied virtual sites after quenching being thus very low.

Quenching experiments thus retain a certain lattice disorder, but only a negligible number of occupied virtual sites, in contrast to low temperature irradiation. In the latter case, those virtual sites which were occupied at the moment where the high energy particle is at the end of its trajectory remain occupied as long as the temperature is sufficiently low, for example <150°C.

The main difference between quenching and irradiation resides in the formation process of the vacancies. In quenched crystals, the occurrence of vacancies is a consequence of the anharmonic thermal vibrations of the atoms around their equilibrium lattice site at a given temperature. In irradiated crystals, the formation of vacancies occurs by means of primary collision events. There is also a difference in the mechanism of disordering:

In the thermal case, disordering is the consequence of random site exchange, the driving force being a function of temperature, while site exchange due to high energy irradiation occurs along focusing directions, the driving energy being due to the incident particle. As discussed above, however, both cases lead to a homogeneously distributed degree of ordering throughout the whole crystal. Both processes, irradiation and quenching, lead to a nonequilibrium state in the crystal, the major difference being the high number of lattice vacancies retained by irradiation. The number of radiation induced vacancies is considerably higher than the equilibrium number of vacancies corresponding to any temperature. This fact is responsible for the occupation of virtual sites and its associated effects, lattice expansion and static displacements.

7. Conclusion

A mechanism is postulated describing the homogeneous decrease of long range atomic ordering in A15 type compounds exposed to high energy particle irradiation. It is based on the occurrence of interstitial atoms on a nonequilibrium site, specified here as "virtual" lattice site, placed midway between two neighbouring A atoms on 6c sites (recent pair potential calculations of Welch et al.[9] have shown that the occupancy of this nonequilibrium site is energetically more favourable than a single 6c vacancy, which is found to be unstable). The most important points can be summarized as follows:

a) Virtual sites are occupied as a consequence of the vacancies (more precisely: unstable 6c vacancies) produced by the primary collision events on irradiations at temperatures below 150°C, where thermal diffusion is unlikely.

b) With the occupation of a small number of virtual sites (<0.3 %), the atomic sequence in the <102> focusing directions changes from ●ABA●ABA● to ●ABAAABA● or ●ABABABA●, depending on the occupancy of the virtual site by an A or by a B atom. This change is decisive for the occurrence of A↔B site exchanges over several interatomic distances by means of focused replacement collision sequences. This is a necessary condition for a homogeneous decrease of the atomic order parameter over the whole crystal.

c) The occurrence of the virtual site exchange mechanism is the last member of a chain of experimental arguments attributing the initial decrease of T_c in typical A15 type compounds after low temperature irradiation at low doses to a decrease of the long range order parameter, as originally proposed by Sweedler and Cox[4] in analogy to thermally induced disorder after quenching[17,18,36]. Together with additional arguments derived from high energy electron irradiation[13], this furnishes the irrevocable proof for the inefficiency of proximity effects on the decrease of T_c after low dose irradiation[6]. The latter are expected to influence T_c after heavy irradiation doses only, close to the region where T_c saturates.

d) Changes in the degree of atomic ordering in A15 type compounds do not occur by simple vacancy diffusion, regardless if produced by thermal or irradiation methods. The type of diffusion in this structure is more complex, and combines both vacancy and interstitialcy diffusion mechanisms. The occurrence of two-step and multi-step processes makes the situation very different from that encountered in bcc or fcc compounds, where only one-step processe are expected to take place.

e) The occupation of virtual sites leads to BAB and BBB sequences, the latter being exclusively encountered after low temperature irradiation. The case of BBB sequences is of particular interest if B is a nontransition element (e.g. Ge, Si,...), the distances between two B atoms in this sequence being very short, a/2. This leads to considerable repulsive forces within the B atoms of this sequence (it may be recalled that nontransition elements ordinarily do not crystallize in close packed structures, in contrast to transition elements). From the very different variation of the lattice parameter after irradiation depending if B is a transition or a nontransition element, it can thus be concluded that the repulsive forces in the sequence BBB are much stronger if the central B atom (which occupies a virtual site) is a nontransition element. By analogy, it would be expected that the static displacements would also be sensitively smaller for A15 type compounds containing a transition B element.

f) The virtual site exchange mechanism proposed here allows to establish a correlation between disordering as produced by quenching or by irradiation, the common point between both being the role of virtual sites. Their occupation is a necessary condition for diffusion processes in the A15 structure. The main difference resides in the fact that these virtual sites are still occupied after low temperature irradiation, in contrast to the quenched case, thus giving rise to the observed lattice expansion and static displacements. This would also explain why considerably lower order parameters can be obtained by low temperature irradiation than by quenching from high temperatures.

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