present calculation gives comparable values of D' and D for the alkali metals, it is quite possible that the former model applies to them. We are inclined to believe that this difference in behavior between the alkali metals and noble metals may be due to the reason that at low temperatures the interaction of long-wavelength phonons with electrons involves only the longitudinal modes if the Fermi surface is a sphere, but a multiply-connected surface which the noble metals have, should be much more sensitive to shear strains in the lattice, and there should be strong interaction with the transverse phonon modes,[24] especially in the neck regions.

Our conclusions about the Fermi surface, though in qualitative agreement with experiments, are weakened by the findings of Bailyn[25,26] that the Umklapp processes dominate the electrical resistivity at all temperatures down to a few degrees Kelvin, and that these are dominated by scattering involving transverse phonons of large wave vector. As a consequence the scattering is affected moderately by whether or not the Fermi surface comes close to Brillouin zone surface. The whole problem of transport properties is of extreme complexity, for it involves almost all the basic properties of the metals, both the electronic band structure and the dynamical properties of the lattice.

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Nuclear Magnetic Resonance of Tc^{99} in Tc Metal and Tc^{99} and V^{51} in Tc-V Alloys*

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The nuclear magnetic resonance of Tc^{99} has been observed in Tc metal and its Knight shift measured relative to a solution of $CsTcO_4$. The Tc^{99} and V^{51} resonances have been studied in 50–50 at. % TcV and TcV_3 alloys as a function of field and temperature. The Tc^{99} resonance curves in TcV and TcV_3 have a Lorentzian shape while V^{51} is Gaussian in TcV and Lorentzian in TcV_3. Probable causes for the shape changes and excess widths encountered are discussed.

NUCLEAR magnetic resonance (NMR) measurements of Tc^{99} in Tc metal and Tc^{99} and V^{51} in Tc-V alloys have been made with a Varian, model V4200, wide-line nuclear magnetic resonance spectrometer and a Varian, model V4012A, electromagnet. The frequency was accurately measured by means of a Beckman/Berkeley model 7175 frequency meter. Temperature-dependent measurements of the line parameters were made by means of a gas-flow Dewar system through which the temperature could be varied from −150 to 300°C.

Technetium metal has the hexagonal close-packed crystal structure with lattice parameters $c_0=4.400\pm0.001$ A, $a_0=2.743\pm0.001$ A, and $c/a=1.604$ and the Tc^{99} nucleus has a nuclear spin $I=9/2$. Figure 1 shows a typical recording trace of Tc^{99} in Tc metal where the central line and its eight satellites are clearly observed. The first reported resonance of Tc^{99} was in an aqueous solution of NH_4TcO_4.[1] A detailed description of the quadrupole interactions and isotropic and anisotropic Knight shifts of Tc^{99} in Tc metal have been given by Jones and Milford.[2] The isotropic Knight shift is $(0.61\pm0.02)\%$ relative to a 350-μg/ml solution of $CsTcO_4$. No chemical shift was observed between the $CsTcO_4$ solution and a 35-mg/ml solution of NH_4TcO_4. Table I gives the central line width versus field strength from which the anisotropic Knight shift and quadrupole effects are calculated. An analysis of the data shows that the anisotropic Knight shift is small. The quadrupole coupling constant e^2qQ/h evaluated from the satellites and central line width are, respectively, 5.05 and 5.15 Mc/sec. Operating in the U mode, the Tc^{99} in the $CsTcO_4$ solution gave rise to the so-called "m" curve and using the theory developed by Hubbard and Rowland[3]

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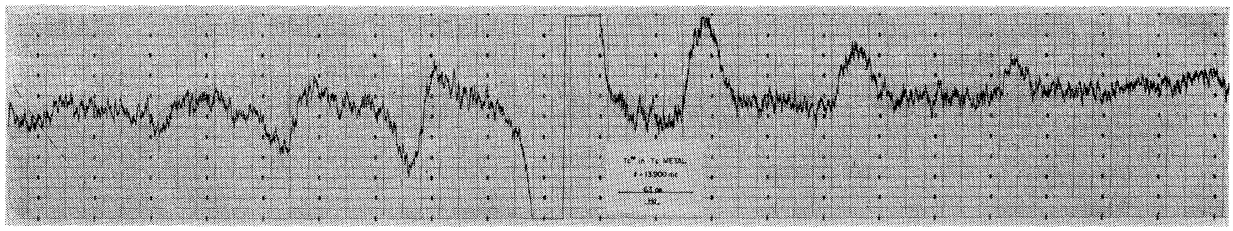

FIG. 1. Derivative of the magnetic absorption of Tc^{99} in Tc metal, at 13.900 Mc/sec. First order quadrupole effects are clearly seen through the appearance of the eight satellites. Second order quadrupole, isotropic, and anisotropic Knight shift effects are evident through the position and asymmetry of the central component.

a spin-lattice relaxation time for Tc^{99} in this liquid in the vicinity of 0.26 sec was calculated.

TcV has the CsCl structure with a lattice parameter of $a_0=3.025\pm0.005$ A. The Tc^{99} resonance curve in TcV shown in Fig. 2 is Lorentzian and the width measured between extreme slopes of the absorption line $\delta H=(11.1\pm1)$ oe is independent of field (3 to 15 koe) within experimental error. A small temperature dependence of the linewidth observed at the lower temperatures is evident in Table II. The frequency shift relative to the $CsTcO_4$ solution is positive and independent of field with a value of $(0.64\pm0.03)\%$. Observation of V^{51} in the same alloy gives a field-independent curve as exemplified in Table IV. The near temperature independence of δH is shown in Table III. The frequency shift relative to vanadium dissolved in HNO_3 is positive with a magnitude of $(0.57\pm0.03)\%$ and field independent. The V^{51} resonance curve in TcV is of Gaussian shape, and the theoretically calculated second moment shows that nuclear dipole-dipole interactions can account for approximately only 60% of the linewidth.

TABLE I. The variation in width (δH) of the central transition in Tc metal as a function of field. An error of ±1.0 oe is to be assigned to δH.

δH(oe)	H_0(oe)
35.6	5196
25.8	7759
14.8	9860
13.2	12 133
12.5	14 691

TABLE II. Temperature dependence of the linewidth (δH) for Tc^{99} in TcV at 12.00 Mc/sec. The modulation width is 4.5 oe and an error of ±1.3 oe is to be assigned to each value of δH.

T(°C)	δH(oe)
182	10.5
100	10.9
25	10.8
−50	11.6
−103	12.0

TcV_3 has the bcc structure with a slight change of lattice parameter from that of pure vanadium. The Tc^{99} line in TcV_3 is Lorentzian and the width $\delta H=(16.5\pm1.5)$ oe is independent of field and temperature. The frequency shift relative to the solution of $CsTcO_4$ is positive and independent of field with a value $(0.93\pm0.035)\%$. Figure 3 shows a Gaussian and Lorentzian curve fitted to the resonance line of technetium. The line shape is the same in each alloy. The resonance absorption of V^{51} in TcV_3 is Lorentzian and Fig. 4 shows that the line changes from Gaussian to Lorentzian as we go from TcV to TcV_3. The linewidth is directly related to the field as seen in Table IV. Frequency shifts relative to the acid solution are positive with a magnitude of $(0.65\pm0.02)\%$ and are independent of field.

TABLE III. Linewidth (δH) of V^{51} as a function of temperature in TcV and TcV_3 at 8.00 Mc/sec (error ±1.0 oe). The modulation width is 2.2 oe.

	δH(oe)	
T°C	TcV	TcV_3
150	10.6	9.4
100	10.6	10.5
25	10.6	10.8
−50	11.2	11.4
−100	11.7	12.3

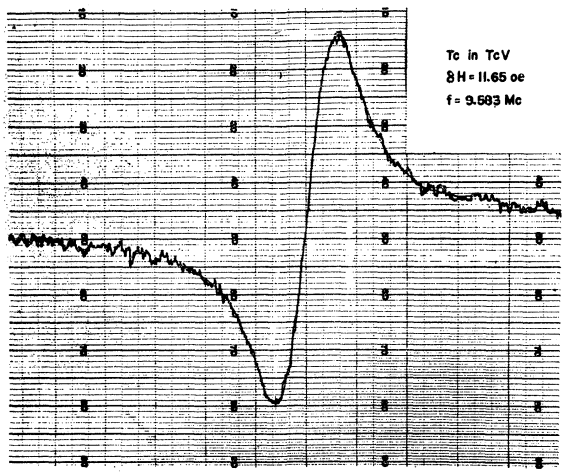

FIG. 2. Derivative of the magnetic absorption of Tc^{99} in TcV.

TABLE IV. Linewidth (δH) of V^{51} as a function of field in TcV and TcV_3 (error ± 1.0 oe).

TcV		TcV_3	
H_0(oe)	δH(oe)	H_0(oe)	δH(oe)
4440	10.8	4437	10.5
7107	11.2	7099	10.9
12 405	10.8	12 391	11.8
13 948	11.1		

The fact that the resonance linewidths of both alloys are larger than can be accounted for by dipolar-dipolar broadening leads one to suspect indirect exchange and/or pseudo-dipolar[4] mechanisms. Spin-lattice relaxation effects are ruled out for the Lorentzian lines because of the temperature independent width over the range studied. Quadrupolar and anisotropic magnetic contributions are eliminated in most cases because of the field independence. The field dependence of δH for V^{51} in TcV_3 can be interpreted in terms of a spatial inhomogeneity of the Knight shift. This is quite often the major source of excess width in disordered alloys and is identified through the linear dependence of δH vs external field. For this alloy δH extrapolated to zero field is just that for pure vanadium within experimental error. The fact that the V^{51} line changes from Gaussian to Lorentzian as the concentration of nonresonant nuclear species is reduced points to the indirect exchange mechanism as another source of excess linewidth. Since the alloy contains essentially two magnetic ingredients with distinct resonant frequencies, line broadening instead of narrowing results.

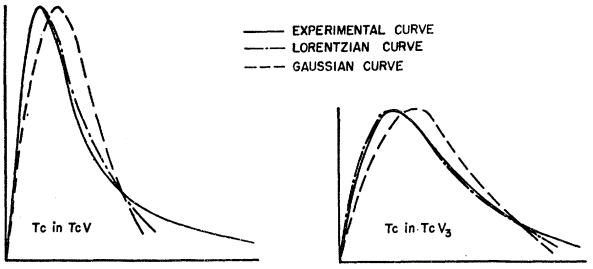

FIG. 3. Lorentzian and Gaussian curves fitted to the experimental derivatives of Tc^{99} in TcV and TcV_3. It is evident that the Tc^{99} line is Lorentzian in each case.

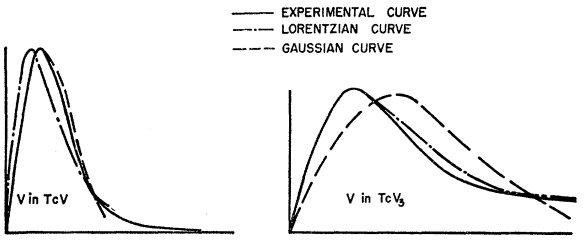

FIG. 4. Lorentzian and Gaussian curves fitted to the experimental derivatives of V^{51} in TcV and TcV_3. It is evident that the V^{51} line changes from a Gaussian shape in TcV to a Lorentzian shape in TcV_3.

Further NMR and magnetic susceptibility measurements in these elements, alloys, and other alloys over larger composition ranges are currently in progress in this laboratory and the results will appear shortly.

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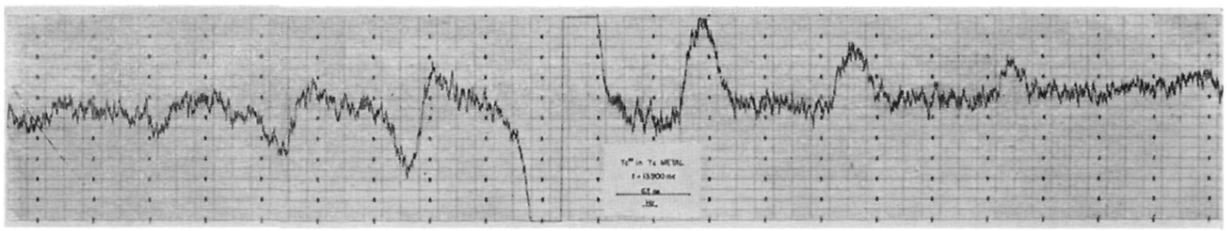

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