Pure Nuclear Quadrupole Resonance in Superconducting and Normal Double-hcp ^{139}La Metal*

W. M. POTEET, R. F. TIPSWORD, AND C. D. WILLIAMS
Department of Physics, Virginia Polytechnic Institute, Blackburg, Virginia 24061
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The $\frac{3}{2}$ - $\frac{5}{2}$ and $\frac{5}{2}$ - $\frac{7}{2}$ pure quadrupole-resonance frequencies for the two inequivalent sites of double hcp ^{139}La metal have been measured in the superconducting and normal states, giving quadrupole coupling constants of 7.700(2) and 6.798(4) MHz in the normal state and shifts of about 0.10 and 0.14%, respectively, in the superconducting state. The asymmetry parameter was experimentally zero.

IN this paper we report a measurement of the pure nuclear-quadrupole-resonance (PQR) frequencies of ^{139}La in double-hcp (α-phase) La metal in both its superconducting and normal states. PQR associated with the $\frac{3}{2}$-$\frac{5}{2}$ and $\frac{5}{2}$-$\frac{7}{2}$ transitions in the spin-$\frac{7}{2}$ ^{139}La nucleus was observed at both inequivalent sites in the double-hcp structure[1] over the temperature range 4.2–12°K, and the results for the corresponding $\frac{5}{2}$-$\frac{7}{2}$ PQR frequencies are indicated by the two sets of data points in Fig. 1. We are of course unable to say which set is associated with the A-site resonance and which with the equivalent B and C sites[1] (in the $ABAC$ stacking sequence for the double-hcp structure), since there exists no sufficiently accurate information on the relative electronic contributions to the electric field gradient (EFG) at these sites. Our results for the $\frac{3}{2}$-$\frac{5}{2}$ and $\frac{5}{2}$-$\frac{7}{2}$ PQR frequencies in the normal state give the values 7.700(2) and 6.798(4) MHz for the quadrupole coupling constant $|e^2qQ/h|$ at the two sites (a difference of about 13%), and the simple average of these values, 7.25 MHz, agrees reasonably well with the average quadrupole coupling constant 7.8(3) MHz observed in recent NMR measurements by Narath.[2] The corresponding shifts in the magnitude of the total EFG on passing from the normal to the superconducting state are +0.10 and +0.14% and occur at about 4.5°K, coinciding with the observed T_c for our sample.

The 99.5%-pure 200-mesh lanthanum powder used in this experiment was obtained from Ronson Metals Corp. The powder samples were sealed in a vacuum tube and after annealing at about 220°C for 24 h the temperature was decreased slowly to room temperature. X-ray diffraction analysis indicated that at least 95% of the sample was in the desired double-hcp structure. The temperature measurements were made with a conventional germanium resistance thermometer and the transition temperature T_c was obtained by means of 100-Hz mutual-inductance measurements. The 4.5°K value for T_c obtained here is about 0.4°K lower than the usual value for pure double-hcp La. This could possibly be due to impurities; 0.1-at. % gadolinium, for example, would account for such a depression of T_c.[3]

The spectrometer, which was first described by Robinson[4] and later modified by Dutcher and Scott,[5] was operated in the superregenerative mode, quenched at a rate of 1.4 kHz, and frequency modulated at 100 Hz. By operating the spectrometer in the superregenerative mode, the most sensitive operating point was utilized to full advantage.[6] Using the appropriate decoupling and filter network, the first stage in the rf oscillator, as shown in Fig. 2, was quenched with an

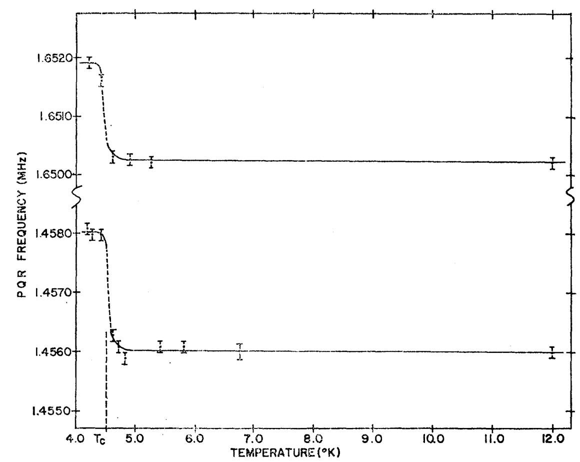

FIG. 1. PQR frequencies for the $\frac{5}{2}$ - $\frac{7}{2}$ transition at the two inequivalent sites of double-hcp ^{139}La metal.

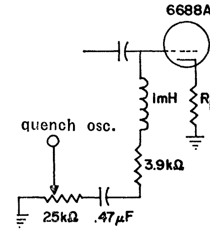

FIG. 2. Quenching circuit for the Robinson spectrometer.

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[1] F. H. Spedding, A. H. Daane, and K. W. Herrmann, Acta Cryst. 9, 559 (1956).

[2] A. Narath, Phys. Rev. 179, 359 (1969).

[3] D. K. Finnemore *et al.*, Phys. Rev. 137, A550 (1965).

[4] F. N. H. Robinson, J. Sci. Instr. 36, 481 (1959).

[5] D. H. Dutcher, Jr., and T. A. Scott, Rev. Sci. Instr. 32, 457 (1961).

[6] J. R. Whitehead, *Super-Regenerative Receivers* (Cambridge University Press, New York, 1950).

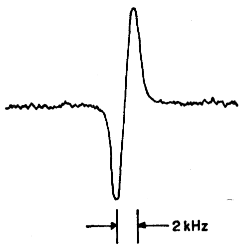

FIG. 3. Recorded signal for the higher-frequency $\frac{5}{2}$-$\frac{7}{2}$ transition in superconducting ^{139}La.

external audio oscillator. With this method and a PAR JB-4 lock-in amplifier detection system, the signal-to-noise ratio on all lines was at least 25:1. The recorded resonance signal for the higher-frequency $\frac{5}{2}$-$\frac{7}{2}$ transition in the superconducting state is shown in Fig. 3. The linewidth estimated from the recorded signal was about 2 kHz for all lines. Turning on the quench oscillator caused a change in the center frequency of the spectrometer relative to that for cw operation with the quench turned off. The data were taken by turning the quench oscillator off and counting the cw frequency with an electronic counter as a resonance was observed. The effect on the frequency by turning off this quench oscillator was determined to be essentially the same for each measurement and was measured by using a calibrated crystal oscillator with several different crystals. The crystal frequency was measured while passing through the observed oscillator signal in the same way as the resonance frequency was measured.

Our original motivation to measure the PQR frequency shifts between superconducting and normal double-hcp lanthanum stemmed from a letter by Hamilton and Jensen[7] in which they proposed a new mechanism for superconductivity in lanthanum and uranium metals. For double-hcp lanthanum this mechanism would presumably take the form of a significant indirect-exchange coupling (via s-f scattering) between opposite-spin electrons occupying $4f$-band states just above the normal Fermi surface. This coupling is suggested by the antiferromagnetic character of double-hcp (β-phase) cerium metal below 12°K.[8] A marked increase in the number of electrons occupying this $4f$ band on passing from the normal to the superconducting state of double-hcp La would then presumably lead to a significant shift in the electronic contribution to the EFG's. A simple model incorporating this mechanism, worked out by Kuper, Jensen, and Hamilton,[9] also indicated that superconducting La might exhibit significant departures from BCS[10] predictions in the case of appreciable $4f$-band occupation.

In the meantime, however, considerable experimental work[11] has indicated that the properties of superconducting double-hcp La are fairly well described in terms of phonon-induced electron-electron interactions as assumed in BCS theory, and that significant departures from BCS behavior of the nature indicated by Hamilton and Jensen are not very likely. Moreover, the BCS-like superconductors indium[12] and gallium,[13] for example, are observed to have PQR frequency shifts (from the normal state) of about -2 and $+0.006\%$, respectively. We conclude that our observations of the PQR frequency shifts in double-hcp La also lend no tangible support to the idea that the Hamilton-Jensen mechanism contributes appreciably to superconductivity in this metal.

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[7] D. C. Hamilton and M. A. Jensen, Phys. Rev. Letters **11**, 205 (1963).

[8] *The Rare Earths*, edited by F. H. Spedding and A. H. Daane (John Wiley & Sons, Inc., New York, 1961).

[9] C. G. Kuper, M. A. Jensen, and D. C. Hamilton, Phys. Rev. **134**, A15 (1964).

[10] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).

[11] See, for example, Ref. 3; W. E. Gardner and T. F. Smith, Phys. Rev. **138**, A484 (1965); J. S. Rogers and S. M. Khanna, Phys. Rev. Letters **20**, 1284 (1968).

[12] W. W. Simmons and C. P. Slichter, Phys. Rev. **121**, 1580 (1961).

[13] R. H. Hammond and W. D. Knight, Phys. Rev. **120**, 762 (1960).