the spin structure of the various phases if at all possible. We note that if our phase diagram is not correct even spiral[17] or more complicated phases are not out of the question. We would also urge a more careful experimental examination of the region near the bottom of the dashed phase line to determine if an actual critical point exists.

[1] M. F. Panczyk and E. D. Adams, Phys. Rev. 187, 321 (1969).

[2] M. F. Panczyk and E. D. Adams, Phys. Rev. A 1, 1356 (1970).

[3] J. M. Dundon and J. M. Goodkind, Phys. Rev. Lett. 32, 1343 (1974).

[4] T. P. Bernat and H. D. Cohen, Phys. Rev. A 7, 1709 (1973).

[5] W. P. Kirk, E. B. Osgood, and M. Garber, Phys. Rev. Lett. 23, 833 (1969).

[6] S. B. Trickey, W. P. Kirk, and E. D. Adams, Rev. Mod. Phys. 44, 668 (1972).

[7] R. B. Kummer, E. D. Adams, W. P. Kirk, A. S. Greenberg, R. M. Mueller, C. V. Britton, and D. M. Lee, Phys Rev. Lett. 34, 517 (1975).

[8] W. P. Halperin, C. N. Archie, F. B. Rasmussen, R. A. Buhrman, and R. C. Richardson, Phys. Rev. Lett. 32, 927 (1974).

[9] A. K. McMahan, J. Low Temp. Phys. 8, 115 (1972).

[10] L. I. Zane, J. Low Temp. Phys. 9, 219 (1972).

[11] A. K. McMahan and J. W. Wilkins, Phys. Rev. Lett. 35, 376 (1975).

[12] A concise method of derivation is given by W. J. Mullin, Phys. Rev. B. (to be published).

[13] G. A. Baker, Jr., H. E. Gilbert, J. Eve, and G. S. Rushbrooke, Phys. Rev. 164, 800 (1967).

[14] W. P. Kirk and E. D. Adams, Phys. Rev. Lett. 27, 392 (1971).

[15] L. Goldstein, Phys. Rev. A 8, 2160 (1973).

[16] R. A. Guyer, Phys. Rev. A 9, 1452 (1974).

[17] T. A. Kaplan, Phys. Rev. 116, 888 (1959).

Neutron-Inelastic-Scattering Measurements of Phonon Perturbations by Defects in Irradiated Copper*

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Neutron-scattering measurements have been made at 10 *K* of phonons in a copper crystal neutron-irradiated at 4 *K*. The results, though clearly showing q-dependent defect-phonon perturbation effects, could not be explained entirely by simplified calculations for the ⟨100⟩ split interstitial. A 300-K anneal removed the irradiation-induced line broadening and frequency shifts but only ~ 50% of the additional peak structure, which was completely removed only after an 800-K anneal.

It is well established that the irradiation of crystals at very low temperatures produces vacancies and interstitials, and extensive research has been focused on determining the stable structure of self-interstitials, particularly in fcc metals. Recent theoretical studies have predicted that the ⟨100⟩ dumbbell configuration is the stable form for the interstitial in Cu[1] and this has been corroborated by diffuse x-ray[2] and elastic-constant measurements.[3] The theoretical work predicted that the dumbbell interstitial possesses low-frequency librational modes.[1] Wood and Mostoller[4] and Schober, Tewary, and Dederichs[5] have shown that these can undergo strong resonant hybridization with the phonons of the host crystal, which possibly could be detected by neutron scattering even for very low concentrations (≪ 1%) as in the somewhat analogous case of $KCl:CN^-$ recently studied by Walton, Mook, and Nicklow.[6] The direct observation of such resonant modes would provide new information about the structure of the interstitial, its dynamical properties, and the interatomic forces which couple it to the lattice.

Here we report the first results of neutron-coherent-inelastic-scattering experiments on perturbed phonons in a neutron-irradiated crystal. The experiment was carried out on a high-purity, low-dislocation-density crystal of dimensions $0.6\times1.8\times3.8$ cm^3, with the $[1\bar{1}0]$ direction parallel to the longest dimension. The crystal was irradiated by *thermal* neutrons at 4.2 K for 24 days in the low-temperature facility at Oak Ridge National Laboratory.[7] The concentration of Frenkel pairs was ≈40 ppm randomly dispersed through the crystal. After irradiation the sample was transferred at 4.2 K to a liquid-helium cryostat on the triple-axis spectrometer at the

Oak Ridge high-flux isotope reactor. Constant-Q measurements were made at temperature $\lesssim 10$ K on the sample as irradiated, after several annealing treatments, and on an unirradiated sample.

The search for resonant-mode effects was carried out for the transverse phonon branch in the [100] direction because theoretical studies[1,4,5] indicated that this branch is strongly perturbed by the interstitials. The predicted perturbation was, however, extremely small because of the very low defect concentration, so that extraordinarily good resolution was required for the measurements. An effective resolution of approximately 0.025 THz [full width at half-maximum (FWHM)] was achieved for phonon frequencies in the range where the effects were expected, 0.3–1.5 THz (1 THz$\approx$4 meV), by the use of the (113) Bragg reflections of Ge crystals having small mosaic spreads of $\sim 0.05°$ as monochromator and analyzer; tight horizontal beam collimation of 10′ (FWHM) before and after the sample; and a scattering configuration which gave nearly perfect focusing conditions.[8] It is important to note, however, that focusing to achieve good frequency resolution did not achieve simultaneously good $\vec{q}$ resolution. Thus a measurement carried out for $\vec{q} = (0, 0, \zeta)2\pi/a$ contained an appreciable sampling of the dispersion relation for $\zeta \pm 0.01$. This resolution was extremely costly in spectrometer time; a scan for each q required at least 18 h and most were run for 30–40 h.

The most complete results were obtained for $\vec{q} = (0, 0, 0.06)2\pi/a$ and are shown in Fig. 1. For the as-irradiated crystal significant excess intensity is observed on the high-frequency side of the main phonon peak, which is itself shifted 0.015 THz below the corresponding peak of the perfect crystal. This extra intensity is reduced and the shift of the phonon peak is eliminated after a room-temperature anneal. A further 800-K anneal for 2 h in high vacuum removed this extra intensity while leaving the peak position unchanged. The peak asymmetry and the high-frequency tail that remain after the 800-K anneal are expected consequences of the relatively large angular divergence ($\sim 1.5°$ FWHM) of the neutron beam in the direction perpendicular to the scattering plane. Peak-shape calculations, obtained by convoluting the instrumental resolution function with the perfect-crystal dispersion relation, are in very good agreement with the 800-K-anneal results, as illustrated in Fig. 1(c). These calculations also explain the 0.005-THz shift of the observed peak away from the "true" frequency calculated for $\vec{q} = (0, 0, 0.06)2\pi/a$ from low-temperature elastic-constant data.[9] This shift is independent of the irradiation-induced shift. The dashed lines in Figs. 1(a) and 1(b) are the peak *shape* of Fig. 1(c) and indicate that there also may be a slight broadening of the phonons as a result of the irradiation. The results for an unirradiated sample (not shown) are virtually indistinguishable from those shown in Fig. 1(c).

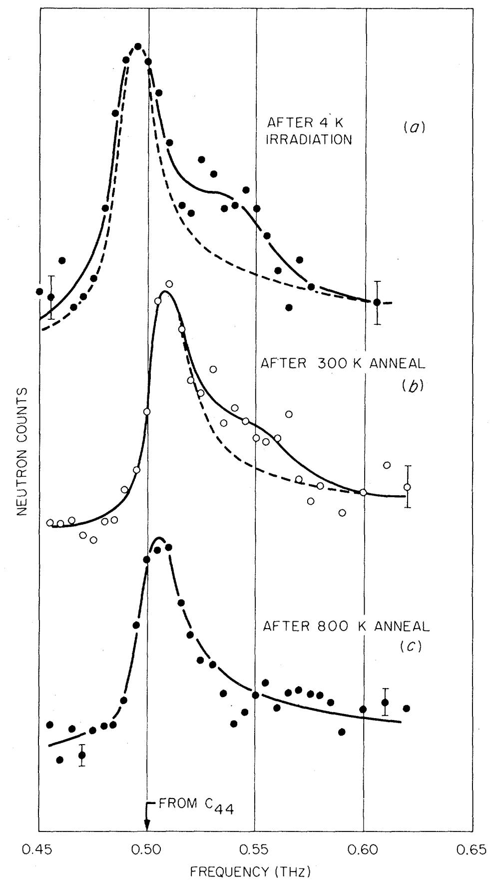

FIG. 1. Frequency distribution of neutrons inelastically scattered from irradiated copper at 10 K for $\vec{q} = (2, 2, 0.06)2\pi/a$. The solid line shown in scan (c) and the dashed lines in scans (a) and (b) are calculations of the peak shape expected from the instrumental resolution. The arrow indicates the frequency calculated from the C_{44} elastic constant measured at 4 K; see Ref. 9.

The peak *shapes* obtained for the as-irradiated sample at several wave vectors are compared to the perfect-crystal data in Fig. 2. Generally the peaks for the irradiated sample were slightly broadened, and additional q-dependent intensity occurred on the high-frequency sides for ζ in the range 0.04–0.07. Data for $\zeta = 0.09$ were essen-

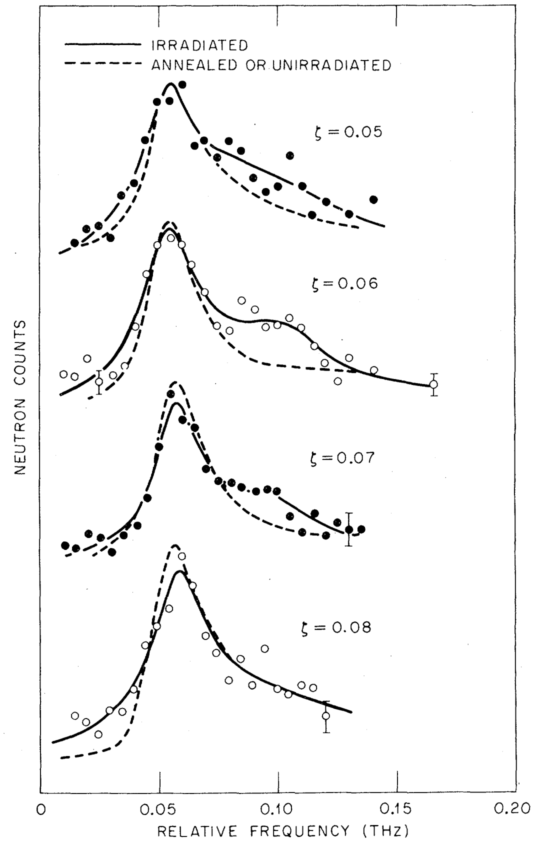

FIG. 2. Frequency distributions of neutrons scattered from irradiated copper 10 K for $\vec{q}=(2,2,\zeta)2\pi/a$. The frequency scale shown is a relative scale to allow visual comparison of the data obtained for different ζ. The frequencies corresponding to the peak positions vary from ~0.415 THz for $\zeta=0.05$ to ~0.665 THz for $\zeta=0.08$. The dashed lines are the peak *shapes* for the perfect crystal.

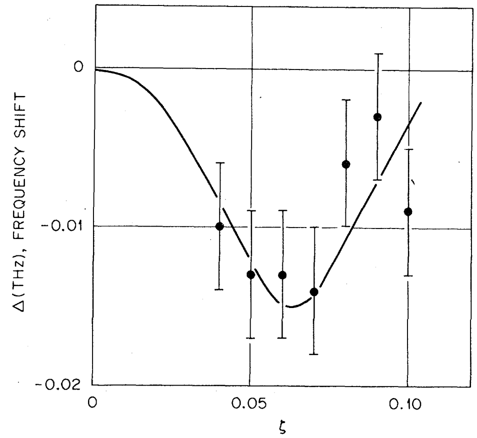

FIG. 3. Phonon frequency shifts for irradiated copper. $\Delta=\nu_{IR}-\nu_{AN}$, where ν_{IR} and ν_{AN} correspond respectively to the frequencies measured for the irradiated crystal and for the crystal annealed at 300 K as explained in the text.

tially the same as those for $\zeta=0.08$. The irradiation had no measurable effect on the peak *shape* observed for $\zeta=0.10$.

The influence of annealing also appears to be somewhat q dependent. After the 300-K anneal the results for peak shapes and peak positions for $\zeta=0.07$–0.10 were indistinguishable from those observed for the unirradiated crystal. However, for $\zeta=0.04$–0.06 the results were similar to those shown in Fig. 1; i.e., the peaks had shifted back to the perfect-crystal positions but some of the high-frequency structure remained. The 800-K anneal restored the crystal to its preirradiated condition.

For all wave vectors investigated, the 300-K anneal eliminated the *shifts* of the phonon frequencies. The results obtained for the peak shift, Δ, as a function of ζ are shown in Fig. 3. The frequencies were determined from the locations of the maxima of lines drawn by eye through the intensity distributions, i.e., the full lines shown in Figs. 1(a), 1(b), and 2. The uncertainties shown in Fig. 3 are estimates, so that the values for Δ should be interpreted with caution. Nevertheless, it appears that Δ is not inconsistent with a quasi resonance type of behavior expected for the case of large damping (discussed below). An estimate of the resonance frequency from these results, i.e., the frequency corresponding to ζ ~0.1 where $\Delta\to 0$, gives a value ~0.8–0.9 THz, which is consistent with theoretical estimates[1] and with the value ~0.8 THz obtained from elastic-constant measurements.[3]

However, serious difficulties remain with the interpretation. Approximate calculations based on a simplified theoretical treatment of the ⟨100⟩ split interstitial[4,5] yield results for the neutron scattering cross section that vary between two extreme cases depending on the assumed interatomic forces and/or defect concentration. At one extreme the damping is small, and a distinct double-peaked structure is predicted for the neutron scattering cross section for $\vec{q}$ near resonance. Calculations for this case were in fact carried out to fit the experimental results at $\vec{q}=(0,0,0.06)2\pi/a$. Although a fairly good fit could be achieved with a reasonable choice of parameters, the experimental results at higher $\vec{q}$ values did not follow the predictions of the simple model. At the other extreme the damping is large, and the scattering cross section has a single broadened peak that is shifted below and above the host-crystal dispersion relation for $\vec{q}$ below or above the resonance region, respectively; approximately at resonance $\Delta \rightarrow 0$. In this case, a combination of focusing and a strongly $\vec{q}$-dependent frequency shift could conceivably lead to double peaks or structure in constant-Q measurements. However, consideration of (1) the resolution used, (2) the shifts required for the observed peak structure, and (3) the results obtained after the 300-K anneal indicate that this explanation for the structure observed is unlikely. For either of these cases double peaks would disappear after an anneal at 300 K.

It would appear that the present results cannot be completely explained in terms of the simplified calculations for the $\langle 100 \rangle$ split interstitial. The absence of structure in the phonon peaks of the unirradiated and the 800-K-annealed samples indicate that this structure is produced by the low-temperature irradiation. The fact that it remains after the 300-K anneal is unexpected and surprising. One possible conclusion is that the split interstitial may be responsible for the frequency shifts and line broadening observed for the irradiated sample as theoretically predicted for the case of large damping, and that the additional structure observed for $\zeta \leq 0.07$ for the irradiated crystal is due to an as yet unspecified form of radiation damage. This interpretation would tend to bring the results of our annealing studies into better conformity with those of other experiments. From diffuse x-ray and resistivity studies on Cu it has been concluded that isolated interstitials anneal well below 100 K. This conclusion is also consistent with the annealing of the irradiation-induced changes in the elastic constants of Cu.[3] We are nevertheless still left with an effect (the peak structure for $\zeta \leq 0.07$) attributable to the low-temperature irradiation, which anneals only ~50% at 300 K, whereas other measurements indicate that 90% of the effect so produced anneals below 300 K.

Although considerable theoretical and experimental work remains it seems clear that the neutron-scattering study of the perturbation of phonons resulting from radiation damage can be very fruitful. The determination of the resonance frequency and of the degrees of hybridization for different crystallographic directions should provide considerable information about the interatomic forces which couple the interstitial to the lattice.

The authors wish to express their gratitude to Mark Mostoller for many helpful discussions. The valuable experimental assistance of C. E. Klabunde, J. M. Williams, and J. L. Sellers is gratefully acknowledged.

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*Research sponsored by the U. S. Energy Research and Development Administration under contract with Union Carbide Corporation.

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

[2]P. Ehrhart, H. G. Houbold, and W. Schilling, in *Festkörperprobleme,* edited by H.-J. Queisser (Pergamon, New York, 1974), Vol. 14, p. 87.

[4]J. Holder, A. V. Granato, and L. E. Rehn, Phys. Rev. Lett. 32, 1054 (1974), and Phys. Rev. B 10, 363 (1974).

[4]R. F. Wood and Mark Mostoller, Phys. Rev. Lett. 35, 45 (1975).

[5]H. R. Shober, V. K. Tewary, and P. H. Dederichs, Z. Phys. B 21, 255 (1975).

[6]D. Walton, H. A. Mook, and R. M. Nicklow, Phys. Rev. Lett. 33, 412 (1974).

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

[8]M. J. Cooper and R. Nathans, Acta Crystallogr. 23, 357 (1967).

[9]W. C. Overton, Jr., and John Gaffney, Phys. Rev. 98, 969 (1955).