

Magnetic Susceptibilities and Nuclear Magnetic Resonance Measurements in V-Fe Alloys*

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Magnetic susceptibilities and nuclear magnetic resonance measurements have been made on V-Fe alloys up to 34 at. % Fe in V. The composition and temperature dependence of the susceptibilities and of the NMR linewidth of V^{51} suggests the appearance of magnetic moments at about 23 at. % Fe. The Knight shifts of V^{51} in the nonmagnetic portion of this alloy system are discussed in terms of the contributions from the Fermi contact term, sd exchange, and induced orbital paramagnetism.

INTRODUCTION

ALTHOUGH the magnetic properties of V-Fe alloys lying in the composition range where ferromagnetism occurs have been investigated in some detail,^{1,2} the corresponding properties of the vanadium-rich non-ferromagnetic alloys have not been studied to the same extent. In the current work, magnetic susceptibilities and Knight shifts of V^{51} have been measured for alloys having iron concentrations varying between 0 and 34 at. %. The susceptibilities have been measured over the temperature range from 4.2 to 300°K, while the nuclear magnetic resonance (NMR) parameters have been measured from 120 to 300°K and at various external magnetic fields. These measurements form a supplement to those made on other V alloys³ which enabled some generalizations to be made about the electronic character at the Fermi surface. In addition, the temperature dependence of the susceptibility and the broadening of the nuclear magnetic resonance line suggests the appearance of moments at about 23 at. % Fe in V.

TABLE I. Compositions and homogenization heat treatments for V-Fe alloys.

Composition (at.%)		Heat treatment		
V	Fe	Temp (°C)	Time (h)	Quench
100.0		900	168	water
98.0	2.0	900	168	water
93.0	7.0	900	168	water
90.1	9.9	900	168	water
84.5	15.5	900	168	water
79.8	20.2	900	168	water
77.1	22.9	900	168	water
72.8	27.2	900	168	water
72.3	27.7	1314	96	oil
69.9	30.1	900	168	water
69.6	30.4	1314	96	oil
69.0	31.0	900	168	water
67.8	32.2	1314	96	oil
66.0	43.0	1220	72	water

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¹ S. Aarj, R. V. Colvin, Henry Chessin, and J. M. Peck, *J. Appl. Phys. Suppl.* **33**, 1353 (1962).

² M. V. Nevitt and A. T. Aldred, *J. Appl. Phys.* **34**, 463 (1963).

³ D. O. Van Ostenburg, D. J. Lam, H. D. Trapp, and D. E. MacLeod, *Phys. Rev.* **128**, 1550 (1962).

EXPERIMENTAL METHOD

The alloys were prepared by arc melting requisite amounts of electrolytic vanadium and puron iron in an argon-helium atmosphere. Table I summarizes the compositions, obtained by chemical analysis, and the heat treatments given to the alloys employed in the study. All of the specimens were in the form of cubes $\frac{3}{8}$ in. on a side except 9, 11, 12, and 13, which were spherical in shape, having a diameter of 0.2 in. Surface contamination produced by the machining of the specimens was removed by chemical etching. Powder specimens for the NMR measurements and for the determination of lattice parameters by x-ray diffraction were prepared from the same alloys.

The susceptibilities were determined by the Faraday method on a microbalance which incorporates automatic weighing and recording. The estimated accuracy is $\pm 1.5\%$, relative to the susceptibility of Ta (0.85×10^{-6} emu/g) used as a standard. The specimen was contained in a cryostat which contained liquid helium for the measurements at 4.2°K. Temperatures above 4.2°K but below room temperature were obtained in the cryostat by achieving a thermal balance between evaporated liquid helium or nitrogen and a heater surrounding the specimen chamber. The temperature was determined by a copper-constantan thermocouple calibrated against a platinum thermometer; it has an estimated accuracy of $\pm 2^\circ\text{K}$ at temperatures below 77°K. The susceptibility was measured as a function of field ($H_{\text{max}} = 11\,000$ Oe) and ferromagnetic corrections were made after it had been shown that the ferromagnetic correction was not a function of temperature.

NMR measurements were performed at 123, 223, and 298°K with a Varian Wide Line NMR spectrometer equipped with a gas-flow Dewar system. The specimens, in the form of powders having a particle size of minus 325 mesh, were kept under silicone oil to prevent oxidation. The shifts of V^{51} were determined relative to V dissolved in nitric acid. No chemical shifts were observed for different nitrate concentrations.

EXPERIMENTAL RESULTS

The mass susceptibilities at 77 and 298°K, the Knight shifts of V^{51} , and the lattice parameters are given in

TABLE II. Magnetic susceptibilities, Knight shifts, linewidths, and lattice parameters of V-Fe alloys.

Specimen	Composition (at.%)	χ (10^{-6} emu/g)		K_V (%) (298°K)	Linewidth (Oe) (7.545 Mc/sec) (298°K)	Lattice parameter (Å) (298°K)
		298°K	77°K			
1	V	5.63		0.567±0.006	10.5±1.0	3.029±0.001
2	V-2 Fe	5.45		0.567±0.006	10.7±0.6	
3	V-7 Fe	5.30		0.584±0.006	11.1±0.6	
4	V-9.9 Fe	5.05	5.15	0.586±0.006	11.2±0.6	3.004±0.001
5	V-15.5 Fe	4.30	4.55	0.596±0.006	11.3±0.6	
6	V-20.2 Fe	4.20	4.60	0.593±0.006	11.5±0.6	2.970±0.001
7	V-22.9 Fe	4.35	6.09	0.584±0.01	12.4±1.2	
8	V-27.2 Fe	5.75	23.00	0.536±0.01	15.1±1.2	
9	V-27.7 Fe	6.00				
10	V-30.1 Fe	7.60	76.00	0.481±0.016	18.0±1.9	2.947±0.001
11	V-30.4 Fe	8.35				
12	V-31.0 Fe	10.20				
13	V-32.2 Fe	11.30				
14	V-34.0 Fe	18.30				

Table II. The room temperature susceptibility as a function of composition is shown in Fig. 1. There is a decrease from pure V to around 20 at. % Fe, and then a rapid increase with higher Fe concentration. The susceptibility of alloys with less than 20 at. % Fe is independent of field up to 11 000 Oe with a small temperature dependence over the range investigated. Alloys containing 20.2 to 30.1 at. % Fe have susceptibility and inverse susceptibility relationships with temperature which are shown in Fig. 2 and Fig. 3, respectively.

Alloys with high Fe content have field-dependent susceptibility at low temperatures, and the values quoted are those at fields of 10 000 Oe. Figure 4 shows the isothermal magnetization curves for the 30.1 at. % Fe alloy; no correction was made for the demagnetizing force. Beginning around 27 at. % Fe, there is a Curie-Weiss-type behavior at higher temperatures, but χ^{-1} versus T curves are convex toward the temperature axis at low temperatures. This general type of curvature is

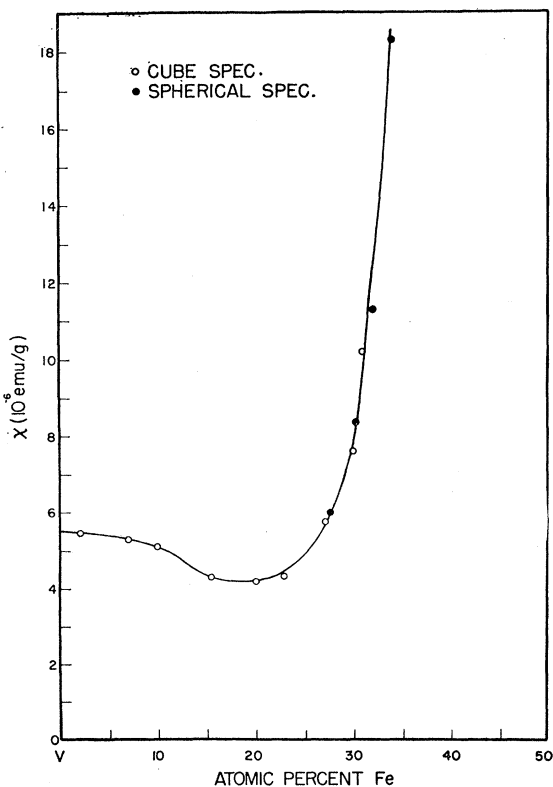


FIG. 1. Paramagnetic susceptibility of V-Fe alloys at room temperature as a function of composition.

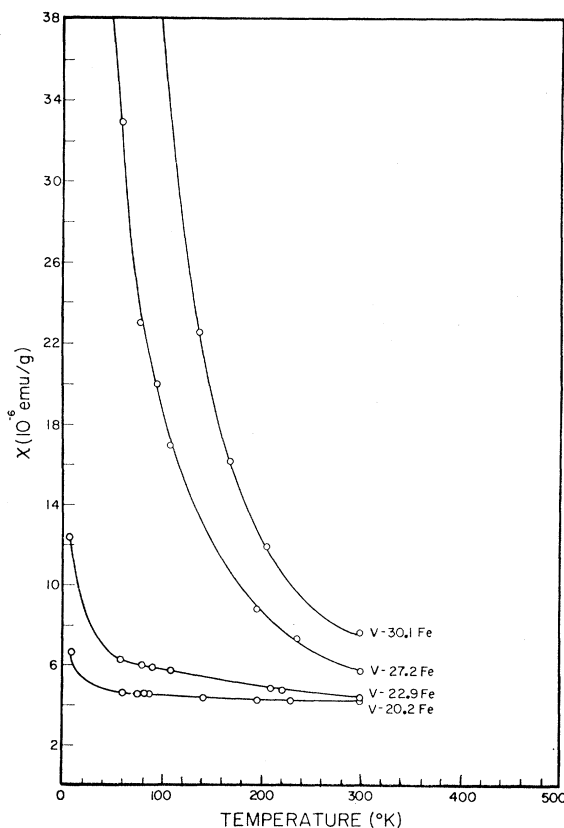


FIG. 2. Paramagnetic susceptibility of V-Fe alloys as a function of temperature.

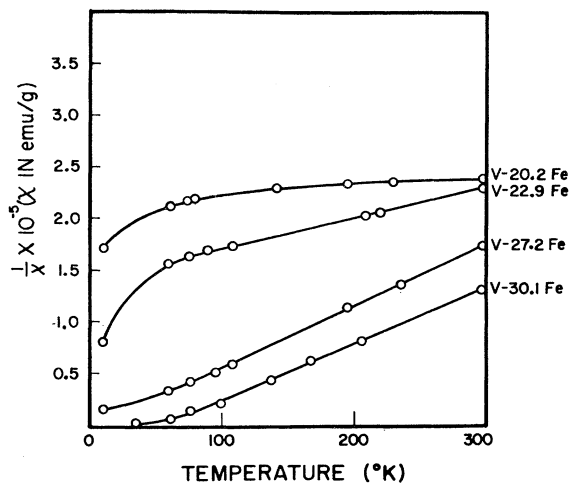


FIG. 3. Inverse paramagnetic susceptibility of V-Fe alloys as a function of temperature.

characteristic of many ferromagnetic elements above their Curie points. A similar behavior was observed in V-Fe alloys with high Fe content by Arajs *et al.*¹

The Knight shift of V^{51} shows a maximum in the vicinity of 16 at.% Fe (Table II and Fig. 5), while the linewidth, measured between derivative maxima, increases slowly up to 20.2 at.% Fe and then rises rapidly at higher Fe contents (Fig. 6). The shifts are independent of temperature and field within experimental error. The linewidths increase linearly with frequency as shown in Fig. 7 and are independent of

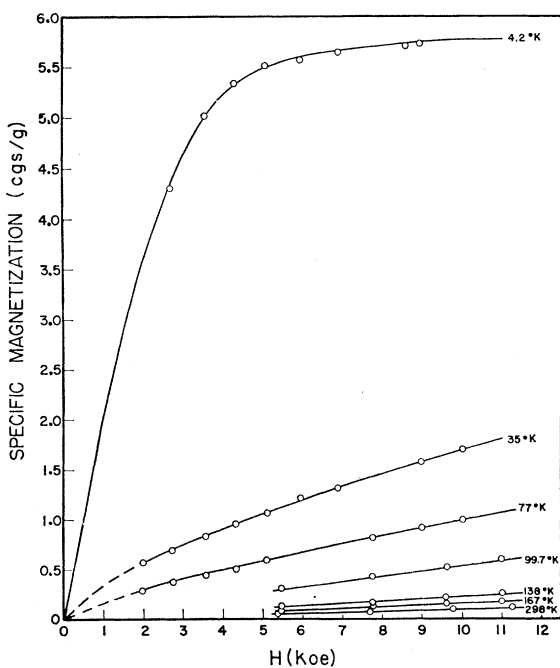


FIG. 4. Specific magnetization of the V-30.1 at.% Fe alloy.

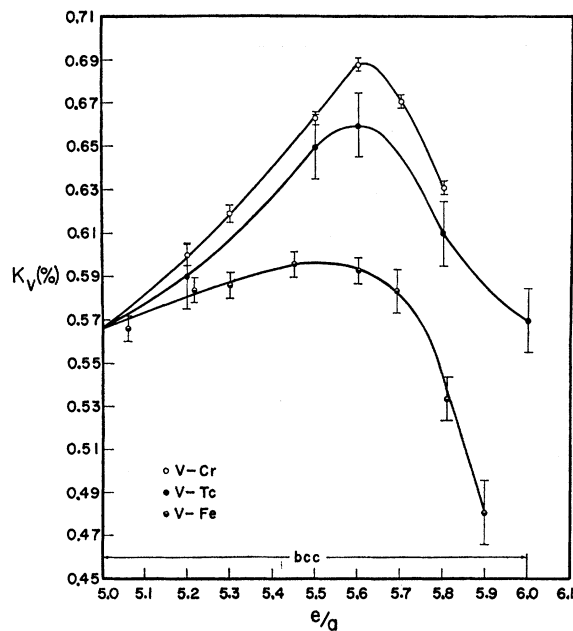


FIG. 5. Knight shifts of V^{51} in V-Fe, V-Cr, and V-Tc alloys as a function of e/a .

temperature up to about 23 at.% Fe; at higher Fe concentration they broaden at low temperatures. These data are given in Table III.

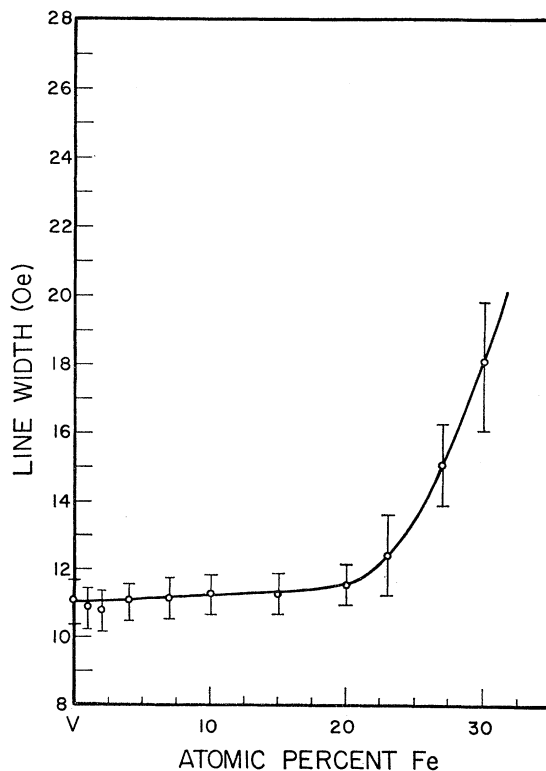


FIG. 6. NMR linewidths of V-Fe as a function of composition.

DISCUSSION

A. Susceptibility and NMR Linewidths

The total susceptibility may be written as follows: $\chi = \chi_P + \chi_{VV} + \chi_{ion} + \chi_{Landau} + \chi(T)$, where χ_P is the Pauli contribution, χ_{VV} is that due to the Van Vleck orbital paramagnetism, which is directly proportional to matrix elements of the electronic magnetic moment and inversely to the separation of the energy levels connected by the orbital angular momentum,⁴ χ_{ion} is that due to the diamagnetism of the ionic cores, χ_{Landau} is the diamagnetic term accounting for the orbital motion of the

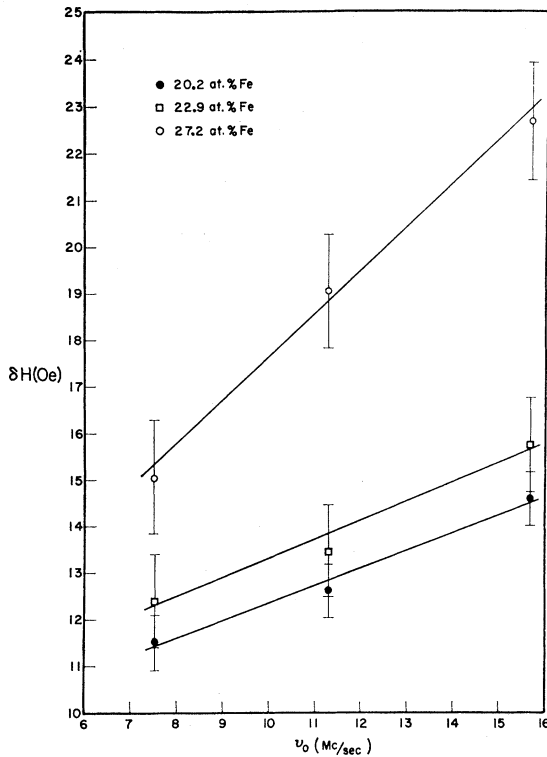


FIG. 7. NMR linewidths of V-Fe alloys as a function of frequency.

conduction electrons, and $\chi(T)$ represents any temperature dependence other than what is found implicitly in the other terms.

The Pauli contribution χ_P can be calculated from the low-temperature specific-heat coefficient γ via the density of states. In the absence of a better theoretical understanding, the effect on the density of states of exchange forces is assumed to be cancelled by the forces of correlation.⁵ Cheng, Wei, and Beck⁶ have measured γ in V-Fe alloys and have found that the density of

⁴ R. Kubo and Y. Obata, J. Phys. Soc. Japan **11**, 547 (1956).

⁵ A. H. Wilson, *The Theory of Metals* (Cambridge University Press, New York, 1953).

⁶ C. H. Cheng, C. T. Wei, and P. A. Beck, Phys. Rev. **120**, 426 (1960).

TABLE III. Frequency and temperature dependences of the linewidth δH (measured between derivative maxima) of the V^{51} line in the V-Fe system.

Alloy (at.%)	ν_0 (Mc/sec)	δH (Oe)	$T^\circ K$	δH (Oe) at 7.545 (Mc/sec)
V-15.5 Fe	7.545	11.3±0.6	298	11.3±0.6
	11.324	12.0±0.6	223	11.3±0.6
	15.670	14.0±0.6	123	11.6±0.6
V-20.2 Fe	7.545	11.5±0.6	298	11.5±0.6
	11.324	12.7±0.6	223	11.6±0.6
	15.670	14.6±0.6	123	12.0±0.6
V-22.9 Fe	7.545	12.4±1.2	298	12.4±1.2
	11.324	13.5±1.2	223	12.7±0.9
	15.670	15.8±0.9	123	12.5±1.2
V-27.2 Fe	7.545	15.1±1.2	298	15.1±1.2
	11.324	19.1±1.8	223	16.7±1.5
	15.670	22.7±1.2	123	40.6±4.7

states at the Fermi surface decreases upon alloying V with Fe up to approximately 21 at.%. Further additions of Fe produce an increase which reaches a peak at about 31 at.% Fe; beyond this composition there is another decrease.

The contribution arising from χ_{ion} is 7.7×10^{-6} emu/g-atom for pure V,⁷ and is not expected to change greatly upon alloying. Calculations of χ_{Landau} ,⁸ based upon effective masses, show that it does not subtract more than a few tenths percent from χ_P , and is negligible. This leaves the Van Vleck and temperature-dependent contributions to account for the differences between the measured and Pauli values.

The lack of a detailed knowledge of the energy-level separations and wave functions in the alloys precludes a calculation of χ_{VV} from first principles. Table IV gives, for several alloys, the measured room-temperature susceptibility, χ_{Pauli} calculated from low-temperature specific-heat coefficients, and their difference $\Delta\chi$. These differences can be used as a rough empirical estimate of the Van Vleck orbital paramagnetism for the alloys with less than 23 at.% Fe, which do not have a Curie-Weiss dependence. The value of $\Delta\chi \equiv \chi_{VV}$ ranges from 160.7×10^{-6} emu/g-atom for pure V to 171.6×10^{-6}

TABLE IV. Values of χ_{meas} , χ_P and their differences (χ at 298°K in units of 10^{-6} emu/g-atom).

Composition (at.%)	χ_{meas}	χ_P	$\Delta\chi \equiv \chi_{VV}$
V	287.0	126.3	160.7
V-2 Fe	278.5	116.8	161.7
V-7 Fe	272.0	95.7	176.3
V-9.9 Fe	259.8	87.0	172.8
V-15.5 Fe	222.4	60.0	153.4
V-20.2 Fe	218.2	54.0	164.2
V-22.9 Fe	226.6	55.0	171.6

⁷ J. H. Van Vleck, *Electric and Magnetic Susceptibilities* (Oxford University Press, New York, 1932).

⁸ B. G. Childs, W. E. Gardner, and J. Penfold, Phil. Mag. **5**, 1267 (1960).

emu/g-atom for the 22.9 at.% Fe alloy. For V-Cr alloys, χ_{VV} calculated in the same way from the experimental susceptibilities⁸ varies between 131.9×10^{-6} emu/g-atom (at 74 at.% Cr) and 189.8×10^{-6} emu/g-atom (at 23 at.% Cr). These seem reasonable for the solid solution alloys in view of the recently calculated theoretical values for the Van Vleck term, 125×10^{-6} emu/g-atom for V and 140×10^{-6} emu/g-atom for Cr.⁹ However, the empirical values of χ_{VV} are not accurate to better than 5% and may be in error by as much as 10% because of the limiting accuracies of the measured susceptibilities and specific-heat coefficients, and the uncertainty in the partitioning of the susceptibility. At the present time, therefore, only limited significance should be attached to apparent composition-dependent variations in χ_{VV} , which are not much larger than the probable error.

Recently, an investigation of ferromagnetism in V-Fe alloys has been made by Nevitt and Aldred.² Their results show that a ferromagnetic alignment of moments does not occur until approximately 28 at.% Fe. However, the 6°K magnetic isotherm for their 27.7 at.% Fe alloy showed a pronounced curvature, suggesting that a transition to the ferromagnetic state might occur at a lower temperature. While they did not give a ferromagnetic Curie point for the 30.4 at.% Fe alloy, they reported that it was ferromagnetic at 6°K. The occurrence of a ferromagnetic state at low temperatures for the alloys with 27.2 and 30.1 at.% Fe is implied by the Curie-Weiss-type behavior in the high-temperature range; a saturation effect at liquid-helium temperature is observed in the 30.1 at.% Fe alloy (Figs. 3 and 4).

The determination of the composition where magnetic moments first appear is augmented by the NMR linewidth measurements shown in Fig. 6. The width increases gradually up to 20 at.% Fe and then shows a marked increase with higher Fe concentrations. The gradual increase below 23 at.% Fe is due to spatially inhomogeneous Knight shifts. This is demonstrated by the linear dependence of the linewidths of the 20.2 and 22.9 at.% Fe alloys upon external magnetic field, depicted in Fig. 7. The rapid rise in width beyond 23 at.% Fe is due to the appearance of magnetic moments. This is borne out by the rapid increase in linewidth versus external field, shown in Fig. 7, for the 27.2 at.% Fe specimen. As expected from the temperature dependence of the susceptibility, the linewidths below 23 at.% Fe are independent of temperature, and above this composition the widths increase at low temperatures (see Table III).

These results suggest that the *d* electrons of iron when alloyed with V first enter a band where they are spin paired. At about 23 at.% Fe, magnetic moments may arise from electron spin polarizations about the Fe atoms. However, cooperative phenomena do not occur

until the Fe content reaches about 27 at.%. This suggestion is in agreement with the model proposed by Cheng, Wei, and Beck based on their low-temperature specific heat measurements, and that by Nevitt and Aldred based on saturation magnetization measurements.

B. Knight Shifts

As shown in Fig. 5, the Knight shift of V⁵¹ increases with Fe content, reaches a maximum in the vicinity of 16 at.% Fe, corresponding to an electron:atom ratio of 5.5, and then decreases sharply with higher Fe content. In deriving *e/a*, all of the electrons outside of the closed 3*p* shell are considered. The shifts of V⁵¹ in the bcc region of the binary systems V-Cr and³ V-Tc are also plotted. The magnitude of the maximum decreases in the order Cr, Tc, Fe, and its position appears to be the same for V-Cr and V-Tc, but to shift toward slightly lower *e/a* in the V-Fe system.

For transition metals the Knight shift, K_V , may be expressed as follows:

$$K_V = K_s + K_d + K_{VV}. \quad (1)$$

K_s is the hyperfine contact term,¹⁰ which is directly proportional to the density of states, atomic volume, and the probability density of *s* electrons at the Fermi surface. K_d is the contribution due to *sd* exchange interactions¹¹ and K_{VV} is that arising from internal fields as a result of the Van Vleck orbital paramagnetism⁹; it is directly proportional to χ_{VV} and $\langle r^{-3} \rangle_{av}$, the latter term being a radial average over the 3*d*-wave functions.

If it is assumed that K_V and its dependence upon *e/a* is due only to K_{VV} , and that $\langle r^{-3} \rangle_{av}$ does not change with alloying, χ_{VV} must increase with *e/a* to 5.6 and then decrease, and must vary in magnitude with the solute elements under consideration. It is, in fact, evident that in V-Cr and V-Fe, χ_{VV} as determined empirically by susceptibility partitioning is not the sole variable in determining K_V . (For V-Fe compare K_V in Table II with χ_{VV} in Table IV.) However, the empirical values of χ_{VV} have only limited usefulness for purposes of analysis, as they are probably subject to considerable error. For V-Tc alloys, χ_{VV} cannot be estimated because there are no electronic specific-heat coefficients from which χ_P can be calculated.

Currently, it is not possible to make theoretical calculations of K_d in the alloys being discussed, but the core polarization calculations of internal magnetic fields by Watson and Freeman on the pure elements¹¹ indicate that this term gives a net negative contribution to the shift. Thus, this term itself cannot explain the positive shifts in these systems.

In the case of V_3X intermetallic compounds in the

¹⁰ E. Fermi, *Z. Physik* **60**, 320 (1930); C. H. Townes, C. Herring, and W. D. Knight, *Phys. Rev.* **77**, 852 (1950).

⁹ L. E. Orgel, *J. Phys. Chem. Solids* **21**, 123 (1961); M. Shimizu, T. Takahashi, and A. Katsuki, *J. Phys. Soc. Japan* **17**, 1740 (1962),

¹¹ A. Abragam, J. Horowitz, and M. H. L. Pryce, *Proc. Roy. Soc. (London)* **A230**, 169 (1955); R. E. Watson and A. J. Freeman, *Phys. Rev.* **123**, 2027 (1961).

normally conducting state it has been proposed¹² that K_d is proportional to the d -electron spin susceptibility, χ_d . By assuming that the strong temperature dependence of the measured susceptibility is due to χ_d , the influence of χ_d on K_V has been deduced. A sharp peak in the density-of-states curve for the d band was offered as one possible explanation for the influence of temperature on χ_d . This argument does not appear useful for V-Fe alloys in the composition range 0 to about 20 at.% Fe, or for V-Cr and V-Tc alloys, for which a strong temperature dependence in the susceptibility and in the Knight shift is not found. It may be significant that the d band in these alloys is not characterized by sharp curvature.

If it were assumed that the composition dependence of K_V is due entirely to K_s , the variation of the latter must enter through the probability density of the s electrons at the Fermi surface rather than through the measured density of states and atomic volume, both of which decrease with Fe concentration in the composition range concerned.

¹²A. M. Clogston, A. C. Gossard, V. Jaccarino, and Y. Yafet, *Phys. Rev. Letters* **9**, 262 (1962); A. M. Clogston and V. Jaccarino, *Phys. Rev.* **121**, 1357 (1961).

It seems likely that an algebraic summing of the three terms in Eq. (1) must be invoked to explain the observed results. For example, the peak in K_V could be due to an increase in K_s and/or K_{VV} on the one hand and a decrease in K_d on the other as e/a increases. However, the occurrence of the peak in K_V in the vicinity of $e/a=5.6$ for three different systems seems to be more than fortuitous. An analysis combining the three terms must account for this electron concentration dependency.

In the composition region where moments and ferromagnetism appear and where the γ term in the specific heat has a large peak, a more detailed study of susceptibility, NMR parameters and saturation magnetization is currently in progress with the purpose of clarifying the nature of the spin interactions which give rise to the observed properties.

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Phonon Scattering by Point Defects*

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Phonon scattering by point defects was studied by measuring the thermal conductivity of KCl containing known amounts of KI, NaCl, and CaCl₂ in solid solution. By also measuring the conductivity in crystals in which the impurities were allowed to coagulate, it was possible to distinguish between the effect of atomically dispersed defects and precipitates.

The experimental data cannot be described by a Rayleigh-type scattering mechanism alone. An additional phonon scattering by impurity modes, as discussed by Wagner in the following paper, is shown to describe the experimental data. The angular frequencies of the impurity modes thus determined are of the order of 10^{13} sec⁻¹ for the defect systems investigated here. A discussion of the magnitude of the Rayleigh scattering is also given.

1. INTRODUCTION

THE strong influence of lattice defects on the low-temperature thermal conductivity of solids was first demonstrated by Berman,¹ and has since been observed in many experiments. In electrically insulating crystals, energy is carried predominantly by elastic waves or phonons, and, therefore, measurements of the lattice thermal conductivity at low temperatures are a useful tool for the study of the interaction between

phonons and defects. For a review of this field we refer to the articles by Klemens,² Carruthers,³ and Bross.⁴

Among the defects which have been most carefully studied are those whose size is comparable to that of the host lattice atoms. In spite of considerably theoretical and experimental effort, the problem of the phonon scattering by these "point defects" must still be considered as unsolved.

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²P. G. Klemens, *Proc. Roy. Soc. (London)* **A208**, 108 (1951); *Proc. Phys. Soc. (London)* **A68**, 1113 (1955); also in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Vol. 7, p. 1.

³P. Carruthers, *Rev. Mod. Phys.* **33**, 92 (1961).

⁴H. Bross, *Physica Status Solidi*, **2**, 481 (1962).