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RELAXATION AND DIFFUSION IN DOPED LEAD CRYSTALS.(U)
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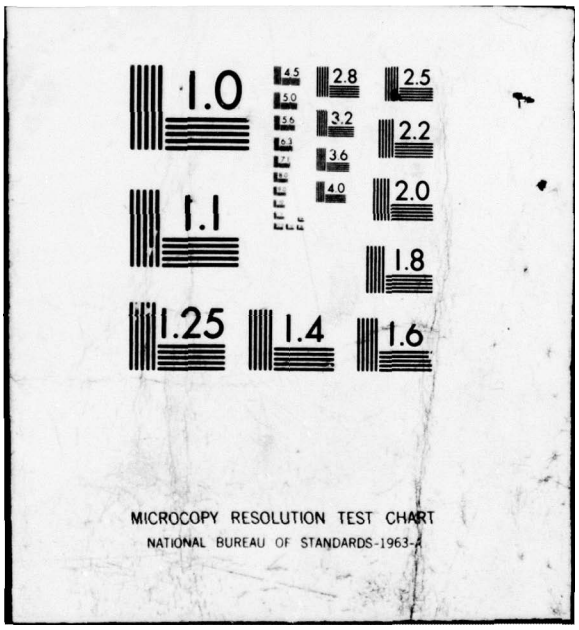
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

This investigation was initiated to determine the nature and cause of four relaxation peaks which occur in single crystals of lead doped with one of the noble metals, gold, silver, or copper. In the case of each of these dopants, studies employing a composite oscillator have revealed a dominant internal friction peak which had the ideal Debye shape and which yielded an activation energy equal to that given in the literature for the diffusion of the particular noble metal into lead.

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Thomas J. Turner

Charles H. Nielsen (M.A. completed)

Robert Melton (Undergraduate student)

George Jones (Undergraduate student)

F. M. McGehee

Relaxation and Diffusion in Doped Lead Crystals

This investigation was initiated to determine the nature and cause of four relaxation peaks which occur in single crystals of lead doped with one of the noble metals, gold, silver, or copper. In the case of each of these dopants, studies employing a composite oscillator have revealed a dominant internal friction peak which had the ideal Debye shape and which yielded an activation energy equal to that given in the literature for the diffusion of the particular noble metal into lead. If the crystals were held for a period of hours at liquid nitrogen temperature it was found that this dominant peak, designated 1, decreased in relaxation strength and a second peak at a lower temperature, designated peak 2, increased. Upon recycling it was found that peak 1 could be returned to its original strength with peak 2 decreasing to its original value. Two other peaks at lower temperatures designated 1′ and 2′ were found to follow the action of the other peaks, that is, when 1 increased 1′ also increased and vice versa. Since these peaks occurred in crystals of <100> orientation, but not in those of <111> orientation it was concluded that two <100> orthorhombic defect configurations were present in these doped crystals.

Since the diffusion of these noble metals into lead was thought to be by means of an interstitial mechanism, and since the interstitial was assumed to occupy the octahedral position in the center of the fcc lattice, no stress relaxation and hence no internal friction peaks were expected. Thus to find evidence of two <100> orthorhombic configurations was quite unexpected. The object of this investigation was to study the kinetics of the transition of the system from one type of interstitial configuration to another and hopefully to determine the nature of these two configurations.

As indicated in the attached reprint[1] an activation energy of 0.098 eV was required to go from configuration 1 to that of 2, while 0.066 eV was required to go from 2 to 1 in Au·Pb. The difference between these values was checked independently from equilibrium measurements and found to be 0.032 eV. A surprising feature of this result is that the activation energy to go either way is considerably less than the activation energy of 0.43 eV for the diffusion of gold into lead and yet the process requires hours for completion. This small activation energy is indicative of a very fast process with any sort of reasonable pre-exponential factor, thus a large number of jumps must be required for the process. Experimental curves plus much more detail of the kinetics of this process are given in the thesis by C. M. Nielsen.

Efforts by Sagues and Nowick[2] at Columbia University to reproduce our results were unsuccessful. In spite of using the same type of equipment and doping by evaporation as well as by plating, they could not observe these peaks. Subsequently we repeated the experiments with crystals grown at Columbia and with some grown at Harvard, and were unable to reproduce the earlier results. Upon analyzing our original crystals we found them to be doped with 300 ppm bismuth even though we had purchased them as crystals of the highest purity available. Thus it appeared that the peaks might be due to a complex made up of bismuth plus the noble metal.

In analyzing resistivity and diffusion studies of the gold-lead system Warburton and Turnbull[3] explained their results in terms of gold, and lead-gold complexes which could give rise to internal friction. Thus they suggested that the effect is intrinsic to the noble metal-lead system and does not require an impurity such as bismuth to produce the effect.

Meanwhile, Ross et al[4] had just published a paper on the diffusion of zinc into lead which illustrated the importance of surface preparation before

plating. This result plus the conclusion of Warburton and Turnbull led us to repeat our experiments with crystals that had been placed in an inert atmosphere.

In collaboration with Dr. Larry Cain and in consultation with Professor Larry Slifkin, both of the University of North Carolina-Chapel Hill, crystals were plated in an argon atmosphere. Crystals grown by Dr. Cain as well as crystals purchased from a new source were used. Once again we were unable to reproduce the earlier data. However, it was suggested by Sagues and Nowick that a dopant such as bismuth might be necessary to pin the dislocations and thus suppress the background so that these internal friction peaks might be observed. We found that with a sufficient waiting period (room temperature anneal) after mounting the crystal we could get a sufficiently low background, $1/Q = 5 \times 10^{-5}$. However, we were still troubled by cold work peaks which occasionally appeared in the temperature region where the small peaks were expected.

If internal friction peaks are not clearly defined or are ambiguous, an aid in positively *identifying* relaxation processes is to check for the change in the modulus with temperature that accompanies the relaxation process. In some cases a well defined break will appear in the modulus plot (frequency squared versus temperature) even though no internal friction peak appears. The earlier result was a copper-doped single crystal of lead which exhibited a well defined break in the modulus plot at the positions of peaks 1 and 1′. In a different run of copper-doped material we observed a well defined modulus break at 180°C, accompanied by a poorly defined relaxation peak. Assuming the energy and frequency factor given in the literature[1] the peak should have occurred at 184°K. Assuming the same frequency factor, this four degree shift in temperature corresponds to a shift of activation energy from 0.338 eV given in the literature to 0.335 eV, well within experimental error.

Similar results were found for gold and are shown in Figure 1. These data illustrate a well defined modulus break and a poorly defined internal friction peak. These data were taken at 36.6 Khz whereas the original work was at 92 Khz. Thus peak 1 which appeared at 235°K in the earlier work should appear at 226°K, done at 92 Khz in this work. The relaxation occurs at 232°K from the modulus change. Again assuming the same frequency factor this corresponds to an activation energy of 0.444 eV whereas earlier we found 0.437, again a difference clearly within experimental error. In addition, keeping the specimen at liquid nitrogen temperature for several hours led to a slight decrease in the relaxation in the region of peak 1 and yielded a small modulus break in the region of peak 2, consistent with our earlier results.

Thus we conclude that the effect observed earlier in bismuth-doped samples can be seen in undoped samples. Unfortunately, the magnitude of the effect is such as to suggest that a complex made up of a noble metal and an impurity may be involved. This calls for an extended study involving doping with a large number of materials to unravel the exact nature of the various interstitial configurations of the noble metals in lead.

An interesting side effect was observed in examining the amplitude dependence of the doped crystals. By driving the crystals at a large strain amplitude for a long period of time one can significantly increase the internal friction by causing dislocations to break away from their pinning points. Upon returning to a small strain amplitude one can monitor the return of the impurities which are pinning the dislocations. This recovery was found to satisfy a $t^{1/3}$ time dependence and yielded an apparent negative activation energy of 0.23 eV. Such effects have been discussed by Kim, Slifkin and Fukai[5] and probably result from clustering of impurities along the dislocation line.

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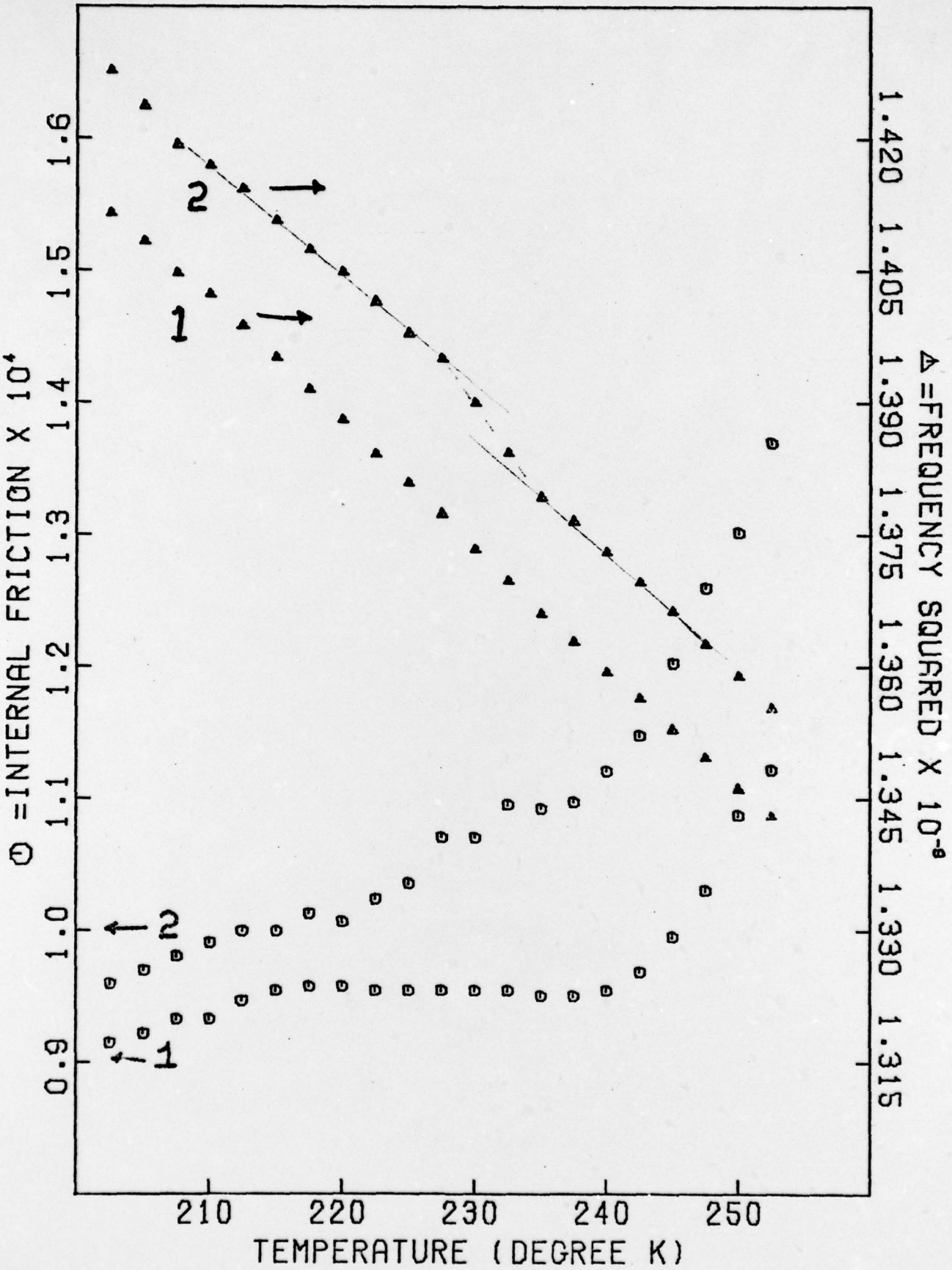
Figure Caption

Fig. 1 Internal friction and frequency squared versus temperature for a <100> crystal of lead before (curves 1) and after (curves 2) doping with gold to a saturation concentration at room temperature.

The scale for the internal friction of curve 1 has been reduced by 0.5×10^{-4} for ease of comparison.

At $240^{o}K$ the initial part of a cold work peak appears following both runs 1 and 2.


Q =INTERNAL FRICTION X 10⁴
Δ =FREQUENCY SQUARED X 10⁻⁸
TEMPERATURE (DEGREE K)
0.9
1.0
1.1
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1.3
1.4
1.5
1.6
1.420
1.405
1.390
1.375
1.360
1.345
1.330
1.315
210
220
230
240
250
1
2
1
2

Figure 1.

Solid State Communications,Vol. 15, pp. 243–247, 1974. Pergamon Press. Printed in Great Britain

THE INTERNAL FRICTION OF LEAD DOPED WITH NOBLE METALS*

Thomas J. Turner and Charles H. Nielsen†

Dept. of Physics, Wake Forest University Winston-Salem, N.C. 27109, U.S.A.

(*Received* 6 *March* 1974 *by S. Amelinckx*)

Internal friction peaks have been observed in Pb–Cu and Pb–Ag similar to those reported earlier for Pb–Au, but it is found that a bismuth impurity is necessary to see the effect. Relaxation peaks from two orthorhombic interstitial configurations have been monitored and reveal unusual kinetics for the transition from one configuration to the other.

IN AN earlier communication[1] we reported a new relaxation effect in gold-doped lead. The activation energy for the relaxation was found to be equal to that reported for the diffusion of gold into lead, hence it was suggested that both the relaxation and diffusion occur by the same process. We report here an extension of this work with ⟨100⟩ single crystals of lead obtained from the same source as that used in the earlier investigation but doped with copper and with silver.[2] These crystals exhibited the same behaviour as the gold doped crystal reported earlier with activation energies obtained for the relaxation process in agreement with those measured in diffusion. In addition, studies on single crystals of lead obtained from two other sources and doped with gold as in our earlier work are presented. However, these crystals yield no relaxation peaks. Upon spectrochemical analysis we found that the crystals which produce the relaxation effects purchased as 99.999% pure actually contained 300 ppm bismuth. Thus the relaxation process observed earlier presumably arises from a complex involving a gold interstitial and a bismuth impurity on a substitutional site. The purpose of this communication is not, however, just to report that bismuth or some other impurity appears to be necessary for the relaxation, but also to present data on what appears to be an unusual effect involving two interstitial configurations.

As reported earlier, the crystals were doped by electroplating and diffusion and the internal friction was measured with a Marx composite oscillator resonating at 92 kHz. All crystals were initially annealed in vacuum for five days at 275°C. They were then doped with gold, electroplated in a cyanide bath and annealed at room temperature to achieve a maximum dopant concentration and then the electrodeposited layer was etched away. The copper doped crystal received identical treatment except a copper sulphate bath was used. The silver crystal was plated with a cyanide bath and given a diffusion anneal at 225°C for 24 hr while mounted on the composite oscillator. In Fig. 1 we illustrate the internal friction as a function of temperature for gold doped ⟨100⟩ single crystals of lead obtained from three sources. Curve *A* shows a major peak at 235°K, designated peak 1, from which we obtain an activation energy equal to that reported for diffusion. Peak No. 2 at 190°K gives an activation energy approximately 10% less than that for diffusion. One can see computer plots of two Debye curves plus a plot of the sum for comparison with the experimental points. Curve *B* illustrates the internal friction as a function of temperature for a crystal grown at Columbia University[3] while Curve *C* is for a crystal grown at Harvard University.[3] It was necessary to allow the crystals of both *B* and *C* to anneal *in situ* for at least

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† Present address Dept. of Materials Science, Cornell University, Ithaca, N.Y.

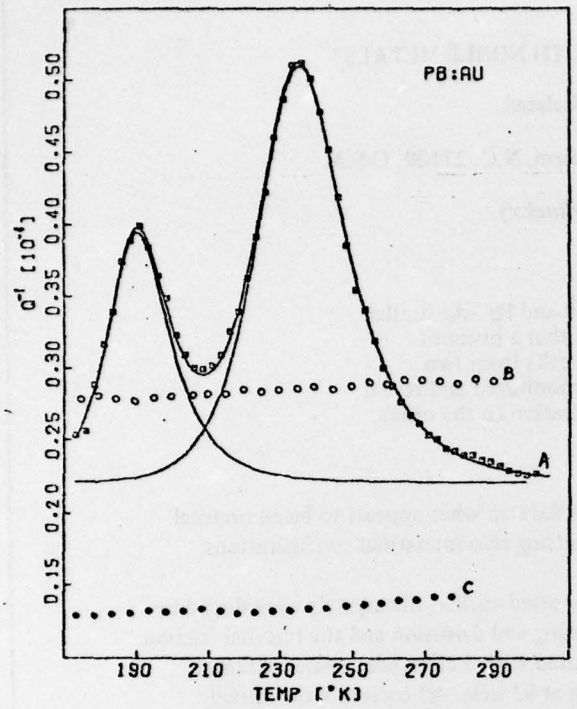

FIG. 1. Internal friction vs temperature for three ⟨100⟩ gold doped crystals obtained from three sources. The crystals received identical treatment and were of the same purity except the crystal of Curve *A* was doped with bismuth.

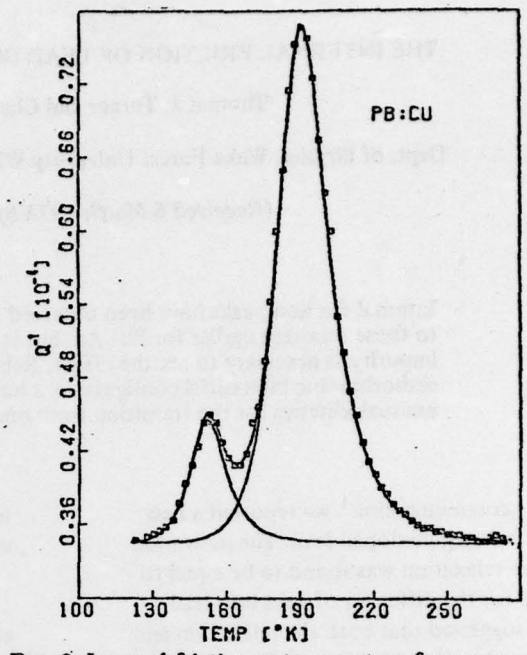

FIG. 2. Internal friction vs temperature for a copper-doped ⟨100⟩ crystal of lead containing bismuth.

a week to achieve this low background. The Columbia crystal was given an additional anneal at 50°C for one week, producing a decrease in the decrement at 235°K from 3.05×10^{-5} to 2.85×10^{-5}. The three crystals of Fig. 1 are essentially of the same purity, except that the Semi-Elements crystal (Curve *A*) contains 300 ppm bismuth. Thus we are forced to conclude that the relaxation observed is not intrinsic to lead doped with gold but requires the presence of an impurity such as bismuth. Nevertheless, it is of interest to note that when these crystals are doped with the other noble metals copper and silver one again obtains identical behavior with each major peak yielding an activation energy equal to that measured for diffusion. The result for copper-doped lead is illustrated in Fig. 2. In Table 1 we give the activation energies and frequency factors for the six peaks in the three systems. In the same table we show for comparison the activation energies and frequency factors measured by diffusion. The agreement between relaxation and diffusion activation energies was regarded as strong evidence that we were measuring an intrinsic effect.

Upon extending this work to lower temperatures we found in each system that four peaks were present rather than two as illustrated in Fig. 3 for the silver-doped lead. In this figure we show Young's modulus as a function of temperature. The breaks in these curves as one moves from the unrelaxed to the relaxed modulus confirm the presence of four relaxation processes. Numbering the peaks in the direction of decreasing temperature 1, 2, 1′ and 2′ we find that peaks 1 and 1′ arise from one defect and peaks 2 and 2′ from another. This can be seen by equilibrating at the temperature of peak 2 and then monitoring the heights of all four peaks. It is found that 2 and 2′ rise while 1 and 1′ decay. The process can be reversed by equilibrating at the temperature of peak 1. In Table 2 we give the positions of the twelve peaks in the three systems and the ratios of various peak temperatures. Again we have strong evidence that the same type defects are present in all three systems. Since these peaks appeared in crystals with ⟨100⟩ symmetry but did not appear in a crystal of ⟨111⟩ symmetry,[1]

Table 1. Diffusion coefficients, $D = D_0 e^{-H/kT}$ and relaxation times, $\tau = \tau_0 e^{E/kT}$ for noble metals in lead

	Internal friction				
Peak	E(eV)	1 τ_0(sec)	E(eV)	2	τ_0(sec)
Copper	0.338	3×10^{-15}	0.305		1.9×10^{-16}
Silver	0.654	0.65×10^{-15}	0.610		0.18×10^{-16}
Gold	0.437	1.1×10^{-15}	0.409		0.377×10^{-16}

	Diffusion		
	H(eV)	D_0(cm^2/sec)	Reference
Copper	0.349	7.9×10^{-3}	4
Silver	0.663	74.5×10^{-3}	5
	0.630	46×10^{-3}	4
Gold	0.436	8.7×10^{-3}	6
	0.407	4.1×10^{-3}	7

Table 2. Temperatures and degrees K in which the peaks appear in the three noble metal-lead systems, plus peak ratios indicating similar processes in all three systems

	Peak position (°K)				Ratio		
	1	*1'*	*2*	*2'*	*1/2*	*1/1'*	*2/2'*
Copper	191	118	152	81	1.26	1.62	1.88
Silver	343	211	275	143	1.25	1.63	1.92
Gold	235	143	190	100	1.24	1.64	1.90

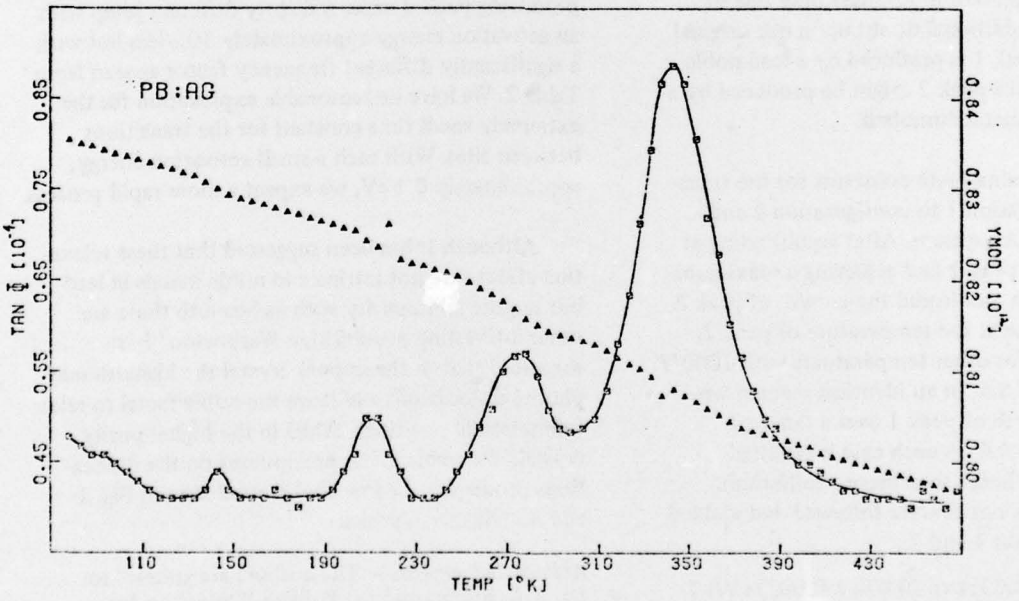

FIG. 3. Young's modulus vs temperature for silver-doped lead.

though it too contained 300 ppm bismuth, it is concluded that the defects have ⟨100⟩ symmetry.

Nowick[8] has shown that the only defect in a cubic system with ⟨100⟩ symmetry with two relaxation times is the ⟨100⟩ orthorhombic defect. Thus these results suggest that we have two ⟨100⟩ orthorhombic defect configurations.

As an aid in completely characterizing these configurations we have performed rate studies of the transition between the two configurations. The change in the defect concentrations producing the relaxation process is obtained by monitoring the relaxation strength Δ_M (in this case twice the peak height) as a function of time. Nowick[8] has shown that the product of Δ_M and T, the absolute temperature at which the relaxation occurs, is proportional to the product of the number of defects producing the relaxation and a term determined by the anelastic dipole strength of the relaxing defect. In each noble metal system a plot of $T\Delta_M$ from peak 1 vs that from peak 2 yields a straight line with a slope of 1. Since processes 1 and 2 have activation energies that differ by approximately 10% we assume that elastic dipole strengths of the relaxing defects are approximately equal. Thus the $T\Delta_M$ plots indicate that the breakup of one type 1 configuration produces only one of type 2. This casts additional doubt upon our original suggestion[1] that peak 1 is produced by a lead-noble metal dumbbell while peak 2 might be produced by a noble metal-noble metal dumbbell.

We have determined rate constants for the transition from configuration 1 to configuration 2 and vice versa in the PbAu system. After equilibrating at the temperature of peak 1 and achieving a maximum peak height we then monitored the growth of peak 2 as a function of time at the temperature of peak 2, and then repeated for other temperatures with $1000/T$ varying from 5.0 to 5.5. In an identical manner we monitored the growth of peak 1 over a range of $1000/T$ from 4.0 to 4.6. In each case it required approximately four hours to achieve equilibrium. Initially first order kinetics were followed and yielded for the decay of peaks 1 and 2.

$$K_1 = (0.032 \pm 0.003) \exp (0.098 \pm 0.002)\ \text{eV/kT}$$

$$K_2 = (0.011 \pm 0.004) \exp (0.066 \pm 0.006)\ \text{eV/kT}$$

A check on these activation energies was obtained by an independent determination of the equilibrium value of the ratio of peak heights as a function of temperature. This yielded the value $\Delta E = 0.032 \pm 0.026$ eV, in reasonable agreement with the results cited above.

In the range of these measurements the mean time of stay of a gold atom diffusing in lead is of the order of 10^{-6} sec. Since the time required to equilibrate from one interstitial configuration to another is approximately four hours it appears that a very large number of atomic jumps is required. Yet the activation energy measured for migration is 0.44 eV while the energy for a transition from one configuration to another is approximately 0.1 eV.

It appears that there are two distinct types of interstitial sites adjacent to a bismuth impurity and that the noble metal ion can make a transition from one of these sites to the other with much less energy than is required for a normal jump in the pure lattice. It further appears that upon the application of a stress interstitials in sites producing peak 1 migrate to equivalent sites around the bismuth impurity to relieve the stress making jumps like those made in the diffusion process. However, interstitials in other sites, producing peak 2 make a slightly different jump with an activation energy approximately 10% less but with a significantly different frequency factor as seen from Table 2. We have no reasonable explanation for the extremely small time constant for the transitions between sites. With such a small activation energy, approximately 0.1 eV, we expect a more rapid process.

Although it has been suggested that these relaxation effects are not intrinsic to noble metals in lead but require an impurity such as bismuth there are other interesting possibilities. Warburton[9] has suggested that in the impure crystal the bismuth may pin the dislocations and leave the noble metal to relax in interstitial positions. While in the higher purity crystals the noble metal precipitates on the dislocations producing the low background seen in Fig. 1 and no relaxation peaks.

Acknowledgements – The authors are grateful to Dr. A.A. Sagues and Dr. William Warburton for supplying crystals and helpful discussions. We are also indebted to Professors A. Nowick and L. Slifkin for enlightening discussions.

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Des pics de frottement interne similaires à ceux rapportés précédemment dans Pb–Au ont été observés dans Pb–Cu et Pb–Ag, mais on a trouvé qu'une impureté de Bismuth est nécessaire pour l'observation de l'effet. Des pics de relaxation de deux configurations intersticielles ortho-rhombiques ont été observés, on en déduit une cinétique particulière pour la transition d'une configuration à une autre.