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Studies of Basic Problems of Metal Physics by the Use of Solid Helium*

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I. Introduction

Solid helium may not be familiar to most scientists or engineers in the field of materials science and technology, but the processes of phenomena caused by relative motion of atoms in solid helium are very similar to those in simple metals and alloys. Plastic deformation, martensitic transformation, recovery of deformed crystals, recrystallization, grain boundary migration, diffusion and precipitation, which have been studied in detail in metals and alloys, occur also in solid helium. There is no qualitative difference in atomic processes of these phenomena between metals and solid helium⁽¹⁾. Of course, solid helium has no conduction electrons, accordingly its properties affected by conduction electrons, such as electrical conductivity, differs from that of metals and alloys. The present author started the experiments on plastic deformation⁽²⁾ of solid helium about 15 years ago and has extend-

ed to the work on sound velocity⁽³⁾, ultrasonic attenuation⁽⁴⁾⁽⁵⁾, temperature dependence of pressure at a constant volume⁽⁶⁾, and X-ray topography⁽⁷⁾⁽⁸⁾ with his coworkers. Experiments on lattice defects in solid helium have been performed in Institute of Physical Problems and Institute of Solid State Physics of Academy of Sciences of the USSR, Alberta University in Canada very actively, and also studied at some institutes in USA, FRG and Japan.

The present author and his coworkers have studied solid helium with the help of the experience of the study of metal physics and also of the knowledge of metal physics which was obtained by the previous investigations. Then our results seem to be more fruitful than that of above mentioned groups. The success of our group suggests that the basic problems of metal physics may be investigated by the use of solid helium. Furthermore it is supposed that in many cases the experiments on solid helium give clearer conclusions than that on metals and alloys for the following reasons.

(1) Solid helium prepared by usual method is the purest among pure materials.

(2) There are two stable isotopes of helium, ^4He and ^3He , and it is rather easy to ob-

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tain isotropically pure helium with impurity less than 1 ppm.

(3) Both ^4He and ^3He crystallize with the bcc, hcp and fcc structures depending on the pressure and the temperature.

(4) Mixtures of ^4He and ^3He behave as simple binary alloys.

(5) Exchange of atomic positions in solid helium takes place by quantum mechanical tunneling, hence diffusion takes place at a measurable rate at any low temperatures.

This paper describes some of problems of metal physics which have been elucidated by the studies on solid helium. For convenience of description of the results, phase diagrams of helium are illustrated in the next section.

II. Phase Diagrams of Helium

There are two stable isotopes ^4He and ^3He . ^4He is extracted from natural gas. The concentration of helium in natural gas differs significantly from gas well to gas well, but the ratio of the concentration of ^3He to that of ^4He in natural gas is about 10^{-7} . Therefore, helium extracted from natural gas is high purity ^4He . Meanwhile, ^3He is obtained by decay of ^3H which was produced by (n, α) nuclear reaction of ^6Li . Commercial ^3He gas contains about 400 ppm ^4He , but it is rather easy to purify ^3He and to decrease the concentration of ^4He to be lower than 1 ppm.

1. Phase diagram of ^4He

The pressure-temperature (P - T) phase diagram of ^4He is shown in Fig. 1(a) and (b). The ordinate of (a) is proportional to $\log [P(\text{Pa}) + 10^6]$ and the abscissa is proportional to $\log [T(\text{K}) + 0.1]$ in order to express wide range of temperature and pressure. Figure 1(b) is the enlarged phase diagram of the part in (a) enclosed by broken lines and by Vignos and Fairbank⁽⁹⁾.

As seen in Fig. 1(a) the hcp structure is stable in a wide range of temperature and pressure and the bcc structure is stable in a narrow region along the melting curve around 1.6 K as shown in (b). The fcc structure is stable in a region of high temperatures above 110 MPa. There are two liquid phases, He I and He II; the former is normal liquid and the later is

Fig. 1 P - T phase diagram of ^4He . (b) is the enlarged figure of the part in (a) enclosed by broken lines and by Vignos and Fairbank⁽⁹⁾.

superfluid.

2. Phase diagram of ^3He

Figure 2 shows the phase diagram of ^3He . Solid ^3He has the bcc structure over a wide range of temperature and pressure. The phase boundaries in solid ^3He are at higher pressures in comparison with those in solid ^4He . It must be mentioned that the melting pressure of ^3He has the minimum around 0.32 K, it increases with decreasing temperature and the increase

Fig. 2 P - T phase diagram of ^3He .

at 0 K is nearly 0.5 MPa (5 atm). Liquid ^3He becomes superfluid below 2.8 mK and there are two superfluid phases A and B. There are also solid phases with different ordered arrangements of nuclear spins below about 1 mK, but these phases are not shown in Fig. 2.

3. Phase diagram of ^4He - ^3He mixture

Isotopes ^3He and ^4He do not form homogeneous solid solution at low temperatures. Helium is an only element which is known to cause phase separation between isotopes. Of course the interatomic force is the same for ^3He - ^3He , ^4He - ^4He and ^3He - ^4He pairs. However, the amplitude of zero-point vibration of He atoms is very large, especially, it is about 30 per cent of atomic distance in bcc ^3He and about 23 per cent in hcp ^4He . An atom with a larger amplitude behaves as an atom with a larger diameter, and a ^3He - ^4He mixture is regarded as a system composed of two kinds of atoms with different diameters. Figure 3 is the phase diagram of ^3He - ^4He mixture at 3.55 MPa (35 atm). It is very similar to that of binary alloys which has no intermetallic compound, and infers the following. Phase separation (precipitation) takes place at temperatures below 1.3 K in this system. Martensitic transformation between the hcp and bcc struc-

Fig. 3 T - C phase diagram of ^4He - ^3He mixture at 3.355 MPa (35 atm). Open circles were measured by Edwards *et al.*⁽¹⁰⁾, filled triangles were measured by Panczyk *et al.*⁽¹¹⁾

tures takes place at temperatures around the phase boundary.

III. Sound Velocity and Ultrasonic Attenuation⁽³⁾

1. Dislocation vibration and sound velocity

Granato and Lücke⁽¹²⁾ have published an excellent theory of the effect of dislocations on sound velocity and ultrasonic attenuation in 1956. Their theory has been used as the standard theory of ultrasonic attenuation or internal friction to analyze experimental results for long years. However, the change in sound velocity is measurable only for the resonant vibration of dislocations under the underdamped condition. The conduction electrons in a normal metal cause a frictional force for the motion of a dislocation, which is nearly independent of temperature. The underdamped vibration of dislocations in metals in MHz region is possible only in the superconducting state and the experiment under this condition is very difficult. Meanwhile, the frictional force for the motion of dislocations in the basal plane of hcp ^4He is caused only by phonon scattering and decreases rapidly at low temperatures.

Figure 4 shows the change of sound velocity of the crystal D at 10 MHz in three runs. Imme-

Fig. 4 Temperature dependence of the velocity of 10 MHz ultrasonic wave in D-crystal by Iwasa *et al.*⁽³⁾

diately after the completion of the crystal growth, the temperature was lowered down to 0.25 K and the data (run D-2) were taken during warming the crystal. The temperature was lowered again from 1.7 K to 0.25 K and then the second run (D-4) was started. By comparing the run D-4 with the run D-2, it is seen that the velocity has been increased, especially below 1 K. When the crystal was further annealed by repeated heating and cooling, the velocity again decreased (run D-28). The change in the anomalous temperature dependence of the same crystal by the cyclic heating implies that it is not intrinsic property of the crystal.

Wanner *et al.*⁽¹³⁾ derived the temperature dependence of sound velocity of a crystalline solid at low temperatures, which is given by

$$v = v_0(1 + aT^4 + bT^6). \quad (1)$$

Here a and b are constants which satisfy relations $a > 0$, $|b| \ll |a|$, v_0 is the sound velocity at 0 K, T the absolute temperature. The curve in Fig. 4 was calculated by eq. (1).

Experimental results on anomalous temperature dependence of sound velocity shown in Fig. 4 were compared with Granato-Lücke theory, and we obtained the average length of vibrating dislocations, L , dislocation density, Λ , the damping constant for dislocation motion, B . Iwasa *et al.*⁽⁶⁾ showed that $L \approx 3 \times 10^{-6}$ m, $\Lambda \approx 10^{10} \text{ m}^{-2}$ and $B \approx 3 \times 10^{-7} T^3$ cgs. The magnitude of B agrees with the calculated value of the frictional force caused by phonon scattering.

In metals, frictional force for the motion of a dislocation by the scattering of conduction electrons is significantly large at low temperatures. Therefore, it is difficult to know the contribution of phonon scattering to the frictional force from the measured values of B . The experimental results in hcp ^4He clearly show that the Ninomiya's result⁽¹⁴⁾ based on fluttering mechanism is most appropriate. And also quantitative experiments, to which Granato-Lücke theory of change in sound velocity is successfully applied, are performed only on solid helium.

2. Interaction between a dislocation and isotope impurity atoms⁽⁴⁾

A ^3He atom in hcp ^4He has a larger amplitude of zero-point vibration than that of ^4He atoms, therefore it pushes away surrounding atoms. For this reason ^3He atoms in solid ^4He interact with dislocations in the same manner as impurity atoms with large atomic radii, and pin the dislocations. Figure 5 shows temperature dependence of sound velocity of hcp ^4He crystal containing 1 at. % ^3He measured at frequencies 10, 30 and 50 MHz. Curves in this figure are calculated by eq. (1). There is no anomalous temperature dependence due to vibration of dislocations. This result strongly supports the idea that the anomalous temperature dependence of sound velocity is caused by vibration of dislocations.

Figure 6 shows the ultrasonic attenuation of hcp ^4He crystals, containing very small amounts of ^3He atoms, as functions of input ultrasonic amplitude. It is seen that the amplitude dependence is negligible above 1.2 K, but it becomes substantial below 0.3 K. The increase of attenuation is due to the motion of

Fig. 5 Temperature dependence of sound velocity in hcp ^4He crystal containing 1 at.% ^3He . The same curve was obtained for the frequency of sound waves of 10, 30, 50 MHz by Iwasa and Suzuki⁽⁴⁾.

Fig. 6 Amplitude dependence of the attenuation at 10 MHz in crystal No. 8 at various temperatures. Open and Solid circles are obtained by increasing and decreasing the amplitude. (Iwasa and Suzuki⁽⁴⁾).

dislocations which were pinned by ^3He atoms. The minimum input amplitude I_c , at which attenuation by dislocations is observed, corresponds to the force required to break away a dislocation from its locked site. Since the diffusion rate of ^3He atoms is independent of temperature at low temperatures, a dislocation is locked by an atmosphere of ^3He atoms in equilibrium at the temperature of measurement. The interaction energy between a dislocation and isotope impurities is then obtained, from the temperature dependence of the critical amplitude, to be 0.3 K.

3. Precipitation of isotope impurities and creation of dislocations⁽⁵⁾

Amplitude dependence of ultrasonic attenuation was measured on bcc ^3He crystals grown from commercial ^3He gas, which contains about 500 ppm ^4He atoms. Figure 7 is an example of the measurements. The attenuation is very small and almost independent of the amplitude at 114 mK, but at 77 mK the attenuation increases rapidly as the amplitude exceeds a critical value provided that the crystal was steadily cooled. Then we measured the attenuation in the course of stepwise heating, and obtained the amplitude dependent attenuation even at 200 mK as shown in Fig. 8. The attenuation remains the same even at 200 mK, but

Fig. 7 Attenuation at 10 MHz versus I in crystal No. 8 at two temperatures above and below T_A on a cooling run. (Iwasa, Saito and Suzuki⁽⁵⁾).

Fig. 8 Attenuation at 10 MHz versus I in crystal No. 1 on a warming run. (Iwasa, Saito and Suzuki⁽⁵⁾).

decreases rapidly around 300 mK and almost disappears at 350 mK. Figure 9 shows the temperature dependence of attenuation for the amplitude 50 dB, at which the attenuation is very large and nearly saturated, and for the amplitude 20 dB, at which the attenuation is not observed, at the lowest temperature. Then it is supposed that the attenuation is caused by the structural change around 100 mK and the structural change remains until the crystal is heated up to 300 mK. Of course the structural change must cause the ultrasonic attenuation.

It is natural to suppose that the structural change is related to the precipitation of nearly pure ^4He particles from the phase diagram of Fig. 3. The solubility limit of ^4He in bcc ^3He shown in Fig. 3 fits to that calculated by the regular solution theory. Hence we extrapolate the solubility limit by the help of regular solution theory to very low concentration region as shown in Fig. 10 and compared it with the critical temperature of the rapid increase of attenuation during the cooling process. It is easily seen in this figure that the attenuation increases at temperatures nearly 10 mK below the solubility limit. Therefore, it is reasonable to conclude that the ultrasonic attenuation is

Fig. 9 (50 dB) and (20 dB) at 10 MHz in crystal No. 19. Runs 1 and 3 are cooling runs, and run 2 is a warming run. (Iwasa, Saito and Suzuki⁽⁵⁾).

Fig. 10 Phase separation temperature versus x^4 . The curve represents T_{PS} calculated from eq. (1). (Iwasa, Saito and Suzuki⁽⁵⁾).

caused by dislocations which are nucleated around precipitates with a certain size, because the specific volume of the precipitates is nearly 20% smaller than that of matrix and the dislocations do not disappear simultaneously with the precipitates during the heating process. Multiplied dislocations contribute to the ultrasonic attenuation until they disappear by pair annihilation through the flow of vacancies.

4. Zero-point vibration and tunneling of dislocations^{(5),(15)}

It is known from the experiment of plastic deformation of bcc ^3He that the Peierls stress of this crystal is about

$$\tau_P = 3 \times 10^{-4} \mu \quad (2)$$

where μ is the shear modulus. The Peierls stress τ_P for a screw dislocation in bcc metals is $2-7 \times 10^{-3} \mu$, consequently the Peierls stress in bcc ^3He is about one order of magnitude lower than that in bcc metals. However, according to the calculation of the effect of the zero-point vibration in the Peierls potential field, the Peierls stress of bcc ^3He decreases to 1/16 of its classical value, while that of bcc transition metals decreases by a few per cent of its classical value⁽¹⁶⁾. Therefore the classical value of the Peierls stress in bcc ^3He is nearly the same as that in bcc transition metals.

In the temperature range, where the flow stress is affected by the Peierls stress, the flow stress increases rapidly with decreasing temperature, because the dislocation must overcome the Peierls potential by thermally activated nucleation of kink pairs. At very low temperatures this process may take place by quantum mechanical tunneling at a higher rate than that of thermal activation. Let us suppose that under the applied stress τ^* the frequency of tunneling becomes to be equal to that of thermal activation at a temperature T^* . At temperatures below T^* the yield stress is τ^* irrespective of temperature as shown in Fig. 11. The critical amplitude I_c in Fig. 7 is proportional to the stress required to move a dislocation. As shown in Fig. 9, I_c is independent of temperature, therefore it is concluded that a dislocation in bcc ^3He moves by tunneling at least below 190 mK. The magnitude of I_c is converted into the maximum stress in the crystal and we have $\tau^*/\mu = 5 \times 10^{-5}$, hence $\tau^*/\tau_P = 1/6$.

There is no reliable measurement of τ^*/τ_P for metals. The value for ionic crystals with the NaCl structure are already obtained⁽¹⁷⁾, and the smallest value is for LiH to be 0.7–0.8⁽¹⁸⁾. Theoretical estimation, which agrees with the experiments on ionic crystals predicts that tunnel-

Fig. 11 Temperature dependence of the yield point. See text.

ing of screw dislocations through the Peierls potential takes place below 1 K in any bcc metals.

IV. X-ray Topography

1. Characteristics of X-ray topography

X-ray topography indicates small local distortion of lattice plane by contrast in the image pattern in a Laue spot, so we can't see enlarged image directly. The images are enlarged from patterns recorded on plates, and the magnification is usually of the order of one hundred times. However, the sensitivity to the distortion is very high, and it is suited to detect lattice defects which are created at a few places in a macroscopic crystals. Therefore, X-ray topography is a complementary method to the high resolution electron microscopy. The thickness of the specimen for X-ray topography is far thicker than that for transmission electron microscopy. Especially we can use a helium crystal several cm in thickness, which is really macroscopic size.

Until recently, X-ray topography requires a very long exposure time more than a few hours and is applied only to crystals of high perfection. However, in recent years we can use synchrotron radiation of the photon factory of National Laboratory of High Energy Physics in Tsukuba, which decreases the exposure time to the order of a second. In solid helium the X-ray scattering cross section by an atom is very small and the extinction distance is of the order

Fig. 12 Schematic figure of X-ray topography.

of a few mm. Hence the dislocation contrast is caused by a different mechanism from usual one and the dislocation image is very faint but very thin compared with those in usual materials. Then we can observe dislocations in imperfect solid helium. Therefore, now difficulties in X-ray topography are removed if we use solid helium.

Figure 12 shows the principle of X-ray topography by synchrotron radiation schematically. X-rays are emitted from 2.5 GeV electron beam with thickness of 0.1 mm irradiate specimen passing a slit of $0.1 \times 6.5 \text{ mm}^2$ or $0.017 \times 6.5 \text{ mm}^2$. The Laue spots of helium crystal by the X-rays are recorded on a nuclear plate behind the cryostat. One of the Laue spot is magnified by an optical microscope. The reason to use an X-ray beam with a wide and thin cross section is to increase the contrast of the image of each lattice defect and to observe wide area of cross section of the crystal.

2. Observed results⁽⁷⁾⁽⁸⁾

By the above mentioned method we observed the crystal growth of ^4He , the relaxation process of internal strain and martensitic transformation between the hcp and bcc structures⁽⁷⁾. Recently we succeeded to observe individual dislocations⁽⁸⁾. Figure 13 shows successive changes of the topograph, 21 $\bar{3}$ 4 reflection of the initial hcp crystal. (a) is just after the crystal growth, (b) after anneal for 780 second. In these two photographs thick zones of white or black are nearly the same, but some parts of

Fig. 13 Successive change of the section topograph, reflection 21 $\bar{3}$ 4 of initial hcp crystal; (a) $p=35.6 \text{ atm}$, $T=1.30 \text{ K}$, (b) $p=30 \text{ atm}$, $T=1.58 \text{ K}$, (c) $p=28 \text{ atm}$, $T=1.62 \text{ K}$. (d) $p=31 \text{ atm}$, $T=1.6 \text{ K}$. (Suzuki, Iwasa and Nakajima⁽⁸⁾).

thin zones differ from each other. These zones represent small angle boundaries and the width of a zone is proportional to the misorientation at the boundary, and the maximum misorientation is of the order of 0.1 degree.

Another important image is the blurred and

whitish regions as lettered by S. The contrast of these region decreases or disappears by annealing without any change in surrounding region. These images are interpreted by high density of dislocations multiplied by nonequilibrium vacancies. Highly magnified photograph of these region shows that images of many helical or tangled dislocations are superposed.

The photograph (c) is 201 reflection of bcc crystal appeared at the same position with $2\bar{1}\bar{3}4$ reflection of the initial hcp crystal. There are many small angle boundaries but the misorientation between two neighboring crystallites is less than 1 degree. There are three possible bcc planes converted from the $(2\bar{1}\bar{3}4)$ hcp atomic plane, but the topograph shows that the whole hcp crystal converted into the same orientation and the $(2\bar{1}\bar{3}4)$ hcp plane converted to the nearly undistorted (201) plane of the bcc structure. Owing to the strain caused by the transformation from the hcp structure into the bcc structure, a martensite grows to a shape of a thin plate and stop the growth, provided there is no slip or twinning to relax the internal stress. However if slip takes place to relax the internal stress, the martensite continues the growth in the direction of thickness⁽¹⁹⁾. Since the vacancies in solid helium is very mobile, multiplied dislocations climb rapidly and annihilate, then only the remained dislocations form subboundaries.

The topograph (d) shows the structure as the reverse transformation from the bcc into hcp structures took place partially. Subboundaries formed by the previous transformation prohibited continuous growth of a hcp crystal or assisted independent nucleations of hcp crystal. Then each crystallite was strongly distorted.

3. Future investigations

As mentioned in previous sections, informations obtained by the studies on solid helium are useful for the investigation on basic problems of metal physics. Though X-ray topography of solid helium is just started, it seems to be most useful. Especially it is most suitable to observe initiation of phenomena, which start from a point in a macroscopic size

of crystal and propagate over the whole of the crystal, such as slip, martensitic transformation, etc. This kind of phenomena are important problems of metal physics, and have been observed mainly by transmission electron microscopy (TEM). We can observe the lattice image by TEM, it is most important in the observation of microstructure in a small region. Its importance does not decrease in future, but it is difficult to observe all parts of a macroscopic crystal.

We can observe the whole volume of a large crystal by X-ray topography, but for metallic samples, we must use thin specimens or reflections from the thin surface. However if we use helium, we can observe the defect structure in a crystal with macroscopic scale as thick as several centimeters and also reconstruct three dimensional structure of lattice defects from many number of topographs of thin parallel zones of solid helium.

V. Conclusions

Plastic deformation, martensitic transformation, recovery of deformed sample, recrystallization, grain boundary migration, diffusion and precipitation, which have been investigated extensively in metals and alloys, occur also in solid helium. The results obtained by measurements of plastic deformation, ultrasonic attenuation, X-ray topography etc. of solid helium contributed to give deeper understanding of these phenomena in metals and alloys. Among these investigations X-ray topography, which is just started, seems to be most promising for the investigation of these basic problems in metal physics. We may be able to observe *in situ* the three dimensional structure of lattice defects by X-ray topography of solid helium. In metals the study of the three dimensional microstructure of macroscopic size is very difficult and requires laborious efforts, so the investigations in this direction using solid helium is quite useful.

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