

be helpful to consider the  $|dI/dV| - V$  curve shown in Fig. 3, as representing an "equivalent density of states" of the combined structure of two superconductors in the presence of a microwave field.

Further characteristics of the interaction will be covered in a future publication.

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<sup>8</sup>Notice that the filled band is on one side of the barrier while the empty band is on the other side.

## NUCLEAR MAGNETIC RESONANCE IN CHROMIUM METAL\*

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The nuclear magnetic resonance of naturally abundant (9.5%)  $\text{Cr}^{53}$  has been observed in pure (crystal-bar) chromium metal at temperatures above the antiferromagnetic ordering temperature  $T_N$  of  $40^\circ\text{C}$ , and the Knight shift of the resonance has been measured. We have also observed the  $\text{Cr}^{53}$  resonance in chromium containing up to 3 at. % (nominal) vanadium, and have measured the Knight shift of the  $\text{V}^{51}$  resonance in these and other vanadium-chromium alloys.

These two metals form a complete solid solution system of body-centered cubic alloys, showing no evidence for the formation of intermetallic compounds.<sup>1</sup> Alloy specimens were prepared by arc-melting crystal-bar vanadium and chromium. Homogenizing anneals of the arc-melted buttons were made in some cases, but this does not appear to affect the Knight shift significantly. Samples suitable for nuclear resonance were obtained from filings of the alloy buttons.

Figure 1 shows the Knight shift  $k_V$  at room temperature for  $\text{V}^{51}$  at composition intervals of 10 at. % (nominal) across the entire V-Cr system. Measurements of  $k_V$  were also made at vanadium concentrations of 0.25, 0.50, 1.5, 3.0, and 5.0 at. %. These latter results are included in Fig. 1 and are shown on an expanded scale in the lower portion of Fig. 2. Measurements of  $k_V$  were also made at  $77^\circ\text{K}$  in all alloys except those containing 3 at. % or less vanadium. In these latter alloys the  $\text{V}^{51}$  resonance was not detectable at  $77^\circ\text{K}$ . The shift at  $77^\circ\text{K}$  is always slightly smaller (by 0.01-0.03 %) than that at room temperature. The Knight

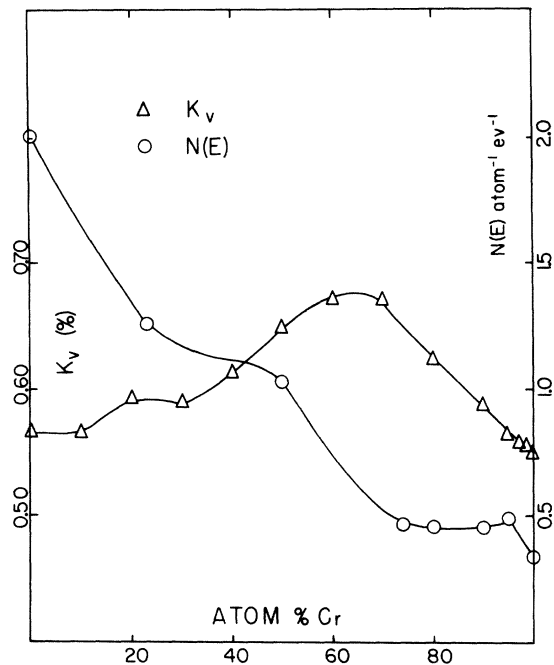


FIG. 1. Knight shift  $k_V$  of the  $\text{V}^{51}$  resonance in the V-Cr alloy system. The density of states at the Fermi level  $N(E)$  calculated from the specific heat data of reference 3 is also shown. The 4s contribution to  $N(E)$  [taken as equal to  $N(E)$  for copper] has not been subtracted from the observed  $\gamma$  values, as was done in reference 3.

shift  $k_{\text{Cr}}$  of the  $\text{Cr}^{53}$  resonance was measured in the range 0-3 at. % vanadium concentration, and these values are shown in the upper portion of

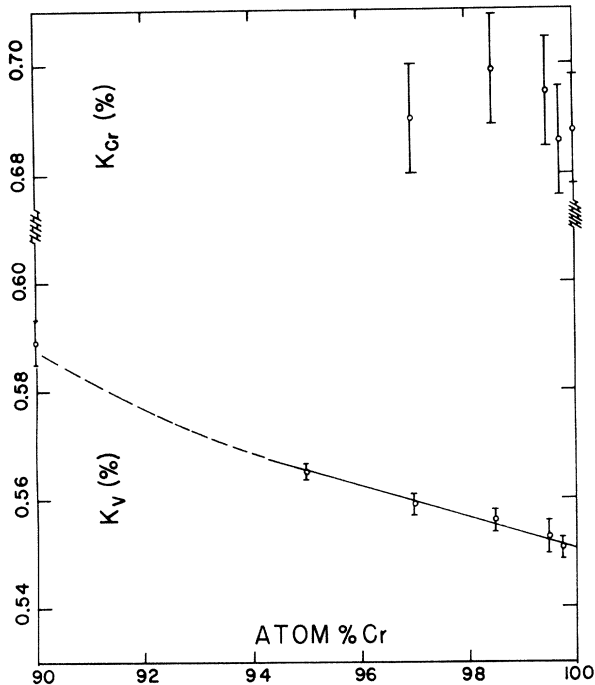


FIG. 2. Knight shifts  $k_V$  and  $k_{Cr}$  at the chromium-rich end of the V-Cr system. The shift of the  $Cr^{53}$  resonance was determined relative to that in  $Na_2CrO_4$  [F. Alder and K. Halbach, *Helv. Phys. Acta* **26**, 426 (1953)] by measuring the frequency ratio  $\nu^{53}/\nu^{39}$  at constant magnetic field (here  $\nu^{53}$  refers to  $Cr^{53}$  in chromium metal and  $\nu^{39}$  to  $K^{39}$  in potassium acetate solution), and employing the reported ratios  $\mu^{53}/\mu^{14}$  (Alder and Halbach, *loc. cit.*) and  $\mu^{39}/\mu^{14}$  [T. L. Collins, *Phys. Rev.* **80**, 103 (1950)] for the ionic species.

Fig. 2. Except for pure chromium, these measurements were made at room temperature. In crystal-bar chromium the  $Cr^{53}$  resonance was observed only at temperatures above the Néel point of approximately  $40^\circ C$ . Within the experimental uncertainty,  $k_{Cr}$  is independent of temperature and vanadium content in the ranges investigated. The  $Cr^{53}$  resonances were observed in a nominal magnetic field of 16 koe, corresponding to a resonance frequency of roughly 3.8 Mc/sec. A reliable determination of the  $Cr^{53}$  resonance linewidth was not obtained because of the very weak strength of the absorption mode signal. After correcting for excessive modulation amplitude, a linewidth  $\delta\nu < 500$  cps was obtained. The calculated nuclear dipolar second moment of naturally abundant  $Cr^{53}$  in Cr metal is only 0.03 (oe)<sup>2</sup>, corresponding to a linewidth of approximately 80 cps.

In the case of the  $Cr^{53}$  shift, it is possible that

the constancy of this quantity over the relatively small composition range investigated may be due to the elimination, by quadrupole interaction, of those  $Cr^{53}$  nuclei situated near vanadium ions, although this seems unlikely in view of the very small quadrupole moment of  $Cr^{53}$ .<sup>2</sup> This argument also seems inappropriate in the case of  $V^{51}$  except perhaps at the extreme vanadium-rich end of the system. The fact that the  $V^{51}$  resonance is clearly distinguished at all intermediate compositions, together with the smooth behavior of  $k_V$  and the gradual decrease in resonance intensity with decreasing vanadium content, implies that the  $V^{51}$  resonance is characteristic of the entire sample. Other evidence also suggests that the nuclear quadrupole moment of  $V^{51}$  may be appreciably smaller than hitherto reported.<sup>3</sup>

Also included in Fig. 1 is a plot of the density of states  $N(E)$  in the V-Cr system as determined from specific heat measurements by Cheng, Wei, and Beck.<sup>4</sup> The Knight shift  $k_V$  does not reflect the sharp decrease in  $N(E)$  indicated by the specific heat data. However, Butterworth's results on  $T_1$  for vanadium,<sup>5</sup> together with Orgel's suggestion of orbital paramagnetism,<sup>6</sup> indicate that the Knight shift very likely does not arise solely from quantities proportional to  $N(E)$  in the case of vanadium, and the same may very well be true of chromium. This same conclusion can also be reached on the basis of Anderson's theory of localized magnetic states<sup>7</sup> without introducing the mechanism of orbital paramagnetism.

Within the composition range 0-3 at. % vanadium, both the  $V^{51}$  and  $Cr^{53}$  resonances are extinguished by the onset of magnetic ordering at temperatures above  $77^\circ K$ . In the case of pure chromium, this extinction occurs within the range  $39.5-41.0^\circ C$ , in excellent agreement with the most recent neutron diffraction studies.<sup>8</sup> The magnetic ordering temperature  $T_N$  is a precipitous function of vanadium content, as indicated qualitatively by the fact that it is below  $77^\circ K$  at 5 at. % V. These observations are in accord with others concerning the effect of metallic impurities on the  $T_N$  of chromium.<sup>9</sup> The fact that the  $Cr^{53}$  resonance is detected at temperatures above the magnetic ordering temperature of chromium, as well as the temperature independence of  $k_{Cr}$ , raises the possibility that the magnetic transition is not an order-disorder type, but rather involves the onset of a local magnetic state.<sup>7</sup> The present observations also suggest that the anomalies reported in vanadium near  $250^\circ K$  are not associated with an antiferromagnetic transition.<sup>10</sup> The extinction of the nuclear magnetic

resonance of  $\text{Cr}^{53}$  by the onset of magnetic ordering provides a convenient and sensitive means of delineating the dependence of  $T_N$  upon alloy composition, and hence upon electron concentration.

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## MAGNETIZATION OF HARD SUPERCONDUCTORS

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It has long been recognized that the magnetic properties of hard superconductors differ qualitatively from those of soft superconductors. Specifically, the hard superconductors often exhibit hysteresis and, in addition, display superconducting properties in fields that are far greater than the critical fields of soft superconductors. In addition it is becoming increasingly clear that these two types of material differ in their microstructure. Confirming Mendelssohn's postulate,<sup>1</sup> the hard superconductors possess, in many cases, a filamentary mesh structure in which the diameter of the filaments is less than the London penetration depth. Shaw and Mapother<sup>2</sup> have recently given a discussion of Mendelssohn's hypothesis and propose a special filamentary arrangement to explain qualitatively the hysteresis they observed in the magnetic transition of plastically deformed lead.

To derive the magnetic properties of such a structure, we could start from first principles. I shall, however, treat the problem macroscopically. I shall assume the filamentary structure to be capable of sustaining lossless macroscopic current up to a critical current density,  $J_C$ . This critical current density is a function of magnetic field. It becomes zero at the critical field of the filaments. In the treatment that follows I assume that the critical current density is independent of field which is equivalent to the assumption that the applied fields are much less than the critical

fields of the filaments. I also assume that the interstices of the mesh are fitted with a soft superconductor of critical field  $H_C$ . Lastly I assume that the magnetic field is shielded by the soft superconductor to a field  $H_C$ ; then further shielding is accomplished by currents flowing in the filamentary mesh. These currents flow to the full amount  $J_C$  for a depth necessary to reduce the field to  $H_C$ .

To derive the magnetization curve of a virgin hard superconductor we must calculate the internal field  $H_i$  as a function of position in the superconductor and as a function of the external field. By definition, the magnetization  $M$  is given by

$$4\pi M = \int (H_i - H) dv / \int dv, \quad (1)$$

where the integrals are over the volume of the specimen. In order to compare the results of this theory with experiment, I shall assume the field to be applied parallel to the axis of a circular cylinder of radius  $R$ . If the applied field is less than  $H_C$ , the shielding is complete if  $R$  is much greater than the London penetration depth. This gives

$$H_i = 0; \quad 0 \leq r \leq R, \quad 0 \leq H \leq H_C. \quad (2)$$

As the field is further increased, the soft superconductor on the outside becomes normal and