helpful discussions.

*Work supported in part by U.S. Atomic Energy Commission.

†Postdoctoral Fellow of the Schweizerischer Nationalfonds.

[1]Y. E. Pokrovskii, Phys. Status Solidi (a) 11, 385 (1972), and references therein.

[2]C. Benoît à la Guillaume, M. Voos, and F. Salvan, Phys. Rev. B 5, 3079 (1972), and 7, 1723 (1973), and references therein.

[3]J. C. Hensel, T. G. Phillips, and T. M. Rice, Phys. Rev. Lett. 30, 227 (1973).

[4]We have fitted by equations using the spatial dependence of the FE density $n_x \propto \exp(-r/L)/r$, and find the homogeneous model of Eqs. (1) and (2) more satisfactory.

[5]Here $\alpha = (g8\pi^2 m^* k_B^2/h^3)(3/4\pi n_0)^{2/3} T^2 \exp(-\varphi/k_B T)$, from the Richardson-Dushman expression. For an e-h pair we use the degeneracy $g=16$, the optical mass $m^* = 0.19 m_0$, the density $n_0 = 2.16 \times 10^{17}$ cm^{-3} and the thermodynamic value $\varphi = 17$ K [see P. Vashishta, P. Bhattacharyya, and K. S. Singwi, Phys. Rev. Lett. 30, 1248 (1973)].

[6]Here $\beta = 4\pi(k_B/2\pi m_d^*)^{1/2}(3/4\pi n_0)^{2/3}$, where for FE the density-of-states mass $m_d^* = 0.335 m_0$ [see T. K. Lo, B. J. Feldman, and C. D. Jeffries, Phys. Rev. Lett. 31, 224 (1973)].

[7]Y. E. Pokrovskii and K. I. Svistunova, Pis'ma Zh. Eksp. Teor. Fiz. 17, 645 (1973) [JETP Lett. 17, 451 (1973)].

[8]J. Barrau, M. Heckmann, and M. Brousseau, J. Phys. Chem. Solids 34, 381 (1973), find for Si the formation time $t_R \sim 10^3 T^2/n_i$ sec; n_i is the initial density.

[9]L. M. Sander, H. B. Shore, and L. J. Sham, Phys. Rev. Lett. 31, 533 (1973); H. Büttner and E. Gerlach, J. Phys. C: Proc. Phys. Soc., London 6, L433 (1973); T. M. Rice, to be published.

[10]B. B. Zubov, V. P. Kalinushkin, T. M. Murina, A. M. Prokhorov, and A. A. Rogachev, Fiz. Tekh. Poluprov. 7, 1614 (1973) [Sov. Phys. Semicond. 7, 1077 (1974)].

[11]R. S. Markiewicz, J. P. Wolfe, and C. D. Jeffries, Bull. Amer. Phys. Soc. 18, 1606 (1973), and to be published.

[12]B. J. Feldman, to be published; a preliminary account was given in B. J. Feldman and R. D. Knight, Bull. Amer. Phys. Soc. 19, 359 (1974).

[13]T. K. Lo, to be published, and references therein.

[14]Vashishta, Bhattacharyya, and Singwi, Ref. 5; Vashishta, Ref. 5. The values of ρ quoted are for unstrained Ge (P. Vashishta, private communication).

[15]T. K. Lo, B. J. Feldman, and C. D. Jeffries, Phys. Rev. Lett. 31, 224 (1973).

Experimental Evidence for Split Interstitials in Copper*

J. Holder
Department of Geology and Materials Research Laboratory, University of Illinois, Urbana, Illinois 61801

and

A. V. Granato and L. E. Rehn†
Department of Physics and Materials Research Laboratory, University of Illinois, Urbana, Illinois 61801
(Received 21 January 1974)

The magnitudes, anisotropy, and temperature dependences of the three independent elastic constants of copper irradiated below 4 K with thermal neutrons provide evidence for the ⟨100⟩ split configuration of free interstitials and thermally excited resonance modes, and lead to a model for the configuration of the I_C close-pair defect.

Much is known about interstitials in copper as a result of intensive research over the past two decades.[1] However, very little is known about the geometry of the interstitial. Calculations for the free interstitial, beginning with the work of Huntington and Seitz,[2] favor[1] the ⟨100⟩ split interstitial geometry over the ⟨110⟩ split configuration (crowdion), or the interstitial located at the bcc position. Recently, Ehrhart and Schilling[3] have excluded the crowdion configuration for Al from measurements of diffuse x-ray scattering. No models have yet been firmly established for the close-pair configurations.

Also recently, Dederichs, Lehmann, and Scholz[4] have found by means of a computer simulation of a copper lattice that a ⟨100⟩ split interstitial should have two resonance modes of frequency of about $\omega_m/7$, where ω_m is the maximum lattice frequency. They point out that the split interstitial is strongly polarizable by an external shear stress, so that the same weak restoring force which leads to the low-frequency libration mode also leads to large negative anisotropic changes of the static elastic shear constants. Since the displacements produced by a C_{44}-type deformation are in the same direction as those of the libration mode (as can be seen from their Fig. 2), C_{44} is more strongly affected than $C' = (C_{11} - C_{12})/2$. One would suspect that this anisotropy would be reversed for a $\langle 110 \rangle$ split interstitial, and detailed calculations[5] show that this is so.

Indeed, elastic constant changes and their temperature dependences are known to be especially well suited for determining the symmetry of defects. This is in contrast with most property-change measurements which merely count the number of defects. There are five different ways which can be identified for point defects to affect the elastic constants. Four of these are well known; the last is introduced here.

(1) *Dislocation pinning.*—This is a relatively large indirect effect which must be eliminated for studies of the direct point defect effects.

(2) *The bulk effect.*—This is a result of the change in number and strength of interatomic bonds caused by the creation of point defects. It is expected[6-8] to be relatively small, but of the same order of magnitude as most property changes ($d \ln c / d\gamma \sim 1$, where c is the elastic constant, and γ is the concentration of point defects).

(3) *Polarization effects.*—These can occur when the atoms associated with the defects are not at perfect crystal lattice sites. In this case, an internal strain can be produced by the application of an applied stress, and the additional strain causes a decrease in the measured elastic constant.[9] This effect may be quite large, and the variation of the magnitude among different elastic constants depends upon the symmetry of the defect.[4]

(4) *Relaxation effects.*—These involve the thermally activated, stress-induced ordering of preferential defect orientations.

(5) *Thermally excited resonance-mode effects.*—These introduce changes in the temperature dependence of the elastic constants, if the defects change the vibrational spectrum by adding new low-frequency Einstein-like oscillator frequencies at the expense of lattice modes.

In summary, since a cubic interstitial is not polarizable, such a defect in a dislocation-free crystal would be expected to produce only a bulk effect, or a change which is small and relatively temperature independent. Isolated split interstitials and close pairs could produce effects (2)–(5), resulting in relatively large elastic constant changes with strong temperature dependence [(3)–(5)]. The effect at zero temperature would be expected to be large and anisotropic for the shear constants, and the temperature dependence should depend on the defect symmetry and the relaxation and resonant frequencies.

The changes were measured in the three independent cubic elastic constants of Cu irradiated below 4 K with thermal neutrons and subsequently annealed through stage I.[10] Details of the experiment and analysis will be given later and only a brief account is presented here. The thermal neutrons create displacements through (n,γ) capture reactions with mean atom recoil energies of 382 eV.[11] Measurements of C_{11}, C_{44}, C', and attenuation were made at 10 MHz with a pulse-echo superposition technique apparatus[12,13] with sensitivity for frequency changes of $1/10^7$ or 1 Hz. At temperatures near 40 K, the precision is limited by temperature control to about $1/10^6$. The dislocation effect was eliminated by using low-dislocation-density specimens irradiated with 10^{17} fast neutrons/cm^2 (approximately 10^{-5} defects[14]) prior to the experiment. The irradiation and annealing were done in the low-temperature irradiation facility at Oak Ridge National Laboratory.[15,16] The defect density was determined from resitivity and attenuation measurements.

The relative elastic-constant changes per unit concentration of Frenkel defects, $d \ln c / d\gamma$, are summarized in Table I for the bulk modulus B and the two shear constants C_{44} and C'. A value of 2.5 $\mu\Omega$ cm/at.% of Frenkel defects was used to calculate the defect concentration, which was $\sim 4 \times 10^{-6}$. Of all the widely varying results reported, the total changes found here during irradiation are in good agreement only[10] with the change found by Townsend *et al.*[7] This total

TABLE I. Irradiation-induced changes in the elastic constants per unit concentration of Frenkel pairs ($d \ln c / d\gamma$).

	Elastic constant		
	B	C_{44}	C'
Total change	−2	−15.8	−18.1
Stage-I_D change	0 ± 1	−31	−15

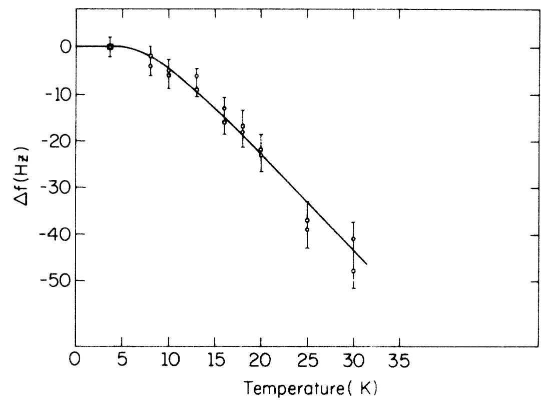

FIG. 1. Difference in the temperature dependence of C' resonant frequency produced by the defects which anneal in the 35–45-K temperature range (stage I_D). Circles, the difference in resonant frequencies after annealing at 45 and 35 K. Since no significant change was observed between 30 and 35 K, both the differences between the 45- and 35-K results and between the 45- and 30-K results (squares) are shown. Solid curve, calculated for Einstein oscillators with $\omega_E = 5\times10^{12}$ Hz. Error bars, our estimate of the experimental uncertainty.

change includes the effects of close pairs, isolated defects, and any clusters which may have been produced during irradiation. The percentage elastic-constant changes measured at 3.6 K after pulse annealing to different temperatures were found to differ for different elastic constants in the same annealing range, and for different annealing regions for the same elastic constant. The last row of Table I gives results for the changes found for stage I_D, which should be a measure of the effect for isolated interstitials.

The bulk modulus should be unaffected by polarization effects. The value of -2 found for irradiation is small and the change observed through stage-I_D annealing was less than 1 in absolute magnitude. We conclude that the relatively large negative effect found for the shear constants is a polarization and not a bulk effect. The sign, magnitude, and anisotropy observed is that expected[4] for a ⟨100⟩ split interstitial. If the calculations of of Dederichs[5] are accepted, then the measured anisotropy is also evidence against the ⟨110⟩ split configuration.

Measurements of the temperature dependence of the C' constant before and after annealing through stage I_D show that the defects responsible for I_D give a change in C' which is strongly temperature dependent, as shown in Fig. 1. In fact, the temperature-dependent part of the change at 30 K is about $\frac{1}{2}$ as large as the temperature-independent part, which is not shown. The temperature dependence is linear above 10 K and levels off below 10 K. This temperature dependence is not that characteristic of a relaxation process. However, thermal excitation of a low-lying resonant mode could contribute a temperature dependence of this form. The theory of the temperature dependence of elastic constants[17] is similar to that for the thermal energy, as given, for example, in the Debye theory. The dependence on temperature arising from lattice modes is quartic (linear) at low (high) temperatures. Einstein oscillators contribute a term which is exponential (linear) at low (high) temperatures. For low-frequency oscillators, the linear dependence occurs in the low-temperature regime of the lattice modes so that even relatively small numbers of low-frequency lattice modes can be detected with sufficiently sensitive apparatus at low temperatures.

The solid line in Fig. 1 is the calculated temperature dependence of the elastic constant change for Einstein oscillators of frequency $\omega_E = 5\times10^{12}$ Hz. In a more detailed discussion given later, we show that the magnitude of the effect is reasonable for the number of defects involved, and that the estimated accuracy of the frequency is about 30%. This value of ω_E is in excellent agreement with the calculation by Dederichs, Lehmann, and Scholz[4] of about 6×10^{12}, providing strong evidence again that the interstitial configuration is split along ⟨100⟩. This is believed to be the first experimental evidence of interstitial resonant modes in metals.

No relaxation effects were found for the free interstitials of stage I_D. However, a sharp relaxation, centered at about 18 K, was observed in the temperature dependence of C_{44}, but not in that of C'. We have determined that the relaxation disappears on annealing through stage I_C. These results are consistent with kilohertz measurements by Nielson and Townsend.[18]

In general, the only condition necessary in order for the relative energies of the equivalent positions involved in the relaxation to be unaffected by a C' measurement is that the positions possess mirror symmetry about a (100) plane containing the vacancy. A relaxation involving motion of the interstitial center of mass seems unlikely in view of the very low activation energy (0.017 eV) determined from the measurements. Thus the symmetry requirements apply to the

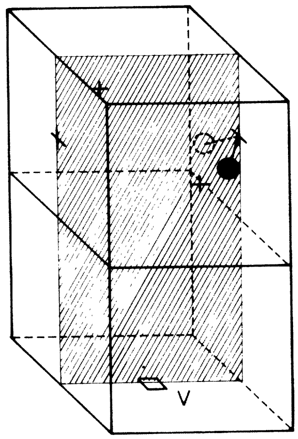

FIG. 2. Proposed model for the I_C defect; 4 of the 24 equivalent sites for the center of mass of the interstitial have been marked with small crosses. The equivalent position into which the split interstitial relaxes is shown by a dashed circle.

interstitial rather than to the close-pair complex as a whole.

These criteria lead to a model for the I_C defect, shown in Fig. 2. The equivalent position into which the interstitial relaxes is indicated by a dashed outline. This configuration places the interstitial center of mass in the same lattice positions as in the model proposed by Peretto *et al.*[19] to explain their observations of a magnetic aftereffect for the I_C defect in nickel. Their model assumes a ⟨100⟩ interstitial orientation inconsistent with the mechanical relaxation. However, they conclude that the magnetic aftereffect involves motion of the interstitial center of mass between equivalent positions (shown by the crosses in Fig. 2), so the present model is consistent with the magnetic measurements in nickel as well as the mechanical measurements in copper.

We thank R. R. Coltman, C. E. Klabunde, and F. W. Young, Jr., of Oak Ridge National Laboratory for providing and operating the low-temperature irradiation facility and for preparing the crystals for this experiment.

---

*Research supported in part by the National Science Foundation under Grant No. GH-33634 and in part by the U. S. Atomic Energy Commission under Contract No. AT(11-1)-1198.

†Present address: Institut für Festkörperforschung der Kernforschungsanlage Jülich, Jülich, Germany.

[1]See articles in *Vacancies and Interstitials in Metals, Proceedings of an International Conference, Jülich, Germany, 1968,* edited by A. Seeger *et al.* (North-Holland, Amsterdam, 1970).

[2]H. B. Huntington and F. Seitz, Phys. Rev. 61, 315 (1942).

[3]P. Ehrhart and W. Schilling, Phys. Rev. 8, 2604 (1973).

[4]P. H. Dederichs, C. Lehmann, and A. Scholz, Phys. Rev. Lett. 31, 1130 (1973).

[5]P. H. Dederichs, unpublished work cited in Ref. 4.

[6]G. J. Dienes, Phys. Rev. 86, 228 (1952).

[7]J. R. Townsend, J. A. DiCarlo, R. L. Nielsen, and D. Stabell, Acta Met. 17, 425 (1969).

[8]J. Holder and A. V. Granato, Phys. Rev. 182, 729 (1968).

[9]M. Pistorious and W. Ludwig, in *Vacancies and Interstitials in Metals, Proceedings of an International Conference, Jülich, Germany, 1968,* edited by A. Seeger *et al.* (North-Holland, Amsterdam, 1970), Vol. 2, p. 558.

[10]L. E. Rehn, J. Holder, A. V. Granato, R. R. Coltman, and F. W. Young, Jr., to be published.

[11]R. R. Coltman, Jr., C. E. Klabunde, D. L. McDonald, and J. K. Redmond, J. Appl. Phys. 33, 3509 (1962).

[12]J. Holder, Rev. Sci. Instrum. 41, 1355 (1970).

[13]D. Read and J. Holder, Rev. Sci. Instrum. 43, 933 (1972).

[14]F. W. Young, Jr., private communication.

[15]R. R. Coltman, T. H. Blewitt, and T. S. Noggle, Rev. Sci. Instrum. 28, 357 (1957).

[16]R. R. Coltman, C. E. Klabunde, and J. K. Redman, Phys. Rev. 156, 715 (1967).

[17]G. Leibfried and W. Ludwig, in *Solid State Physics,* edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1961), Vol. 12, p. 275.

[18]R. L. Nielsen and J. R. Townsend, Phys. Rev. Lett. 21, 1749 (1968).