

The Anomalous Temperatures of Cu and Their Physical Significance. (II, 3)

著者	SATO Mitsuru
journal or publication title	Science reports of the Research Institutes, Tohoku University. Ser. A, Physics, chemistry and metallurgy
volume	3
page range	661-686
year	1951
URL	http://hdl.handle.net/10097/26470

The Anomalous Temperatures of Cu and Their Physical Significance. (II, 3)*

Mitsuru SATO

The Research Institute for Iron, Steel and Other Metals

(Received September 15, 1951)

Synopsis

The experimental evidences concerning anomalous changes of various properties of Cu, with temperature, were studied in literature, and it was found that four anomalous temperatures, including the melting point, exist, the values being 503°, 553°, 823° and 1356°K (mp), and that in these temperatures and the absolute zero, there exists a regularity as shown in the following table where the numbers in parentheses show the ratios of the intervals between the adjacent temperatures in each group. This regularity was understood by the writer to be identical, in nature, with Landé's interval rule in atomic spectra in the case of odd multiplicity, and, accordingly, it was inferred that the temperatures in each of the groups, II and I, would correspond to the components of the fine structures of the energy levels, E_1 and E_2 , respectively. These levels, as well as E_3 and E_4 had been determined from experimental data, as those associated with the valence electron, their energy positions being in the order of E_1 , E_2 , E_3 and E_4 . Further, it was considered that each of E_1 and E_2 is associated with two electrons and two atoms, hence, they may be denoted as,

Group	Anomalous temperature (°K)				
I	0	(3)	503	(2)	823
II	0	(2)	553	(3)	1356

$$E_1 : (A_1, B_1) \ ^3D_{1,2,3} \quad E_2 : (A_2, B_2) \ ^3D_{3,2,1}$$

where A_1, B_1 and A_2, B_2 denote two pairs of atoms which associate respectively with the levels, E_1 and E_2 , forming the diatomic molecules, (A_1, B_1) and (A_2, B_2) . Concerning E_3 and E_4 , it was assumed that, as in the case of Zn, there exist two groups of anomalies in low temperature range, which show the multiple structures of E_3 and E_4 , respectively. Further it was assumed that the electrons associating with E_3 and E_4 are identical with those which associate to E_1 and E_2 , respectively, and they oscillate between E_1 and E_3 , E_2 and E_4 , respectively. Furthermore, that these oscillations take place, in resonance, in the group of the above molecules of the same kind, and, accordingly the molecules in the above group are bound mutually by the energy of the resonance exchange. On the other hand, it was proved previously that, when the electron is in E_3 or E_4 , it plays the role of electric conduction, but, in E_1 or E_2 , it binds the atoms firmly, and so, with the above idea the important properties of metals were explained consistently.

I. Introduction

In his previous paper on Zn,⁽¹⁾ the present writer studied closely in literature the experimental evidences concerning anomalous changes of various properties of Zn with temperature, in solid as well as in molten state; and it was concluded that there are, at least, eleven anomalies, and that they can be classified into four

* The 655th report of the Research Institute for Iron, Steel and Other Metals.

(1) M. Satô, Sci. Rep. 27 (1939), 278.

groups as shown in Table 1. That is, if we take the absolute zero as belonging to each of the groups, then each of them excepting the last, consists of odd anomalies and the temperature intervals between the adjacent ones in each are

Table 1. Anomalous temperatures of Zn, the number in parenthesis being interval ratio.

Group	Anomalous temperatures ($^{\circ}\text{K}$)								
I	0	(5)	247	(4)	443	(3)	593	(2)	692(mp)
II	0	(4)	473	(3)	823	(2)	1069	(1)	1178
III	0	(2)	36	(3)	90				
IV	0		?		0.79	(trans. pt. of spra-cond.)			

in the ratio of a sequence of simple natural numbers. For the last group in whose range of temperature Zn is in spra-conductive state, we had no evidence supporting the validity of the above rule. But it became very expectable to be so from the investigation of W. J. De Haas and A. Rademakers⁽²⁾ who measured the thermal resistances of lead in spra as well as in nonspra-state, over the same range of temperature, and obtained the result shown in Fig. 1. From this figure, it is seen

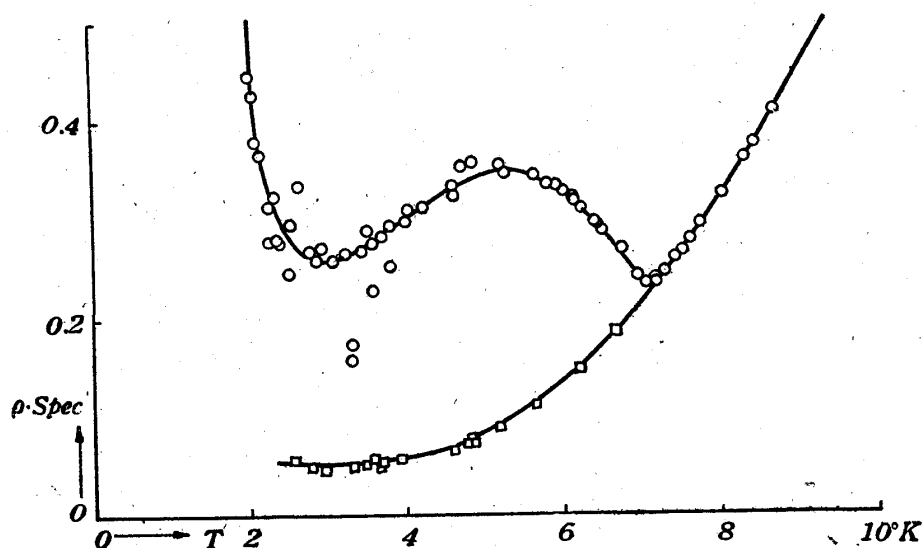


Fig. 1. Specific heat resistance vs. temperature curves for Pb in spra (○) and nonspra (□) conductive state: taken from W. J. De Haas and A. Rademakers, *Physica* 7 (1940), 992.

that the thermal resistance of lead in spraconductive state, gives two minima at the temperatures, 7.2°K (transition point) and about 3°K , respectively, and the intervals, as above considered, are in the ratio of 3:4, satisfying the above rule.

Now, since the temperature may be taken as a measure of a kind of energy, so, in his subsequent paper,⁽³⁾ the above regularity was taken by him as to be the identical in nature with Landé's interval rule in the case of odd multiplicity in atomic spectra. Accordingly, the anomalous temperatures, including 0°K , in the groups I, II, III and IV, respectively represent the components of the multiple

(2) W. J. De Haas and A. Rademakers, *Physica* 7 (1940), 992.

(3) M. Satô, *Sci. Rep.* 28 (1939), 143.

structures of the energy levels, E_2 , E_1 , E_3 and E_4 , whose existence and their relative positions had been determined from X-ray spectrum⁽⁴⁾ and confirmed from photoelectric effect and others.⁽⁵⁾ For the above correspondence, it was assumed that when the level is lower in energy, its total separation is larger. Further, it was inferred that, since the above rule in atomic spectra is explained as having resulted from the Russel-Saunders coupling of optical electrons, so, in the present case, each of the energy levels, E_1 , E_2 , E_3 and E_4 , is formed by valence electrons in the same way as above; and from the numerical values of the interval ratio in Table 1, we have $S=2$, $L=2$, and $S=2$, $L=3$ for E_1 and E_2 , respectively; accordingly, the fine structures of E_1 and E_2 may be represented respectively as

$${}^5D_{1,3,2,1,0} \quad \text{and} \quad {}^5F_{5,4,3,2,1}$$

where the suffix showing the value of J is written in order of the energy position from the lowest. Similarly for E_3 , $S=1$, $L=2$ or $S=2$, $L=1$, but by the reason which will be given below, it was taken that the latter is more probable, hence the fine structure of E_3 may be represented as

$${}^5P_{1,2,3}$$

the suffix being written in the same way as described above. Concerning the structure of E_4 , there is no direct evidence, but it was supposed to be $S=2$, by the same reason as above.

As the result of the above investigation, we obtained for each of the levels, $E_1 \sim E_4$, $S=2$; hence it was inferred that, at least, four electrons have to associate with each of the above levels. But more than two of valence electrons do not belong to an atom of Zn, provided that the electron in the inner shell is excited to behave as the valence electron, and the latter case is very unlikely to occur. Therefore, it was inferred that to each of the levels, $E_1 \sim E_4$, belong, at least, two Zn-atoms; and assuming that the simplest is the case in reality, it was taken as that each of the levels, $E_1 \sim E_4$, is formed by two Zn-atoms. In other words, Zn-atoms in their condensed state, form diatomic molecules, in general, the binding energy being that of the coupling of the four valence electrons in Russel-Saunders type.

The result obtained above differs entirely from the prevailing idea concerning the electronic structure of a metal in its condensed state, but a remark was made there that the above result might easily be expected from the following experimental evidence. Namely, it is spectroscopically observed that Zn-atoms, even in the vaporous state, combine, though partially, to the diatomic molecule, when it is sufficiently dense. Hence, it is highly probable that, most of Zn-atoms in condensed state combine to molecules, at least, of the diatomic. Further, if really so, it is very expectable that the electrons forming the above diatomic molecule are in the coupling of Russel-Saunders type. This expectation comes from the feature of the coupling of the quantum vectors in a free Zn_2 -molecule, and, though it was not known directly, but it was expectable to be,

(4) M. Satô, Sci. Rep. Honda Anniv. Vol. (1936), 136.

(5) M. Satô, Sci. Rep. 25 (1936), 771.

$$\{ [(\sum \vec{l}) \vec{S}] \text{rot} \}$$

in the usual notation, as suggested by W. Weizel.⁽⁶⁾ Hence, it may be said that the former expectation is also very reasonable.

Next, he proceeded to explain the mechanism of the intermolecular binding in constructing the crystal as follows:

On the basis of an experimental evidence, though it is not so reliable, it was supposed that both of the energy levels, E_2 and E_3 are formed by four common electrons belonging to a molecule which was designated as (A_2, B_2) ; consequently, at least, one of the above four electrons, must be in different energy states in forming different energy levels; but, since no electron can be in the different states at the same time, so it was natural to suppose that, at least, one of the above four electrons is in oscillation between the above two levels, this being denoted as $E_2 \rightleftharpoons E_3$. Further, in order to be sustained from damping, the above oscillation is naturally to be expected to take place in resonance with a neighbour of the same kind in the manner which may be denoted as $E_2 \rightleftharpoons E_3, E_2 \leftrightarrow E_3$. Accordingly, these two molecules must be bound by the energy of resonance exchange of the electrons. Moreover, such a resonating oscillation can take place in a group of molecules, all of them being of the same kind, (A_2, B_2) , and, accordingly, these molecules are bound. Similarly, it was taken that, the molecules of the other kind, (A_1, B_1) , are bound mutually by the resonating oscillation, $E_1 \rightleftharpoons E_4, E_1 \leftrightarrow E_4$. Thus the intermolecular action, under consideration, was explained attributing to the resonating oscillation, and it seems that the characteristic mechanical properties of metals, such as toughness, can be well explained from the above idea; and not only that but it is in harmony with the interpretations which were given by the writer⁽⁷⁾ to the phenomenon of the electric conduction of metals and that of photoelectric effect.

Now, in the above oscillations, the electron transitions between E_1 and E_4 and E_2 and E_3 take place constantly, and it is presumable that the selectivity, $\Delta S=0$, which widely holds in the combination of the atomic terms, is valid also in the present case. This is the reason that S for E_3 and E_4 was determined above as 2.

Finally, the energy state of the individual electron in the levels E_1, E_2 and E_3 was considered. For this, he analysed the experimental result given by M. Straumanis⁽⁹⁾ who measured the electrode potentials for the surfaces, (0001), (10 $\bar{1}$ 0), (11 $\bar{2}$ 0), (10 $\bar{1}$ 1) and (11 $\bar{2}$ 1) of Zn-single crystal. On the basis of the regularity which was taken by him to exist in the above values, it was inferred that E_2 is formed by the electrons in the states, (4s, 4p) and (4 or 5s, 4d)*, and that the two electrons in E_3 are in the state (4s, 5p). Accordingly, it was designated as

(6) W. Weizel, Bandenspektren (Handbuch exp. Phys. Erg. Bd. 1.) (1931), 102, 109.

(7) M. Satô, Sci. Rep. RITU, 2 (1950), 725.

(8) M. Satô, Sci. Rep. 25 (1937), 829.

(9) M. Straumanis, Zeits. phys. Chem., A 147 (1930), 161.

* In the former paper⁽³⁾ it was written as (4s, 4d), but it must be corrected as above.

$$E_2: (4s, 4p)(5s, 4d) \ ^5F_{5,4,3,2,1}^{**}$$

$$E_3: (4s, 5p)(n_1s, n_2d) \ ^5P_{1,2,3}$$

Since E_1 is lower in energy than E_2 , it was determined as

$$E_1: (4s, 4p)(5s, 4p) \ ^5D_{4,3,2,1,0}$$

Thus, we have reproduced above the main result of the previous investigation on the anomalous temperature of Zn, and briefly that which was inferred from the former. Now it is very expectable that, the similar fact will be found in the case of Cu, and further that the similar inference is possible also in the latter case. So, in the following the investigation on the entitled subject will be carried out in the light of the findings described above.

II. Experimental evidences

In this section the change of various properties of Cu with temperature was closely studied in literature.

1. Specific heat and electric resistance

A. Seikichi Satô⁽¹⁰⁾ measured the heat evolution of cold-worked Cu and others, for the purpose of obtaining the strained energy stored in the above materials. The test piece was a circular bar which was previously twisted to give torsional strain, the degree of the cold-work being given by the twisted angle, θ . The method of measurement was analogous to that which was devised by C. Sykes⁽¹¹⁾ and is well known by his name; the rate of heating was 5°C per minute. The result of measurement on Cu is shown in Fig. 2. From this figure it is seen that a maximum appears in heating, and the temperature corresponding to the peak was given by him as shown in Table 2. It is also seen that on the low temperature side of the above maximum, a flat maximum seems to exist but it is impossible to determine the corresponding temperature; also on the high temperature side, though very faint, a maximum seems to exist. Thus, in all, there are three maxima, and they will be called the first, second and third maximum, respectively, from the lowest.

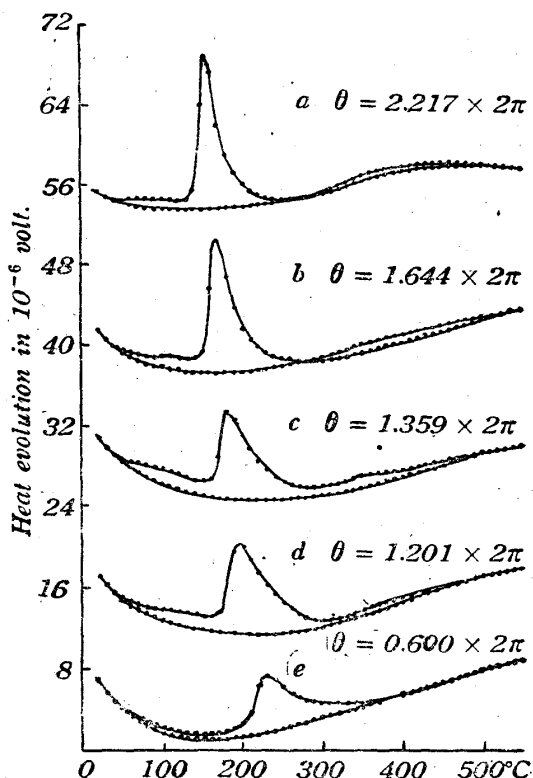


Fig. 2. Heat evolutions vs. temperature curves for cold-worked Cu by torsion: Taken from seikichi Satô, Sci. Rep. 20 (1931), 140.

** $(4s, 4p)(4s, 4d)^5F_{5,4,3,2,1}$ in (3) is to be corrected as above.

(10) Seikichi Satô, Sci. Rep. 20 (1931), 140.

(11) C. Sykes and F. W. Jones, J. Inst. Met. 59 (1936), 257.

Table 2. Temperatures of maximum heat evolution of strained Cu.

Specimen	a	b	c	d	e
Temperature (°C)	155	165	180	195	230
θ (2π unit)	2.217	1.644	1.359	1.201	0.690

As generally accepted, the evolution of heat in the present case is due to the release of the internal stress; expressing in atomistic term, it is the conversion of the potential energy stored between Cu atoms into that of their thermal vibrations, hence, it may be said roughly that the number of atoms which are released from stress per unit time is maximum at the temperature corresponding to the peak in the heating curve in Fig. 2. But there is a very important problem with regard to the cause of the release stated above; of course, it is not questionable that the ultimate cause of this phenomenon is the thermal motion of the atom, speaking more rigorously, the atom-core excluding the valence electron which binds it with its neighbours. But, it must be questioned further that whether this is the sufficient or not, that is, some more is in need for the occurrence of the above phenomenon. If the former is true, it is probably very difficult to explain satisfactorily the appearance of the maximum, especially from the viewpoint of atom physics, because the energy as well as the frequency of the thermal vibration of the atom increase monotonously with the rise of temperature. Hence, there must exist, at least, a secondary cause for the above phenomenon; and if we remember that the atom-cores are bound mutually by the valence electron, the cause stated above must be considered to exist in the energy state of this electron. From this point of view, the explanation of the above phenomenon may be given as follows:

First, we consider an atom-core within the strained specimen at the room temperature. The forces acting upon it must be in an equilibrium when it is situated at the centre of the thermal vibration. The forces, stated above may be considered to consist, ultimately, of Coulomb's, electric as well as magnetic, and the exchange of the valence electron which binds the above atom-core with its neighbours. As a matter of fact, the magnitudes, the directions and even the senses of the above forces may differ according to the degree and the feature of the strain around the above atom-core. Further, the exchange force considered above changes discontinuously, in general with the change of the quantum state of the electron under consideration.

We consider further the case where the temperature is raised at a moderate rate. The energy of the thermal vibration of the atom-core above considered increases also gradually in macroscopic sense, and the forces mentioned above change also continuously, and accordingly its equilibrium position may be shifted gradually. But, when the above energy attains such a value as is suitable to disturb the motion of the electron under consideration, its quantum state may be changed discontinuously. Accordingly the equilibrium of the above forces may be broken down, suddenly; consequently, the centre of the vibration of the

atom-core under consideration may be shifted to the new equilibrium position. Therefore, in short, the secondary cause stated above is the electronic transition, which is caused by the thermal vibration of the atom-core.

Now, as seen from Fig. 2, the position of the temperature range in which the heat evolves is shifted, as a whole, towards high temperature side with the decrease of the degree of the cold-work; and this means that the temperature at which the electronic transition considered above occurs, rises with the decrease of the degree of the cold-work. From this fact it may be inferred that even in a single specimen the strain is not uniform and, accordingly, the release from the stress does not take place at a definite temperature, but in a certain range, the releasing temperature being higher in the region which is less strained. Expressing in atomistic term, the temperature for the transition stated above rises with the decrease of the stress (the forces), acting upon the atom-core, with which the electron, under consideration, is associated. From the above consideration it may be said roughly that at the temperature corresponding to the peak in Fig. 2, the occurrence of the above transition is most abundant, and hence this temperature may be taken as the "transition temperature" corresponding to the degree of the cold-work which is assigned to the specimen under consideration. Thus, it may be concluded that the transition temperature rises with the decrease of the degree of the cold-work assigned to the specimen. This temperature for the perfectly annealed specimen can be determined by the method of extrapolation from the numerical values in Table 2. In fact, omitting the first value in Table 2, it was done as shown in Fig. 3, and obtained the value, 280°C.

Here it may be worthy to remark that in the case of the specimen described above, the heat evolution coming from the release of the internal stress must be zero, but, this notwithstanding, the electron transition described above, must occur, if our conception concerning the

secondary cause for the release of the internal stress is correct. Further, if it is really so, the temperature at which the above transition occurs must be confined in a very narrow range as seen in the case of the transition of spraconduction, because, according to the idea entertained by the present writer, the cause of the latter phenomenon is to be found also in the electron transition which is identical in nature with the one considered above.

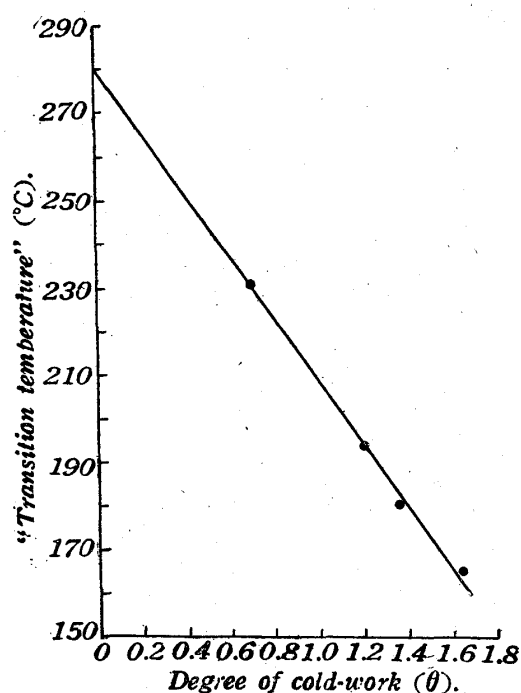


Fig. 3. "Transition temperature" vs. degree of cold-work curve.

B. Taira Suzuki⁽¹²⁾ measured the true specific heat of cold-worked Cu by modified Syke's method for the same purpose as above. In the present investigation the cold-work was given by compression, and the rate of heating was 2°C per minute.

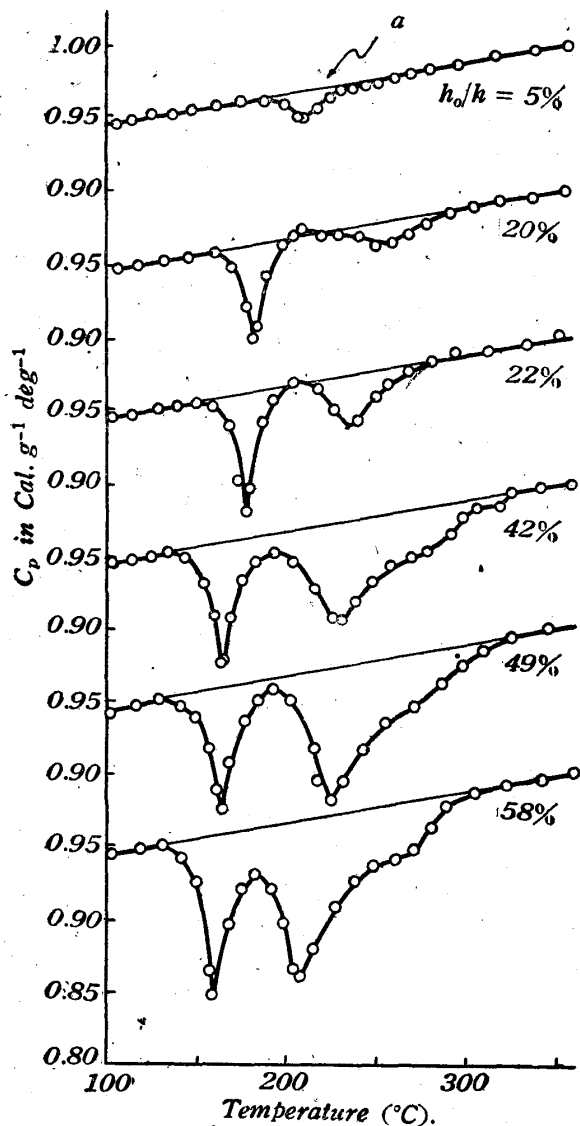


Fig. 4. Specific heats vs. temperature curves for cold-worked Cu by compression: Taken from Taira Suzuki, Sci. Rep. RITU. 1 (1949), 193.

The result of measurement is shown in Fig. 4. In this figure two minima appear prominently, except in the uppermost curve; and in the three specimens which are most severely compressed, a very weak one appears on the high temperature side of the formers. These three minima respectively correspond to the three maxima in Fig. 2. The temperatures corresponding to the minima were determined, for convenience, from the original curves which had been plotted by the experimenter on a section paper,* and obtained the values as shown in Table 3, the degree of cold-work being given by the value of h_0/h , where h and h_0 are respectively the heights of the specimen (circular rod), before and after compression.

Similarly as in the case of A, the temperature in Table 3 was plotted for the degree of cold-work, and the values for the annealed-Cu was determined to be 230°C and 280°C, as shown in Fig. 5; and the latter is in good agreement with that determined previously.

From this result it is clearly seen

Table 3. Temperatures giving minimum specific heat for compressed Cu.

Degree of cold-work (h_0/h %)	58	49	42	26	22	20	5
Anomalous temperature	162 207 Ca. 250	164 225 Ca. 270	165 230 Ca. 275	178 240 —	180 249 —	183 253 —	212 — —

(12) Taira Suzuki, Sci. Rep. RITU, 1 (1949), 193.

* The writer thanks to the present investigator for the kind permission of the use of the above figure.

that the higher one is identical with the second in the case of A; It is very remarkable and interesting that the feature of the appearance of the lower in the present case is entirely different from the first in the case of A, that is, in the previous case it is very faint, and now it is very prominent. This difference is attributable to the difference in the manner of giving the stress, namely, in the previous by twist, and in the present by compression. In a latter section a discussion on the above problem will be made. Next, it is seen from Fig. 4 that with the decrease of the cold-work, the lower minimum weakens more slowly than the higher. This fact will be also discussed later on.

C. T. Suzuki⁽¹²⁾ studied the change of the electric resistance for cold-worked Cu in heating. In the present experiment the Cu-wire which is previously annealed well was stretched up to be

$l_0/l\% = 49\%$ where l_0 and l were the initial and the final length of the specimen, and the temperature was raised in the same rate as in the case of the specific heat. As the result of the measurement, it was found that the resistance changes slightly at about 180°C and at about 230°C ; these values are roughly in coincidence respectively with 164°C and 225°C in Table 3, of which the degree of cold-work is same as the above. From this result it is expected that when the study on the electric resistance is carried out in the similar way as in the case of the specific heat, we can have the same result as obtained above.

D. A. Avramescu⁽¹³⁾ measured the true specific heat of Cu in the temperature range, $100^\circ\sim 1,000^\circ\text{C}$. The specimen was a drawn Cu-wire of high purity and the method of measurement was as follows: A heavy direct current, about 1,200 Am in about 30 V was passed through the specimen and the temperature was raised very quickly up to its melting point; the time duration for this was less than two seconds and during this interval the terminal voltage of the specimen and the current were measured by an oscillograph. Now from the above results, the resistance of the specimen at any instant is computable; accordingly, from the result obtained previously in which the relation between the temperature and

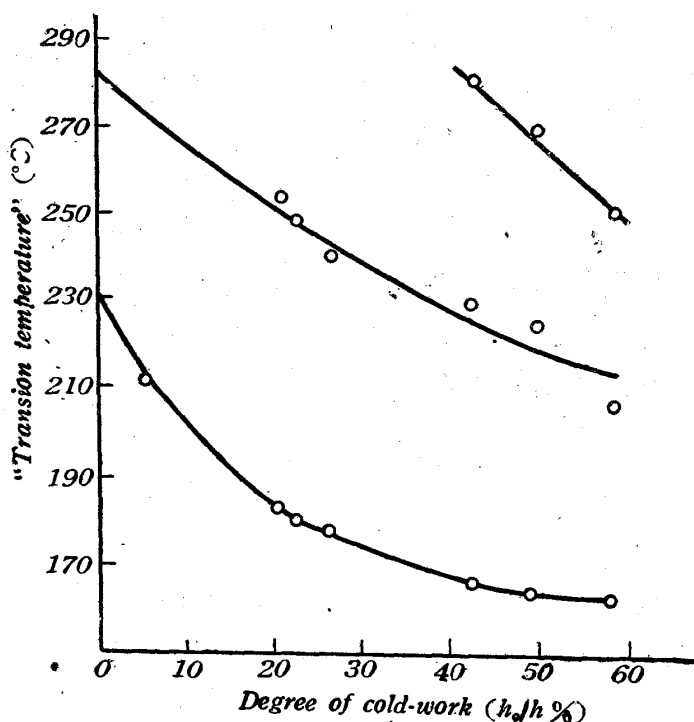


Fig. 5. "Transition temperatures" vs. degree of cold-work curve.

(13) A. Avramescu, Zeit. tech. Phys. 20 (1939), 213.

the resistance of the specimen is expressed, the temperature at a given instant within the above interval can be computable; consequently, the time rate of the temperature rise is obtainable. On the other hand, the rate of the consumption

Table 4. True specific heat of Cu, obtained by A. Avramescu
Zeit. tech. Phys. 20 (1939), 213.

Temperature (°C)	100	200	300	400	500	600	700	800	900	1,000
Specific heat Cal/g deg	0.0946	0.0972	0.0999	0.1027	0.1057	0.1089	0.1125	0.1162	0.1208	0.1265

of electric energy by the specimen at any instant is also to be known from the record of the above oscillograph; and when we combine the above two results,

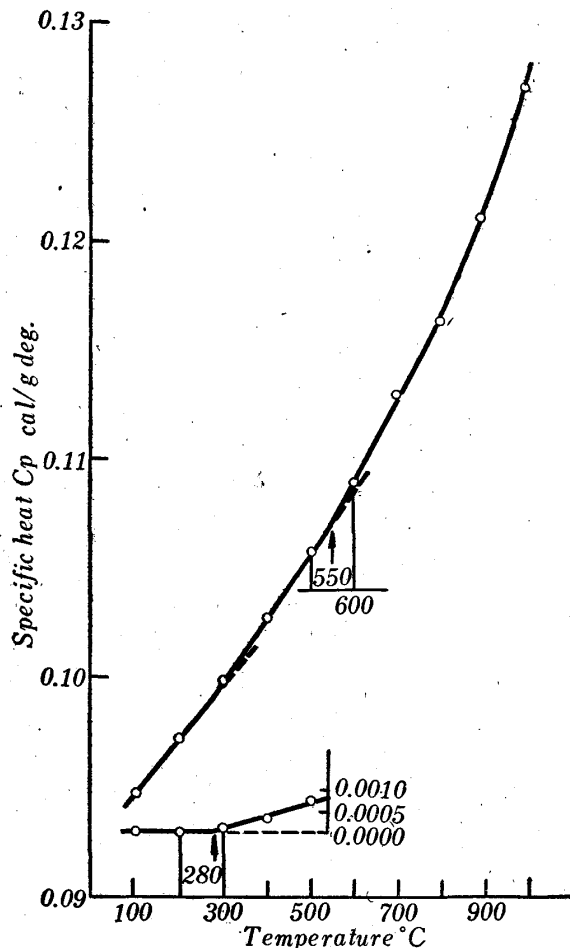


Fig. 6. Specific heat of Cu vs. temperature curve; and curve of ΔC_p (deviation from the linearity of the lowest part of the former) vs. temperature.

Further in this figure the curve was so drawn as to run upward gradually from about 800°C, departing from its linearity. This means that the energy loss which was considered above as negligibly small, became sensible at about this temperature and increased more and more with the rise of temperature.

Here a remark must be made, concerning the relation between the first anomaly

the temperature coefficient of the above energy consumption at any temperature is to be known. In this way the author obtained the true specific heat of Cu as shown in Table 4; here the energy loss by radiation, etc, was taken as to be negligibly small, because the time duration was very short. Further, the values in this table may be illustrated by the curve shown in Fig. 6. From the upper curve in this figure it is seen that the curve suddenly bends at the temperatures, 280° and 550°C, respectively; and to show the former more clearly the lower curve is affixed in which the deviation, ΔC_p from the upward elongation of the lowest part of the upper curve is plotted for the temperature.

Of the above two anomalous points the former temperature is in good agreement with the second anomalous temperature previously determined; so the latter may be taken as the third which appeared very weakly in the experiments, described in A and B.

and the third. From the result obtained above nothing can be said of the existence of the first anomaly, owing to rareness of the measured points; but from the feature of their distribution, it may be presumed that even in the case where it appears, it is probably very weak; and in spite of all these the third appears clearly as seen from Fig. 6. This is quite contrary to the result shown in Fig. 4, that is, in the latter case, the first, strongly, and the third, weakly. Such difference must be attributed to the rate of heating. When it is heated slowly, the first is strong and the third, weak, while when it is heated very quickly the first weak, and the third strong. From this it seems that the first and the third belong to the same class of anomaly, i. e., the release of the internal stress of the same kind. Therefore when the heating rate is slow, most part of it is released at the first and the rest is very small, while when quickly heated, most part is retained till the third anomalous temperature. The above finding will be discussed more fully in a latter section.

2. Diffusion and Sintering

A. Shinsuke Tanaka⁽¹⁴⁾ studied the diffusion between Cu and Au in solid state by the following method. The above two metals were electro-plated, alternately one on the other, layer by layer, and prepared a ribbon consisting of many thin layers, and its resistance was measured in heating; the result given by him is shown in Fig. 7. From this figure, it is seen that the resistance increases slowly in the initial period, and then, from 230°C according to him, very rapidly, with the rise of the temperature. His explanation for this fact is that; the first part of this curve shows that the resistances of the above metals separately increase with the rise of temperature; but, from 230°C the diffusion between Cu and Au begins to take place and, because the resistance of the alloy thus formed is higher than that when the components had existed separately, the curve runs steeper. So it may be said that the diffusion stated above commences at 230°C.

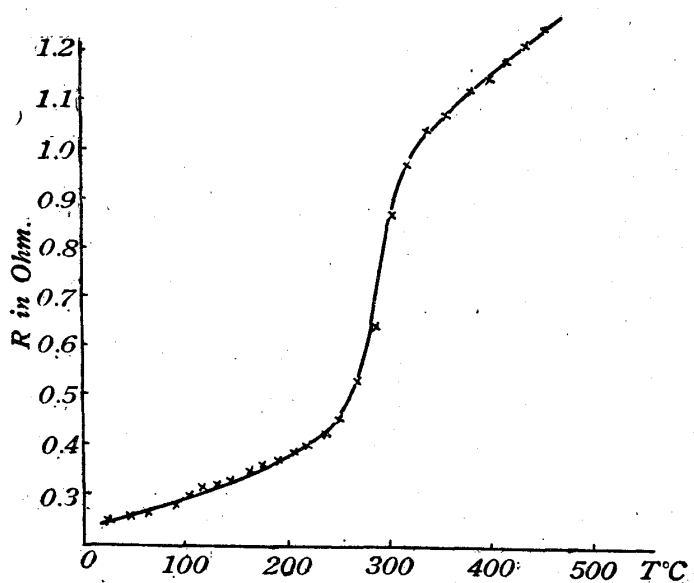


Fig. 7. Resistance vs. temperature curve: Taken from Shinsuke Tanaka, Mem. Collg. Sci. Kyôto Univ. A. 13 (1930), 343.

For the confirmation of the above inference, a further experiment was made by him as follows: the resistance of the specimen described above, was measured in various constant high temperatures, and obtained the result shown in Fig. 8.

(14) Shinsuke Tanaka, Mem. Collg. Sci. Kyôto Univ. A 13 (1930), 343.

Thus it was found that, the increasing speed of the resistance in the initial period became remarkably rapid in the temperature range, $200^{\circ}\sim 250^{\circ}\text{C}$, in which 230°C is included.

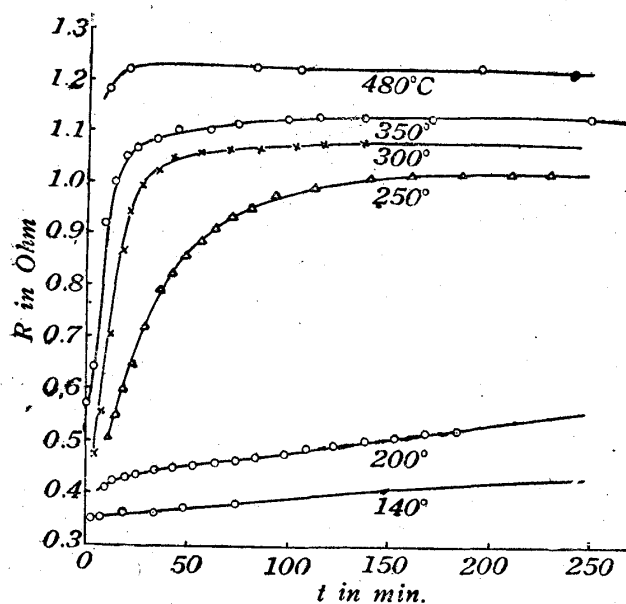


Fig. 8. Resistance vs. time curves at various constant temperatures: Taken from Shinsuke Tanaka, Mem. Collg. Sci. Kyōto Univ. A 13 (1930), 343.

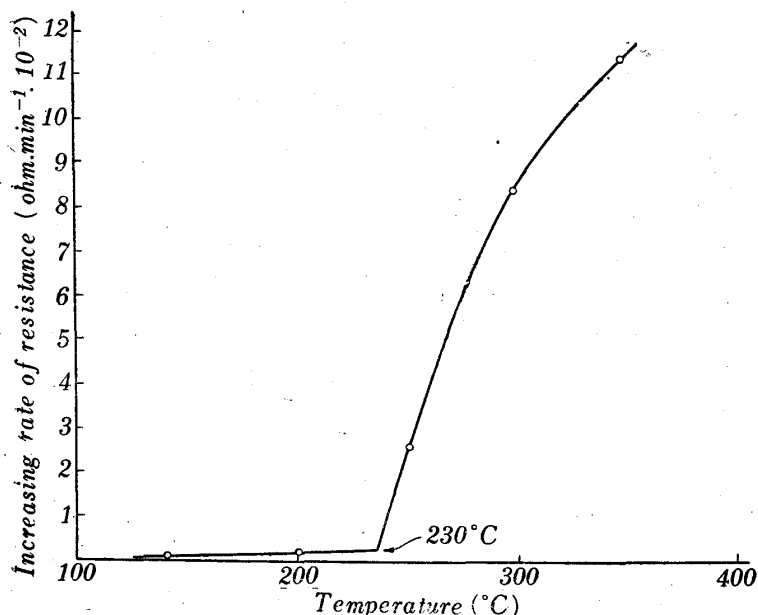


Fig. 9. Curve showing the increasing rate of resistance changes discontinuously at 230°C .

but it must necessarily be considered that a discontinuous change in the state of the valence electron, which binds the atoms of each element mentioned above, takes place at the temperature, 230°C ; in detail, there occurs an electronic transition, by the excitation of the thermal motion of the atom-core, and as a consequence of this, a discontinuous change in the force which binds the atoms in one or both of the components, Cu and Au, takes place and the diffusion under

Thus, the previous result was confirmed, but unfortunately, it was not clarified that the temperature at which the inclination of the curve in Fig. 8, changes, is 230°C . So, for this purpose the following treatment was made by the writer: from Fig. 8 the increasing rate of the resistance for each constant temperature was computed graphically, and it was plotted against the temperature as shown in Fig. 9. It shows that the temperature stated above, is 230°C , and thus the previous result was confirmed satisfactorily.

Now from the above considerations, it may be inferred that at the temperature 230°C , the diffusion of the one or both of the elements, Cu and Au, into the other, begins to take place sensibly; and it may further be taken that the diffusion commences to be appreciable rather suddenly than gradually at the above temperature. If this is the case in reality, the above phenomenon can not be explained satisfactorily only from the thermal motion of the atom, as described above in 1, A,

consideration begins. From this point of view, the above electronic transition must be the same in nature with that described above in 1, A; and further, from the fact that the above temperature is in good agreement with the lower anomalous temperature of annealed Cu, determined above in 1, B, by the method of extrapolation, it may be safely inferred that the discontinuous change, described above takes place, at least, in Cu, and, accordingly, the diffusion, at least, from Cu into Au, begins to take place at the above temperature. The fact whether the diffusion of the opposite direction also begins to take place or not at the same time, will be needless to consider in the present work.

B. Toshihiko Okamura, Yoshimichi Masuda and Sadao Kikuta⁽¹⁵⁾ studied the sintering of Cu powder by measuring the shrinkage and the breaking strength of the specimen which was previously compacted under the pressure 1, 2 or 3 t/cm² for 30 sec and then sintered at the constant temperature, 500°, 550°, 660° or 720°C. The typical isotherms of breaking strength given by them are shown in Fig. 10. In this figure it is seen that the isotherm for 500°C is approximately straight, that for 660°C S-shape and that for 550°C intermediate; that for 720°C, though omitted here, is similar to that for 660°C. To be more exact, the above second one shows that the breaking strength very rapidly increases in the period of 30~60 minutes, and it seems that this phenomenon implies a certain important thing in clarifying the mechanism of the sintering. But, from their microscopic examination it was clarified that in the above period most open pores in the specimen changed into the enclosed ones. Hence, they inferred that the isotherm of breaking strength mainly represents the binding condition rather than the substantial process of sintering.

It may be so, but we think the origin which makes the above condition is to be found in the sintering itself; it may be said therefore that the shape of the above diagram is an indicator showing the intensity of the sintering. Seeing the above diagram from this point of view, it may be said that the sintering takes place certainly at 660°C, never occurs at 500°C, and it is critical at 550°C; in other words, the temperature at which the sintering begins to occur appreciably is 550°C or very near to this. Therefore, it may be said that the temperature, under consideration, is 550°C, in the accuracy of the present observation.

Now, according to the view as already stated, the above workers studied the mechanism of the sintering, applying chiefly the experimental data of shrinkage

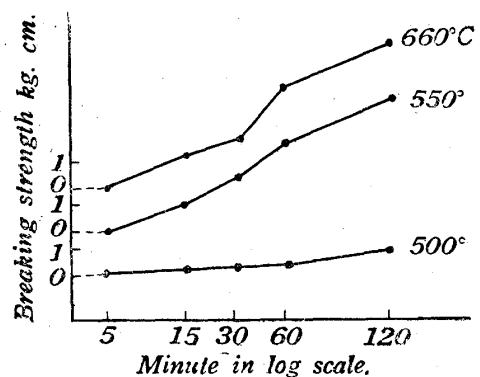


Fig. 10. Curves of breaking strength vs. sintering time for the specimens, pressed at 1t/cm² and sintered at constant temperatures: Taken from T. Okamura, Y. Masuda and S. Kikuta, Sci. Rep. RITU 1 (1949), 357.

(15) Toshihiko Okamura, Yoshimichi Masuda and Sadao Kikuta, Sci. Rep. RITU, 1 (1949), 357.

obtained by them. Firstly, it was inferred that the sintering takes place appreciably from 550°C. This assertion is in agreement with that described above. In the further treatment, they considered the total volume of the pores in the specific volume of the specimen, and the ratio in which the value for the sintered specimen was compared with that for the one, compacted but not yet sintered, was taken to be the measure of the degree of the sintering which was denoted by w . From the experimental data, the relation

$$w = At^{\frac{1}{3}}$$

was obtained, where A is a constant, depending on the temperature of sintering and t is its time duration. Accordingly it follows

$$\frac{\partial w}{\partial t} = -Dw^{-2}$$

where D is a constant depending on the temperature. This equation means that the velocity of the decrease of the total volume of the pores mentioned above is inversely proportional to the square of its amount at the instant considered; in other words, the velocity of filling the vacant space of the above pores by the displacement of the Cu-atom is inversely proportional to square of the total volume of the vacant space still left. Thus, they deduced an equation, expressing the velocity of the sintering. Here, it may be worth to remark that this equation is equivalent in nature to Fick's first equation in diffusion

$$m = -D \frac{dc}{dx}$$

where m is the mass of the considered substance passing through the unit area which is perpendicular to the direction x ; D is a constant depending on the temperature, and dc/dx , the gradient of the concentration of the above substance along x -direction. The equivalence stated above means, (1) both of the above equations concern the system in which the density of the considered substance is not distributed uniformly, that is it changes discontinuously in the former case, and continuously in the latter, (2) the term in the left hand side of the above equations represents the velocity of forming a system in which the density is distributed more uniformly, by the displacement of the atoms or molecules, under consideration, (3) about the first factor D , in the right hand side, it will be needless to explain, (4) the last factor expresses the dependency of the above velocity on the degree of the nonuniformity of the above density, this degree being expressed in an integrated form and in the differential, respectively, in correspondence to the features of the nonuniformity, mentioned above.

From this point of view, the former equation shows that the sintering is the phenomenon that belongs to the same category as the diffusion. But, even in the elementary process, whether the above two phenomena are identical with each other or not must be the problem to be discussed further.

Further, the workers, from the experimental data of the shrinkage determined the functional form of D and obtained the familiar one

$$D = be^{-\frac{a}{T}}$$

where a and b are constants and T is the absolute temperature; further, they computed the activation energy of the sintering for Cu as

$$E = 56 \text{ kcal/mol}$$

and this is in good agreement with the activation energy of the selfdiffusion of Cu,

$$E = 57.2 \text{ kcal/mol}$$

which was obtained by J. Steigmann, W. Shockley and F. C. Nix.⁽¹⁶⁾ From the above finding, it may be expected that, even in its atomistic sense, the process of the sintering will be the same as that of the selfdiffusion. In fact, this view is asserted by some workers, especially by G. C. Kuczynski,⁽¹⁷⁾ though this opinion is not yet so widely accepted. This problem, we think, will be answered conclusively when the physical meaning of the activation energy in the above cases is clarified. This will be done in our paper to be published later. But here it will be simply assumed that the above view is correct. Then it may be inferred that the diffusion considered above begins to take place appreciably at the temperature 550°C. Further, in analogy with the case of 230°C described above in 2, A, it may be taken that, the above diffusion begins to take place appreciably in a discontinuous way, and that it results, accordingly from a transition occurring in the valence electron which binds Cu-atoms. Therefore the above anomalous temperature is not only in coincidence in its numerical value, but also identical in its nature with that designated as the third in 1, A.

From the above consideration, it is expectable that even in the experimental condition where the contact between the powders is not good as in the present case, the sintering begins to occur at 230°C, though very faintly, and at 550°C, it begins to be appreciable. The fact that the two anomalies, at 230°C and at 550°C, are in intimate connection as described above in 1, D, may be support of the above expectation.

3. Annealing

The phenomenon of the recovering of cold-worked Cu by annealing has been studied by many workers, but the experimental results given by N. Kôda⁽¹⁸⁾ seems to be most preferable to the present investigation in that various methods of investigation were applied to the same specimen. The above methods consisted of the mechanical testings on tensile strength, elongation, and number of bending, and the X-ray studies on lattice distortion and recrystallization. The specimen was cold-drawn wire of electrolytic Cu and its degree of cold-work was measured by

$$\frac{(\text{cross section of annealed wire}) - (\text{cross section of cold-drawn wire})}{(\text{cross section of annealed wire})} \times 100\%$$

(16) J. Steigmann, W. Shockley and F. C. Nix, *Phys. Rev.* 56 (1939), 13.

(17) G. C. Kuczynski, *J. Appl. Phys.* 21 (1950), 632.

(18) Nariyasu Kôda, *Furukawa Denkô-Denshen* (in Japanese), No. 12 (1940).

and the specimens actually experimented by him were of 97.6, 84.0, 55.5 and 35.5%. The process of the experiment was as follows. The above specimen was annealed for 30 minutes at several constant temperatures which were not higher than 500°C, and the above testing was applied, after cooling. The results of the investigation are illustrated in the way as shown in Fig. 11.

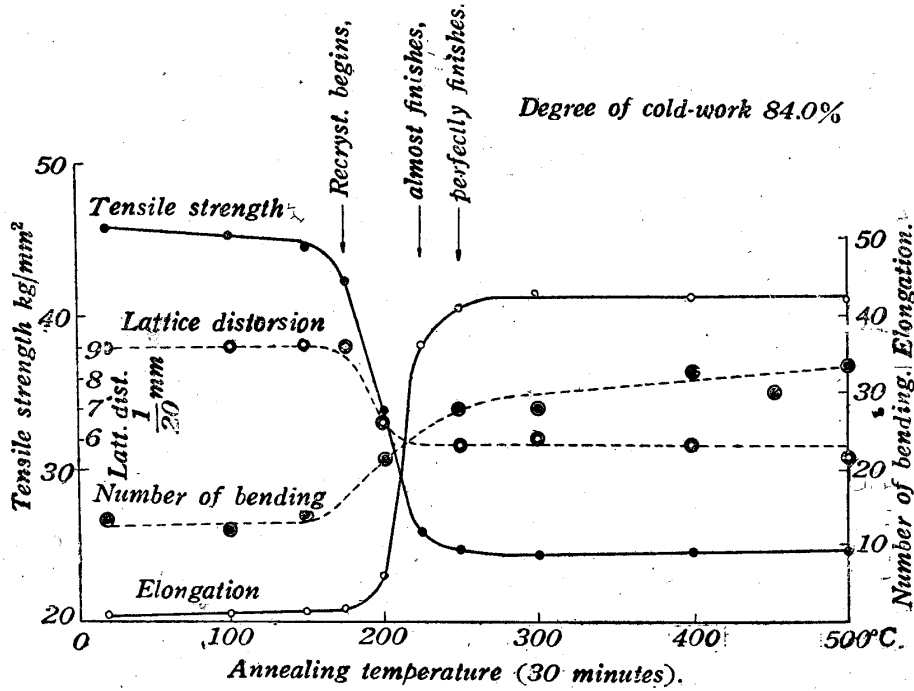


Fig. 11. Curves, illustrating the recovery from internal stress in Cu by annealing : Taken from N. Kōda, Furukawa Denkō-Denshen (in Japanese), No. 12 (1940).

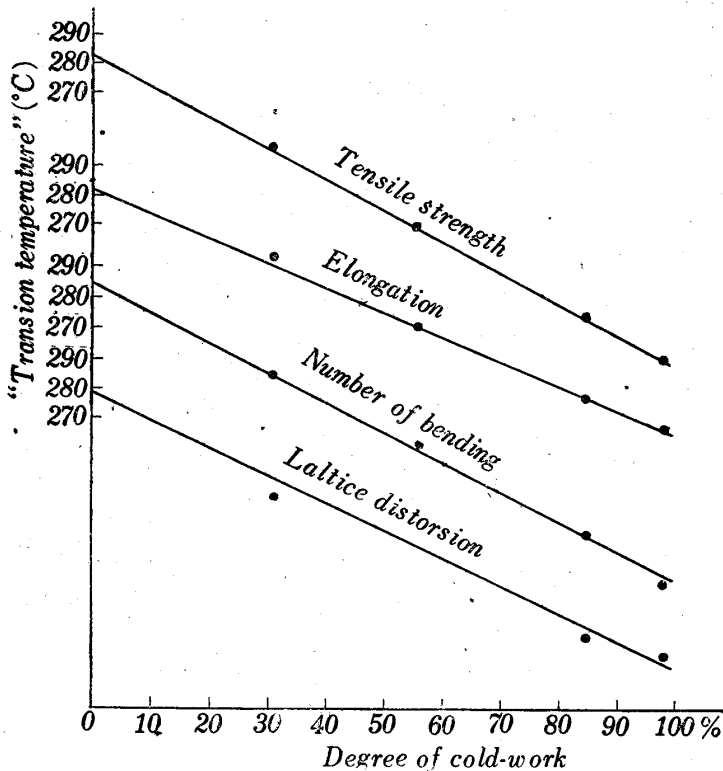


Fig. 12. Curves of "transition temperature" vs. degree of cold-work.

Now, in a curve in the above figure, the inflection point must correspond to the temperature at which the Cu atoms are released from internal stress most abundantly, and so with the same idea as described in 1, A, the above temperatures were graphically determined, and these temperatures which are given by the same testing, say by tensile strength, were plotted as the function of the degree of the cold-work, as illustrated in Fig. 12; and by the method of extrapolation the anomalous temperature of the annealed specimen was determined as

shown in Table 12. These values are in good agreement with that determined above in 1, A and B as the second anomalous temperature.

Table 12. Anomalous temperature of Cu, determined from annealing.

Method	Tensile strength	Elongation	Number of bending	Lattice distortion
Temperature(°C)	280	280	284	278

Finally, it must be added here a remark that from the present investigation, the following fact is clarified; in the case of Cu, the phenomenon of recrystallization occurs in the temperature range of the second anomalous change as shown in Fig. 12.

4. Hardness in high temperature range

The hardness of Cu at high temperatures was measured by several workers of which the result given by J. Engl and G. Heidkamp⁽¹⁹⁾ seems to be most valuable for the present investigation. In the above work the hardness H is defined by the expression

$$H = \frac{P}{0.25 d^2} \frac{\text{kg}}{\text{mm}^2}$$

where P is the pressure applied to the conical indenter and d the impression diameter. In high temperature, however, d increases with the time duration of impression, even when the temperature is kept constant, hence, H is a function of the temperature and the time of impressing. From the present investigation, however, the above function was determined as

$$H = H_1 t^{-n}$$

where t is the above time duration, which is valid in the range, 5~300 sec, and H_1 and n are the constants depending on the temperature; these constants called by them, "hardness number" and "softening number", respectively and were determined experimentally as represented graphically in Figs. 13 and 14, respectively. Thus, according to the present workers, the hardness of Cu in high

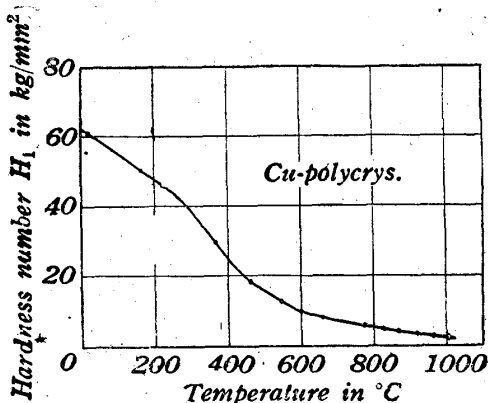


Fig. 13. Curve of hardness number H_1 for Cu vs. temperature: Taken from J. Engl and G. Heidkamp, Zeits. Phys. 95 (1935), 30.

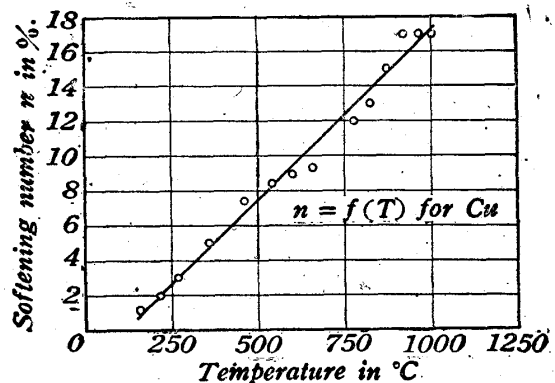


Fig. 14. Curve of softening number n for Cu vs. temperature.

(19) J. Engl and G. Heidkamp, Zeits. Phys. 95 (1935), 30.

temperature is defined by two constants, H_1 and n .

Now, from the above equation it follows that

$$F = -\frac{\partial H}{\partial t} = n H_1 t^{-(n+1)},$$

and, since our object is to study the property of Cu in most annealed state as possible, it will be appropriate to put $t=5$ sec in the present case as

$$F_0 = n H_1 5^{-(n+1)}.$$

Further, this equation may be taken as expressing the deformation velocity of the specimen, and so it may be put as usual,

$$F_0 = AD$$

where A is a constant, depending on the external pressure, and the dimension and the form of the impression; D is the constant, expressing the temperature dependency which may be put

$$D = e^{-b/T},$$

where b is a constant having the nature of the activation energy for the phenomena which occur in the specimen in the course of impressing, and T , the absolute temperature; thus we have

$$\ln F_0 = \ln A - \frac{b}{T}.$$

The values of $\ln F_0$ for the temperatures which correspond to the measuring points in Fig. 14 were computed graphically from Figs. 13 and 14 as shown in Table 13, and they were plotted against $1/T$ as shown in Fig. 15.

Table 13. Numerical values of $\ln F_0$.

$T^\circ\text{K}$	431	485	546	631	732	809	875	932	1043	1093	1141	1188	1228	1273
$\frac{1}{T} \times 10^4$	23.2	20.6	18.3	15.9	13.7	12.4	11.4	10.7	9.59	9.15	8.76	8.42	8.14	7.86
$\ln F_0$	-4.6	-4.0	-3.7	-3.6	-3.7	-4.0	-4.2	-4.4	-4.6	-4.7	-4.7	-4.9	-5.0	-5.3

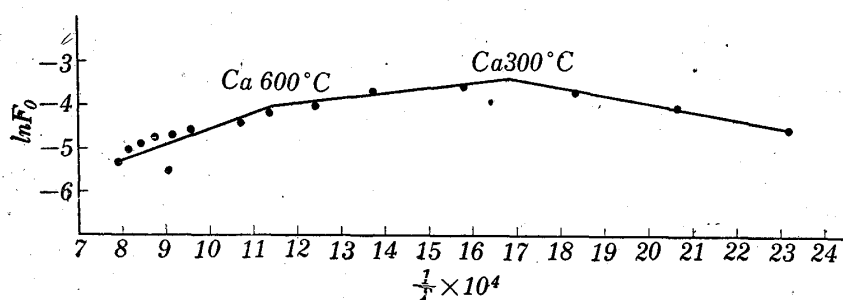


Fig. 15. $\ln F_0$ vis. $\frac{1}{T} \times 10^4$ curve.

Table 14. Numerical values of b .

$t^\circ\text{C}$	158°~Ca 300°	Ca 300°~Ca 600°	Ca 600°~1000°
$b \times 10^5$	-2	1	4

From Fig. 15 it is seen that the value of b is not constant throughout the whole range of temperature, but constant in each of the three ranges, respectively, as shown in Table 14. Accordingly, b changes its value discontinuously at the temperatures, about 300°C and about 600°C, and

from the nature of the above determination, these temperatures may be considered to be in agreement respectively with 280°C and 550°C which are determined in the former sections as the anomalous temperatures of Cu in annealed state. Further, in order to clarify the physical meaning of b , we differentiated F_0 with respect T and obtained

$$\frac{dF_0}{dT} = b \frac{F_0}{T^2} .$$

In the further treatment, it will be convenient to consider the three temperature ranges separately. First, in the lowest range, b is negative, hence the deformation velocity F_0 decreases with the rise of the temperature; saying in other words, with the rise of the temperature, the time of impression required for a constant small increment of deformation becomes longer, or the amount of the increment of deformation in a constant short time decreases. So, in such a sense as above stated, the hardness of the specimen under the above condition increases with the rise of temperature. Next, in the second range, b is positive, hence, the hardness decreases with the rise of temperature; and this fact may be explained as follows: as described above in 3, in this temperature range, the phenomenon of the recrystallization takes place, and it is very likely that this phenomenon or, at least, its underlying process facilitates the deformation of the specimen and it is affected more effectively with the rise of the temperature. Finally, the highest range will be considered. In this range, the sintering takes place, as described above in 2, B, and accordingly, it may be true with the selfdiffusion in the present case. Therefore, similarly to the case of the second range, the above phenomenon or, at least, its underlying process facilitates the above deformation and it is affected more effectively with the rise of the temperature. Moreover, the agency which is effective in the second range is probably cooperative in the present range, at least at the considered instant. Therefore the value of b is larger than that for the second range, its sign being of course positive.

5. Summary

The results of investigation obtained above in this section may be summarized as shown in Table 15.

Table 15. Summarizing table.

Observer (reference)	Phenomena	Anomalous temperature (°C)		
S. Satō(10)	Heat evolution	—	280	—
T. Suzuki(12)	Specific heat	230	280	—
A. Avramescu(13)	Specific heat	—	280	550
S. Tanaka(14)	Diffusion	230	—	—
T. Okamura, Y. Masuda S. Kikuta(15)	Sintering	—	—	550
N. Kōda(18)	Annealing	(tensile strength	280	—
		elongation	280	
		numb. of bend.	284	
		lattice distort.	278	
J. Engl, G. Heidkamp(19)	Hardness	—	Ca 300	Ca 600
Most probable value		230	280	550

As already shown in Table 1 for Zn, the melting point is clearly an anomalous temperature of the substance, under consideration, and as its value for Cu, 1083°C⁽²⁰⁾ may be taken as the most reliable. So, it may be concluded that the anomalous temperatures of Cu obtained above are as shown in Table 16. Here, in concluding

Table 16. Anomalous temperature of Cu (°K).

503	553	823	1356
-----	-----	-----	------

for Zn concerning the anomaly in low temperature, shown in Table 1, it is very expectable that the similar fact will exist also for Cu. But, unfortunately any work is hardly found in literature available for the investigation along this line, and so it must be left to the experimental work in future.

III. The regularity, existing in the anomalous temperatures of Cu

As already stated at the end of I, it is very expectable that from the fact shown in Table 1, a similar rule as mentioned above will be valid also for the anomalous temperatures of Cu which are obtained and shown in Table 16. In the first place, it is presumable that from the fact described in II, 1, D, the anomalous temperatures, 503° and 823°K belong to the same group, and taking the absolute zero as belonging to this group, as in the case of Zn, we considered the ratio of the intervals between the adjacent temperatures of the above three, and obtained the following result:

$$0^{\circ} \sim 503^{\circ} = 503^{\circ} \quad 503^{\circ} \sim 823^{\circ} = 320^{\circ}$$

and

$$503^{\circ} : 320^{\circ} = 1.57 : 1 \\ \doteq 3 : 2$$

Thus, it satisfies formally, at least, the separation rule of Landé concerning the fine structure of the term in the atomic spectra, the above three temperatures corresponding respectively to the components of the fine structure of an inverted triplet term.

In the second place, the other two in Table 16 were treated in the same way as above and obtained the following result:

$$0^{\circ} \sim 553^{\circ} = 553^{\circ}, \quad 553^{\circ} \sim 1356^{\circ} = 803^{\circ},$$

and

$$553 : 803 = 1 : 1.45 \\ \doteq 2 : 3$$

Table 17. The regularity in anomalous temperatures of Cu, the number in the parenthesis being interval ratio.

Group	Anomalous temperatures (°K)				
I	0	(3)	503	(2)	823
II	0	(2)	553	(3)	1356

this section, the following remark is to be added: from the experimental evidence

for Zn concerning the anomaly in low temperature, shown in Table 1, it is very expectable that the similar fact will exist also for Cu. But, unfortunately any work is hardly found in literature available for the investigation along this line, and so it must be left to the experimental work in future.

III. The regularity, existing in the anomalous temperatures of Cu

As already stated at the end of I, it is very expectable that from the fact shown in Table 1, a similar rule as mentioned above will be valid also for the anomalous temperatures of Cu which are obtained and shown in Table 16. In the first place, it is presumable that from the fact described in II, 1, D, the anomalous temperatures, 503° and 823°K belong to the same group, and taking the absolute zero as belonging to this group, as in the case of Zn, we considered the ratio of the intervals between the adjacent temperatures of the above three, and obtained the following result:

$$0^{\circ} \sim 503^{\circ} = 503^{\circ} \quad 503^{\circ} \sim 823^{\circ} = 320^{\circ}$$

and

$$503^{\circ} : 320^{\circ} = 1.57 : 1 \\ \doteq 3 : 2$$

Thus, it satisfies formally, at least, the separation rule of Landé concerning the fine structure of the term in the atomic spectra, the above three temperatures corresponding respectively to the components of the fine structure of an inverted triplet term.

In the second place, the other two in Table 16 were treated in the same way as above and obtained the following result:

$$0^{\circ} \sim 553^{\circ} = 553^{\circ}, \quad 553^{\circ} \sim 1356^{\circ} = 803^{\circ},$$

and

$$553 : 803 = 1 : 1.45 \\ \doteq 2 : 3$$

Thus, it also satisfies the same rule as above. In the present case, however, the above three temperatures correspond respectively to the components of the fine structure of a regular triplet

(20) Critical Tables, I (1926), 104.

term. The results obtained in this section are tabulated, for convenient of later use, in Table 17.

IV. Physical significance of the anomalous temperatures of Cu

1. The correspondence between the anomalous temperatures and the energy levels, of the valence electron in Cu

As already stated in I, the temperature under consideration may be taken to be a measure of the energy of the thermal vibration of Cu-atom. Hence, the rule in table 17 can be taken not only as formal but also in nature identical with Landé's rule in the case of odd multiplicity. Further, in the theory of atomic spectra, the above rule can be explained as having resulted from Russel-Saunders coupling of optical electrons, hence, the above rule in Table 17 may be explained as being due to the above coupling of the valence electrons in Cu, as in the case of Zn described in I.

On the other hand, we inferred from the analysis of X-ray spectrum that the valence electron of Cu is in the four levels, E_1 , E_2 , E_3 and E_4 ,⁽²¹⁾ and this fact is confirmed from the photoelectric effect and the absorption of light by the thin film of Cu.⁽²²⁾ Accordingly, it may be taken that the above two groups of the anomalous temperatures represent the fine structures of the two levels, E_1 and E_2 , respectively, and assuming that when the energy position of the level is lower, the total separation will be larger, it may be taken here that I and II in Table 17 correspond to the levels E_2 and E_1 , respectively.

Concerning E_3 and E_4 , though we have no experimental evidence as stated above but in analogy with the case of Zn, it may be

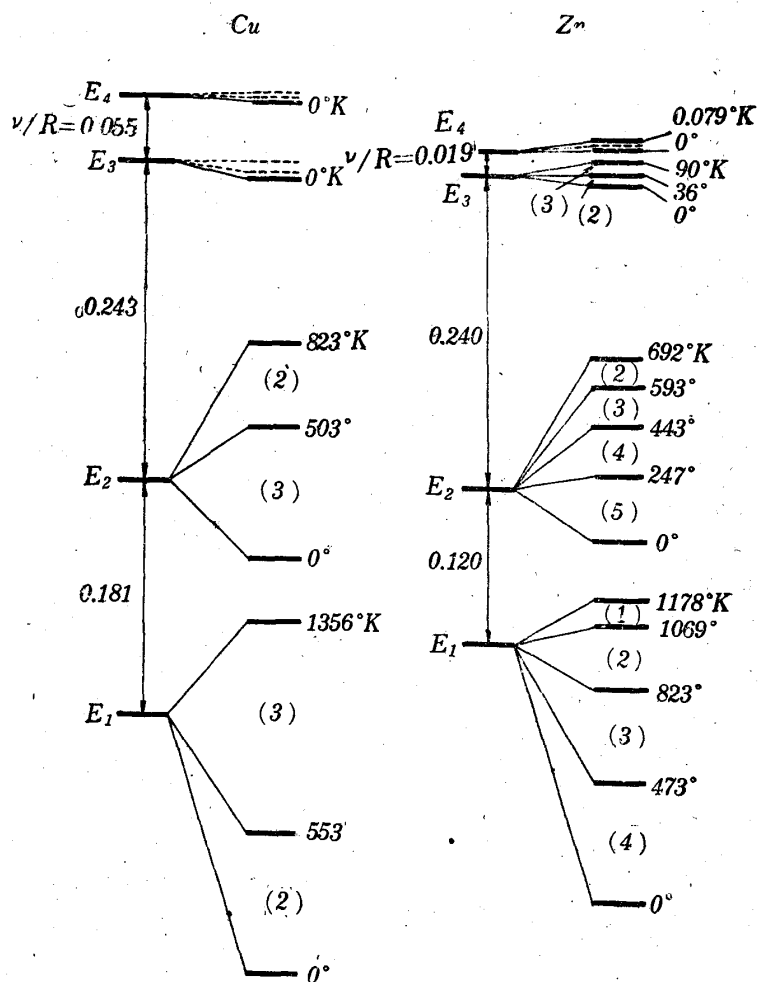


Fig. 16. Diagrams showing the fine structures of the energy levels of the valence electrons in Cu and Zn.

(21) M. Satô, Sci. Rep. RITU, 2 (1950), 424.

(22) M. Satô, Sci. Rep. RITU, 2 (1950), 725.

assumed here that in low temperature range, there are two groups of anomalous temperatures, corresponding to the multiple structures of E_3 and *E_4 , respectively.

The result mentioned above and that obtained previously for Zn,⁽³⁾ are illustrated together diagrammatically in Fig. 16.

2. The multiple structures of the energy levels E_1 and E_2

From the correspondences made above in 1, the multiple structures of the energy levels, E_1 and E_2 , can be determined in the usual way as follows:

For both E_1 and E_2 .

$$J = 3, 2, 1$$

and

$$L + S = 3 \quad \text{and} \quad L - S = 1 \quad \text{or} \quad S - L = 1.$$

Accordingly, two solutions

$$\left. \begin{array}{l} L = 2 \\ S = 1 \end{array} \right\} \quad \text{and} \quad \left. \begin{array}{l} L = 1 \\ S = 2 \end{array} \right\}$$

are possible, but the former seems to be more probable than the latter, hence, the multiple structure of E_1 and E_2 may be designated, respectively, as

$$E_1: {}^3D_{1,2,3} \quad E_2: {}^3D_{3,2,1}$$

where the suffix numbers, showing the value of J , are written in order of the energy position from the lowest, that is E_1 is regular and E_2 , inverted. Next, the electrons associating with the levels, E_1 and E_2 , are to be considered. From $S = 1$, the number of the electrons, associating with each of the above levels must be 2 or its multiple. But in the ordinary state of an isolated Cu-atom, a single electron behaves as the valence electron, therefore, it is assumed here that the above is in reality true with the present case. Accordingly, each of the energy levels, E_1 and E_2 , must be associated with the atoms, 2 or its multiple in number; it will be also assumed here that the simplest is with the case in reality. In other words, each of the above levels is associated with two electrons which are supplied by two atoms. In order to represent clearly the above fact, the following notations will be used:

$$E_1: (A_1, B_1) {}^3D_{1,2,3} \quad \text{and} \quad E_2: (A_2, B_2) {}^3D_{3,2,1}$$

where A_1 and B_1 , A_2 and B_2 , represent the two pairs of Cu-atoms, each associating with the levels, E_1 and E_2 , respectively. So, it may be said that the above two pairs form respectively two kinds of diatomic molecules. This result, though inconsistent with the prevailing idea concerning the structure of a metal, is the very probable thing as described above in I for Zn.

Further, in order to show that the above assertion is possible also from the quantitative point of view, the total separations of the triplets of E_1 and E_2 will be compared with those of ZnI. Now, since the energy of the thermal vibration of Cu-atom at $T^\circ\text{K}$ may be taken as kT , as usual, where k is Boltzmann constant, amounting to 1.379×10^{-16} erg/deg, the above separations are computed as shown in Table 18. On the other hand, the total separations of the lowest three terms

Table 18. Total separations of E_1 and E_2 .

Energy level	E_1	E_2
Total separation (erg)	1.870×10^{-13}	1.135×10^{-13}

in the triplet system of ZnI, are computed from the data in Critical Tables⁽²³⁾ as shown in Table 19. From these tables, it is seen that the total separation of

Table 19. Total separations of the lowest three triplets of ZnI.

Triplet	(4s, 4p) 3P	(4s, 5p) 3P	(4s, 4d) 3D
Total separation (erg)	1.145×10^{-13}	1.643×10^{-14}	1.76×10^{-15}

E_1 and E_2 , is respectively comparable with that of (4s,4p) 3P of ZnI. Hence, from the consideration on the electronic structures of Zn-atom and the molecules mentioned above it may be said that our view described above is reasonable.

Finally, the quantum state of the individual electron in E_1 and E_2 will be discussed. From the fact that E_1 is a regular 3D and (4s,4d) 3D of ZnI is also regular, it seems that the quantum states of the individual electrons in E_1 are identical with those in the latter. So, here it will be assumed provisionally as

$$E_1: (A_1, B_1)(4s, 4d) ^3D_{1,2,3}$$

and, on an appropriate occasion, this result will be confirmed or revised from some experimental evidence, if possible. For E_2 , the inference as made above is impossible, because there is no inverted 3D in the lowest part of ZnI, but for convenience sake, it will be assumed here to be

$$E_2: (A_2, B_2)(4p, 5p) ^3D_{3,2,1}$$

and if possible, the same treatment as stated above must be made.

Thus, the multiple structures of the energy levels, E_1 and E_2 , are determined as far as possible. For convenience in later use, the results obtained above are tabulated in Table 20.

Table 20. Structures of E_1 and E_2 .

Energy level	E_1	E_2
Structure	$(A_1, B_1)(4s, 4d) ^3D_{1,2,3}$	$(A_2, B_2)(4p, 5p) ^3D_{3,2,1}$

3. The multiple structures of the energy levels, E_3 and E_4

As mentioned above in 1 there are likely to be two groups of the anomalous temperatures, indicating the multiple structures of E_3 and E_4 respectively, which are probably triplets. Accordingly, also in the present case, similar inference as made above in 2, must valid. In otherwords E_3 and E_4 are formed by two atoms, respectively. Hence, it appears as if four kinds of diatomic molecules would be found constantly, but this is not in concordance with the experimental evidence which will be described in another paper; it shows that any kind of

(23) Critical tables, 5, 398.

molecule other than (A_1, B_1) and (A_2, B_2) , does not exist. So, in order to consider these facts to be consistent, it was supposed similarly as in the case of Zn, described in I, that E_3 and E_4 are associated with the atoms, (A_1, B_1) and (A_2, B_2) , respectively, and the electrons in (A_1, B_1) and those in (A_2, B_2) are constantly in oscillation between the levels, E_1 and E_3 , and E_2 and E_4 , respectively; these oscillations may be represented as $E_1 \rightleftharpoons E_3$ and $E_2 \rightleftharpoons E_4$, respectively.

Here it will be worth to add a remark about the pairing of the levels in the above oscillations. In the case of Zn, it was assumed to be $E_2 \rightleftharpoons E_3$, and, consequently, $E_1 \rightleftharpoons E_4$, as described above in I; this comes from an experimental evidence, though it may be less reliable. This pairing seems to be favourable in the explanation of the anisotropic property of Zn-crystal. In the present case, however, we have no experimental evidence, as mentioned above, but from the fact that the property of Cu-crystal is isotropic, it must be reasonable to pair the four levels so that the level distance in each will be equal as possible. So it was done in the way as described above.

Now, in the previous paper,⁽²²⁾ we named E_1 and E_2 the "structure level", after Richardson,⁽²⁴⁾ because when the electron is in these levels they bind the atoms firmly; E_3 and E_4 , the "conduction level" as usual, because when the electron is in these level, it plays the role of the electric conduction. Accordingly, it may be said that the valence electron within the bulk mass of Cu behaves both the conduction electron and of the structure electron not simultaneously but alternately.

4. The nature and the mechanism of the transition at the anomalous temperature

Above in II, A, we have expected that at the anomalous temperature, there would occur a transition in the energy state of the valence electron, and now we are ready to clarify the nature and the mechanism of it. For this purpose, the energy level E_1 will be considered for an example. First suppose that it is at 0°K . Under such a condition, the vectors, \vec{S} and \vec{L} of E_1 make precessional rotation about the invariant axis \vec{J} , its quantum number being 1; the Cu-atom in (A_1, B_1) , associating with E_1 , vibrates with zero point energy. Next, suppose that the temperature is raised gradually; then the vibrational energy of Cu-atom will practically be increased, continuously. But, in the above precessional motion, the feature is entirely different, that is only the three values of the rotational energy corresponding to $J = 1, 2, 3$ are permitted. Accordingly, when the temperature is raised from 0°K , as stated above the energy of the above precessional motion can not be increased as it is in the thermal vibration of Cu-atom, hence, it keeps the state of motion at 0°K , not disturbed by the thermal vibration of the associating Cu-atom, until the energy of the latter attains the value, corresponding to $J=2$ of the former. But, when the vibrational energy of the Cu-atom reaches the above value, the precessional motion, under consideration, is disturbed by the former, and there occurs the translation of energy from the thermal to the electronic, and the transition, ${}^3D_1 \rightarrow {}^3D_2$ is executed. This is the nature and the

(24) O. W. Richardson, Proc. Roy. Soc. A 128 (1930), 68.

mechanism for the transition which takes place at the temperature 553°K. Further, in raising the temperature from 553°K, similar phenomena take place, and when the thermal energy of the Cu-atom attains the value of the above precessional motion for $J=3$, then there occurs ${}^3D_2 \rightarrow {}^3D_3$, and this is the transition at the temperature 1356°K. In the similar way the transitions at the anomalous temperatures 503° and 823°K as well as those which are expected above as corresponding to E_3 and E_4 , may be explained. Thus, the nature and the mechanism of the transition, which has been considered above to be the ultimate cause of the anomalous change of the various properties of the present metal, are explained, satisfactorily.

5. The nature of the cohesive force

From the considerations made above in 2, it is clarified that the binding energies between the atoms, A_1 and B_1 , A_2 and B_2 , are respectively those of the coupling of the electrons in Russel-Saunders type. But, in order to build the crystal from these molecules, there must be an energy which binds them firmly and this fact may be explained as follows:

As already explained in I for Zn, in order to be preserved from damping, the oscillations $E_1 \rightleftharpoons E_3$ and $E_2 \rightleftharpoons E_4$ are presumed to be carried out in resonance with their neighbours of the same kind, as illustrated in Fig. 17; in this figure, the mutual orientations of the molecules are disregarded.

As a consequence of the above resonating oscillations the pair of molecules of the same kind must be bound by the energy of resonance exchange of the electrons in oscillation. Further, these resonating oscillations can take place in a group of the molecules of the same kind, as illustrated by a simple example in Fig. 18; the mutual orientations of the molecules are, also, disregarded. Thus, it may be supposed that within the bulk mass of Cu, innumerable molecules are bound mutually, each atom

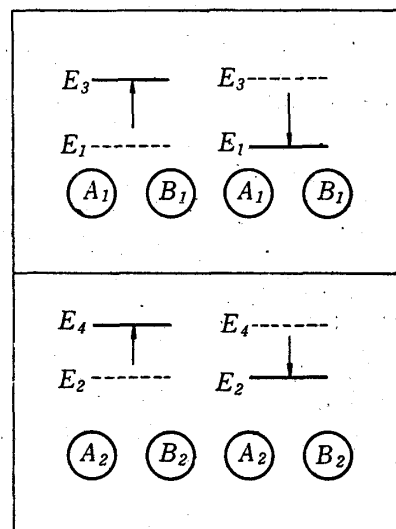


Fig. 17. Diagrammatic illustration of resonating oscillations between E_1 and E_3 , E_2 and E_4 associated with two molecules.

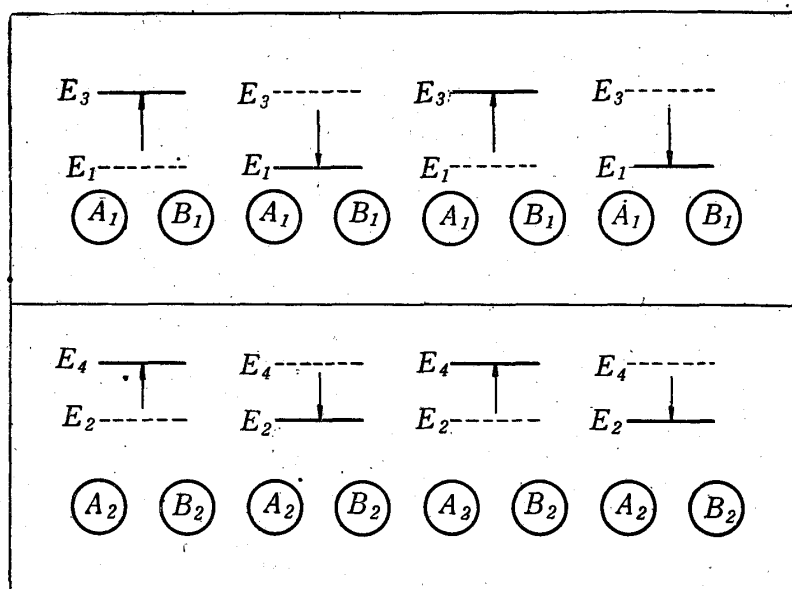


Fig. 18. Diagrammatic illustration of resonating oscillations between E_1 and E_3 , E_2 and E_4 associated with four molecules.

occupying the lattice point of the crystal.

In the surface layer, the feature of the above binding must be somewhat different, though the geometrical arrangement of the atoms may be the same as that in the inner part, that is, as we described in a previous paper,⁽²¹⁾ in the upper most surface of the metal, most of the levels, E_3 and E_4 are vacant, and this means that most of the oscillations stated above are in stop. Further, it was continued in the above paper that, when we proceed from the surface into the inner part of the metal, the numbers of E_3 and E_4 , which are occupied by electrons, increase with increase of the depth. This can be explained as having resulted from the fact that the numbers of the molecules in each of the group in the oscillation mentioned above increase with depth. Thus, excepting in the very thin layer of surface, the atoms, being situated at the lattice point of Cu-crystal, are bound as if they were woven from two kinds of the elastic strings. All metallic crystals are probably built up similarly; this seems to be very favourable in the explanation of the characteristic properties of metals, such as good conductivity of the electric energy as well as of the thermal and toughness. Further, the fact that the properties stated above differ from metal to metal may be explained as being due to the property of the binding string stated above and the manner in which the crystal is woven.

V. Conclusion and the plan for the further investigation

From the analysis of many experimental evidences, it was found that in the case of Cu, at least, four anomalous temperatures, including the melting point,

Group	Anomalous temperatures ($^{\circ}$ K)				
I	0	(3)	503	(2)	823
II	0	(2)	553	(3)	1356

exist, their values being 503, 553, 823 and 1356 $^{\circ}$ K, and that their interval ratios satisfy Landé's interval rule as

shown in the above table. Accordingly, it was inferred that the energy levels E_1 and E_2 have the structures which may be represented, respectively, by the following notations:

$$E_1: (A_1, B_1)(4s, 4d) {}^3D_{1,2,3} \quad E_2: (A_2, B_2)(4p, 5p) {}^3D_{3,2,1}$$

where A_1 , B_1 and A_2 , B_2 denote the Cu-atoms, forming diatomic molecules, respectively. Further, assuming that a number of each kind of molecules are bound by the energy of the resonating oscillations between E_1 and E_3 , E_2 and E_4 , the cohesive force was explained similarly as in the case of Zn.

Now, in the course of the study of the experimental evidences in I, it has been stated frequently that explanations will be given more satisfactorily later in the present paper but in writing the above section it has been noticed that it will be done better after the confirmation of the assumption stated above is made as satisfactorily as possible, and the electronic structure of Cu-crystal is also clarified as far as possible. Hence, it will be given on an appropriate occasion in another paper.

Here the writer wishes to express his hearty thanks to Mr. T. Suzuoka for his assistance.