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Nuclear Magnetic Resonance in Vanadium Allovs

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In the study of the magnetic properties of transition metals and their alloys, vanadium is particularly interesting as this metal forms a useful range of solid solutions with all of the elements in the first transition period from titanium to nickel. In this work, the behaviour of the V^{51} nuclear magnetic resonance has been studied in some dilute solid solutions of Cr, Mn, Fe, Co and Ni in vanadium at room temperature. The V^{51} isotope has a nuclear moment of 5.139 nuclear magnetons and a spin of 7/2. Experiments were made at a frequency of 10.73 Mc/s in a field of approximately 9,500 gauss.

The constituents of the alloys were melted together in an argon arc furnace and the resulting buttons were ground and sieved. 300 mesh (maximum particle diameter, 52μ) powders were used. The vanadium used was obtained from two sources, Johnson, Matthey and Company (J. M.) and U.S. Bureau of Mines (U.S.B.M.). Material from the latter source is appreciably purer. A detailed analysis of the impurities in vanadium from the two sources is given in reference [1]. Unfortunately, the source of vanadium appears to make some difference to the results and in figures 1, 2 and 3, results obtained with J.M. vanadium are plotted with open symbols and those with U.S.B.M. vanadium plotted with filled symbols.

In solid solutions of cubic crystal structure containing transition metals, there are two important sources of line broadening of the solvent nuclear resonance in addition to those present in the pure solvent metal. These are

a) local magnetic fields produced by magnetic moments of unpaired electron spins on solute atoms, and

b) the interaction of nuclear electric quadrupole moments with electric field gradients in the crystal.

Both these effects will be discussed for the vanadium alloys.

MAGNETIC INTERACTIONS.

The results of measurements of nuclear magnetic resonance line widths and intensities are shown in figures 1 and 3. For convenience the 1% Co alloy is used as a reference for intensity measurements and all intensities are normalized to a constant amount of vanadium.

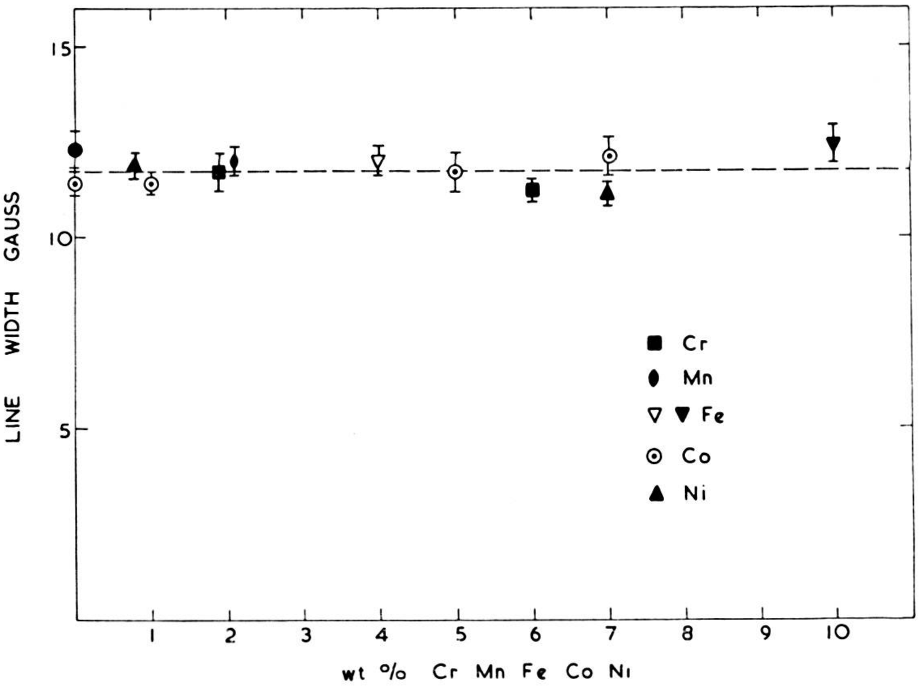

Fig. 1.
The variation with composition of the line width of the V^{51} resonance in alloys of vanadium with some other transition metals.

Compared with similar systems that have been investigated (e.g. CuZn, CuNi, CuMn), the changes in line width and intensity of the vanadium resonance are small. It must be concluded that both sources of line broadening are very much weaker than in the copper alloys.

Line broadening by magnetic interactions is illustrated by the system Cu-Mn [2] in which there are definitely electronic magnetic moments localized on the manganese atoms. It is to be noted that the orientation of these moments changes at a high frequency (about 10^{11} sec^{-1} at ordinary temperatures) due to spinlattice relaxation [3]. Thus the effective field at a neighbouring nucleus is just that due to the average moment on a solute atom and consists both of the direct dipole field and of the indirect field produced via the polarization of the conduction electrons [4]. Since the field at a nucleus is now dependent on its distance from a solute atom and on crystal orientation, the result for a powdered alloy is a general broadening of the nuclear resonance.

From the absence of an appreciable increase in line width on adding transition metals to vanadium, it can be concluded that the field produced at a vanadium nucleus by a neighbouring solute atom is less than 2 gauss for all the alloys investigated. If it is assumed that the constants for the indirect coupling of solute electronic moments and solvent nuclear spins are the same as in the Cu-Mn system [2] and that Curie's law is obeyed, it may be estimated that the localized moment on a solute atom in vanadium is less than 0.2 Bohr magnetons. This is in agreement with recent magnetic susceptibility results [5] on these alloys. Their magnetic susceptibility is practically temperature independent, i.e. there is no Curie-Weiss term which would be associated with localized moments at least until solute concentrations well in excess of those used here.

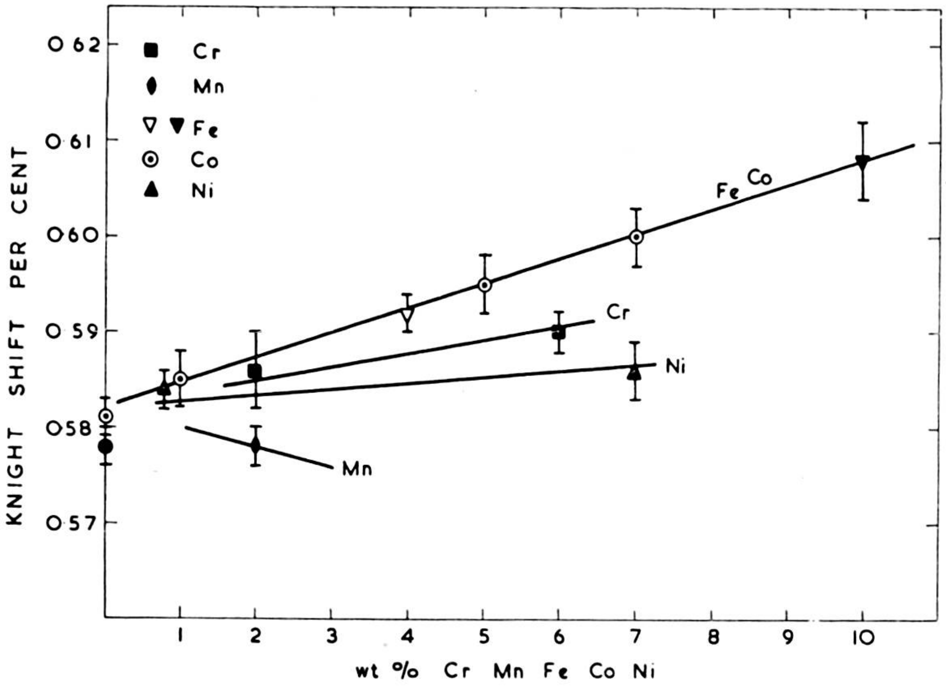

Fig. 2.

Knight shift of the V^{51} magnetic resonance in vanadium alloys. The reference is a solution of sodium metavanadate.

The magnetic susceptibility of the alloys is found to be almost solely a function of the electron concentration of the alloy. Thus the approximation in which the electrons are assumed to be in a common band of constant shape appears to be valid. Since the Knight shift of nuclear resonance is closely connected with the Pauli paramagnetism of the conduction band, it is disappointing that the change in Knight shift with solute concentration (fig. 2) appears to show no relation to the excess valency of the solute.

QUADRUPOLE INTERACTIONS.

It is characteristic of line broadening of nuclear magnetic resonance by quadrupole interactions for nuclei of half-integral spin, that broadening takes place in two stages corresponding to first and second order perturbations. To a first order, the electric field gradient splits the nuclear resonance line into an evenly spaced multiplet but leaves the position of the central line of multiplet unchanged. Since quadrupole splitting is dependent on the orientation of the crystal with respect to the magnetic field, in a powdered sample the resonance from the satellite (i.e. not central) lines is spread over a wide range and is effectively obliterated. To a first order, the central line is unaffected. Considerably more field gradient is required to produce second order perturbation and consequent reduction in the intensity of the central line.

Bloembergen and Rowland [6] found that the cold-working of copper produced enough distortion to remove the satellite lines from the Cu^{63} resonance and the addition of a few per cent zinc to copper produced a considerable diminution of the central line. By contrast it will be shown that in the vanadium alloys studied (except possibly 2% Mn and 10% Fe) the central line intensity is not reduced appreciably and in some alloys even part of the satellite intensity is present.

It is suggested that the intensity of the V^{51} resonance in the Co alloys and some others approximates to that of the pure central line of the resonance. This level is shown by a dotted line in figure 3. An attempt was made to prove this by using the V^{51} resonance from a sample of V_2O_5 as a reference for intensity. Since this compound has an orthorhombic structure, the V^{51} resonance intensity must come from the central line of the quadrupole multiplet only. However the translation of the intensity observed in this compound to the intensity scale of figure 3 was difficult because of the presence of long tails on the alloy resonances which made the calculation of the integrated resonance intensity subject to error. In the 1% Co alloy, tails could be detected up to ± 120 gauss away from the centre of resonance and it was estimated that they contained over 70% of the resonance intensity. If all the tails that could be detected were included, the ratio of V^{51} integrated resonance intensity (per V atom) in the 1% Co alloy to that in V_2O_5 is 2.7 whereas if the tails are ignored by approximating the resonance line shape by a gaussian curve, the ratio obtained is 0.76. It therefore appears that the resonance intensity as usually measured in the Co alloys is essentially that of the central line of the quadrupole multiplet but that a large part of the satellite intensity is present in the tails.

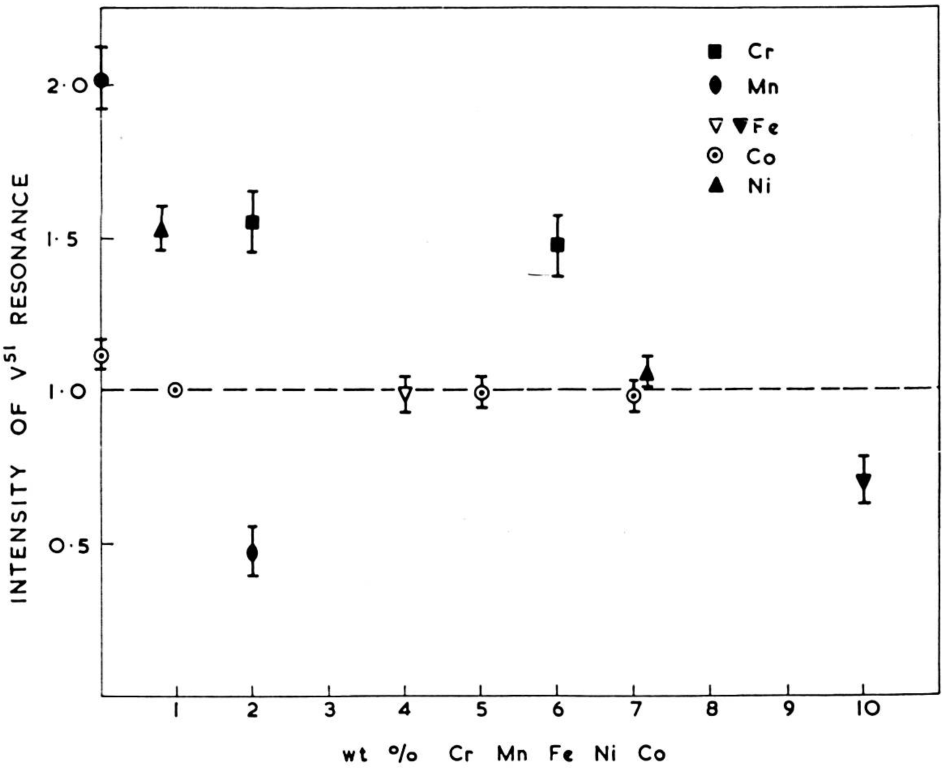

Fig. 3.

The relative intensities of V^{51} resonances in vanadium alloys as a function of composition. The measure of intensity used is the peak to peak amplitude of the derivative of the absorption curve normalized to a constant amount of vanadium. The intensity in the 1% Co alloy is taken as unity. Open symbols refer to alloys made with J.M. vanadium Solid symbols refer to alloys made with U.S.B.M. vanadium.

It is remarkable that the resonance intensity in the chromium alloys made with U.S.B.M. vanadium (99.8% pure) is higher than that in a sample of nominally pure (99.6%) J.M. vanadium. It appears that the resonance intensity is much more sensitive to the extra interstitial impurities (chiefly N, O, Si) present in the latter vanadium than to transition metal additions. Similar effects have been observed on the magnetic susceptibility [5] and hardness [7]. The shapes of the V^{51} resonance lines from samples of vanadium from the two sources are somewhat different, the purer sample having a slightly increased line width but less pronounced tails. Both these facts are consistent with the supposition that in the purer sample, the centre part of the resonance contains a larger contribution from the satellite lines. For a spin of 7/2, the second moment of the line width due to direct nuclear dipole interaction is 13% less for the central line only than for the full resonance [8]. The calculated dipolar widths assuming a gaussian line shape are 8.2 gauss and 8.8 gauss respectively.

There are two possible explanations for the comparatively small magnitude of quadrupole effects in vanadium alloys, a small value of the nuclear quadrupole moment or small electric field gradients. There are reasons for suspecting that both factors may contribute. From the negligible contribution of second order quadrupole interaction to the line width of the V^{51} resonance in V_2O_5 at 2,000 gauss, it may be deduced that the quadrupole coupling constant in this compound is less than 1 Mc/s. This suggests that the nuclear quadrupole moment is small. In copper alloys, Rowland [9] has been able to account for the electric field gradients by the imperfect screening of the extra charge on an impurity atom. In vanadium alloys this effect would be smaller because the higher conduction electron density would lead to more rapid screening.

MAGNETIC RESONANCES FROM SOLUTE NUCLEI.

Since there have been shown to be no localized magnetic moments on transition metal atoms dissolved in vanadium, the magnetic resonances of the nuclei of the solute atoms should be observable if they have suitable magnetic moments. A calculation showed that it should be possible to detect the Co^{59} and Mn^{55} resonances at 1% solute concentration where second order quadrupole effects should be negligible. Searches in the 2% Mn and 1% Co alloys proved unsuccessful but resonances attributable to Co^{59} were found in 5% and 7% Co alloys. The resonance intensity was about 1/12 of that expected if 2nd order quadrupole interaction can be ignored. The line width was found to be 20 gauss and the shift relative to $K_3Co(CN)_6$ solution, $+ 1.13\% \pm 0.05\%$. Measurements were made at 9.58 Mc/s and 7.70 Mc/s and the line width and shift were the same within experimental error at both frequencies and for both alloys.

The small resonance intensity and its variation with solute concentration are difficult to explain by a quadrupole mechanism unless the assumption of a random distribution of Co atoms is abandoned. It is equally possible however that the broadening observed has a connection with the transition metal character of the solute. If it is assumed that fluctuating moments do exist on the cobalt atoms, the local fields produced at the cobalt nuclei will be an order of magnitude larger than those produced at the vanadium nuclei. It is possible that the rate of fluctuation of these fields may be high enough to give an insignificant broadening of the V^{51} resonance but not high enough to narrow the Co^{59} resonance to the same extent. If a fluctuation frequency of 10^{12} sec^{-1} is assumed and a field at a cobalt nucleus of 10^5 gauss is produced by the electronic moment on the atom, the resonance line width of the Co^{59} resonance would be 10 gauss. This is nearly of the right order of magnitude to explain the resonance broadening observed.

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Summary.

Measurements have been made of the shift, line width and intensity of the V^{51} resonance in dilute alloys of vanadium with chromium, manganese, iron, cobalt and nickel. The absence of an appreciable increase in line width or decrease in intensity in the alloys suggests that there are no localized moments on the solute atoms. Quadrupole interactions are also small probably due to both a small electric quadrupole moment of the V^{51} nucleus and effective screening of excess charges in the alloys by conduction electrons. The Co^{59} nuclear resonance has been observed in two cobalt alloys. The weak intensity and width of this resonance cannot be satisfactorily explained.

Résumé.

Nous avons effectué des mesures de shifts, de largeurs de raies et d'intensités sur la résonance de V^{51} dans des alliages dilués de vanadium avec du chrome, du fer, du cobalt et du nickel.

L'absence d'un élargissement appréciable de la raie ou d'une diminution de son intensité dans ces alliages suggère qu'il n'existe pas de moments localisés sur les atomes du soluté. Les interactions quadrupolaires sont également faibles, ceci sans doute pour deux raisons: d'une part le faible moment électrique quadrupolaire du noyau V^{51}, d'autre part l'existence d'un écran effectif des charges en excès dans les alliages par les électrons de conduction. La résonance nucléaire de Co^{59} a été observée dans deux alliages de cobalt. La faible intensité de cette résonance et sa largeur n'ont pu être expliquées de façon satisfaisante.