

Hall-Effect Measurements on Chromium-Iron and Chromium-Vanadium Alloys at Room and Liquid-Nitrogen Temperatures

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Hall-effect measurements at room and liquid-nitrogen temperatures show a Hall coefficient maximum for pure chromium at room temperature and a maximum for an alloy with 5% iron in chromium at liquid-nitrogen temperatures. This is close to the minimum in the density-of-state curve.

INTRODUCTION

EXPERIMENTAL investigations on bcc transition elements and their alloys, especially of their specific heat^{1,2} and magnetic properties,^{3,4} have made it possible to construct a detailed model of the electronic energy band structure of these systems.⁵ The magnetic moment as a function of electron concentration (Slater-Pauling curve) has been used to determine the shape and position of *d*-electron subbands. One could deduce from this model that one of the *d*-electron subbands would begin in chromium-iron alloys with about 10% iron where the onset of ferromagnetism occurs.⁶ Yet low-temperature specific-heat measurements on Cr-V and Cr-Fe alloys by Beck *et al.*¹ show that a minimum of the density-of-state curve is found at pure chromium. This indicates that the new subband starts at this metal. Goodenough⁵ deduces, from the occurrence of localized and collective electrons in transition elements and their alloys, an electronic structure which makes it possible to correlate with a few basic assumptions most known physical properties of these alloy systems. He proposes that a minimum in the density-of-state curve exists near pure chromium. A t_{2g} electron bonding subband ends there and a higher energy e_g sub-band begins. This e_g subband contains localized electrons which may propagate ferromagnetism. The Hall coefficient R_H for pure chromium is very large and positive which corresponds to a small number of "holes" as dominant charge carriers. This implies according to Goodenough that an energy band is nearly filled, confirming thereby the results of specific-heat measurements. Further, R_H is rather temperature-dependent.⁷ Goodenough ascribes this to the fact that the Fermi surface is very close to a nearly full or empty band. Yet it is obviously more

advisable to know R_H over an extended composition and temperature range in order to obtain information on the band structure. It was therefore decided to measure R_H of a series of Cr-V and Cr-Fe alloys.

The Hall coefficient in a simple system is inversely proportional to the carrier concentration. Transition elements and alloys have unfilled *d* and *s* bands. Both bands may be subdivided. Therefore, a straightforward analysis of the charge carrier concentration from R_H values is not possible.⁸ Only the dominant carrier concentration and the trend in the change in band structure as a function of the electron concentration can be estimated.

SPECIMEN-PREPARATION, MEASUREMENTS, AND EXPERIMENTAL RESULTS

Alloys were melted several times in an arc furnace under an argon atmosphere, then annealed in a He atmosphere at 1350°C for 2 hours and quenched in water. Their weights varied from 20 to 30 g. Only one of three pure chromium specimens was annealed. Within experimental error, the Hall coefficient and resistivity agreed with previously published data,^{7,9,10} except for only qualitative agreement with the R_H (liquid N₂) value of pure chromium,⁷ showing that possible contamination and oxidation during annealing did not influence their electrical properties markedly. The wet analysis agreed within ($\frac{1}{2}$)% with the nominal composition from the calculated inweight. A qualitative analysis of several specimens showed that they consisted of approximately 99% chromium and iron, or chromium and vanadium. Remaining metallic impurities were approximately: Si (<0.05%), Al (<0.01%), Ag (<0.01%), K (<0.01%), Mo (<0.01%), Li (<0.01%), Ni (<0.01%), Ca (<0.01%), Mg (<0.01%), Na (<0.01%). Tungsten and copper were major impurities and of the order of a few 0.1%. Both apparently came from the arc furnace with its copper crucible and tungsten tip. The following elements were looked for

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² K. Schröder, *Phys. Rev.* **125**, 1209 (1962).

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⁴ M. N. Newman and K. W. H. Stevens, *Proc. Phys. Soc. (London)* **74**, 290 (1959).

⁵ J. B. Goodenough, *Phys. Rev.* **120**, 67 (1960).

⁶ M. V. Nevitt and A. T. Aldred, *J. Appl. Phys.* **34**, 463 (1963).

⁷ G. DeVries and G. W. Rathenau, *Phys. Chem. Solids* **2**, 339 (1957).

⁸ E. M. Pugh, *Phys. Rev.* **97**, 647 (1955).

⁹ S. Foner, *Phys. Rev.* **107**, 1513 (1957).

¹⁰ N. S. Rajan, R. M. Waterstrat, and P. A. Beck, *J. Appl. Phys.* **31**, 731 (1960).

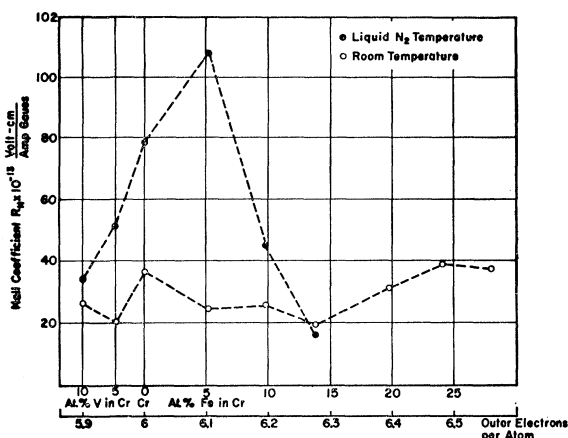


FIG. 1. Hall coefficient of iron-chromium and vanadium-chromium alloys, measured at room and liquid N₂ temperatures. Abscissa: Atomic % V in Cr, Atomic % Fe in Cr, Outer electrons per atom. Ordinate: Hall coefficient $R_H \times 10^{-13}$ V-cm/A-G.

and not detected in these samples: Ti, Mn, Bi, Zr, Pb, Sn, Co, Sb, As, B, Zn, Ba, Sr, Cb, and Cd.

Specimens were machined to an approximate size of $20 \times 6 \times 2$ mm. Current leads were silver soldered to the ends. One potential lead was spot welded to the specimen on one side, two were spot-welded on the opposite side. These two were connected to the ends of a slide wire with its center tap adjusted in such a way that it had the same potential as the single opposite probe with a current passing through the specimen at $H=0$.

The Hall voltage V_H was measured with a dc-null method at room and liquid-nitrogen temperatures. V_H was balanced against a known emf source. An L and N high sensitivity galvanometer was used as the null detector. It was possible, in combination with an optical magnification of the light beam movement, to measure voltages to 2×10^{-8} V.¹¹ Parasitic voltages of the order of 10^{-7} V were quite stable and could be compensated. Currents through the specimens were of the order of 10 A and constant to $\pm 1\frac{1}{2}\%$. The magnetic field was 10.6 ± 0.01 kG for room temperature measurements and 6.3 ± 0.01 kG for liquid-nitrogen tests. The thickness of the specimen was constant in the test section to $\pm 2\%$. This would correspond to an over-all error of approximately $\pm 4\%$. The conductivity of the specimen could be measured to about 10% .

The experimental results are given in Fig. 1 and Table I.

DISCUSSION OF RESULTS

The interpretation of Hall coefficient data has to take into account that electrons move in several sub-bands. Goodenough's analysis of low-temperature specific-heat data indicates that a bonding band with t_{2g} electrons is nearly filled at pure chromium and that the e_g band begins there.

TABLE I. Electrical conductivity and Hall coefficient of Cr-Fe and Cr-V alloys at room and liquid N₂ temperatures.

Specimen Nominal composition (weight %)	Conductivity σ [10^4 (Ω -cm) $^{-1}$]		Hall coefficient R_H [10^{-13} V-cm/A-G]	
	Room temp.	Liq. N ₂ temp.	Room temp.	Liq. N ₂ temp.
100% Cr;	5.8	(57.0) ^a	36.4	79.0
94.43% Cr; 5.57% Fe	2.3	1.76	24.6	108
90.0% Cr; 10.0% Fe	2.2	1.73	26.4	45.6
85.1% Cr; 14.9% Fe	2.1	2.8	18.9	15.8
78.97% Cr; 21.03% Fe	1.9	...	31.3	...
74.8% Cr; 25.2% Fe	1.5	...	39.1	...
70.1% Cr; 29.9% Fe	2.6	...	38.4	...
95.0% Cr; 5.0% V	6.7	25.0	20.7	51.6
90.0% Cr; 10.0% V	5.4	14.6	26.7	34.5

^a $\pm 20\%$ for pure chromium at liquid N₂ temperatures.

It is usually assumed that the electrical current is carried predominantly by s and p electrons ($=t_{2u}$ electrons). In other words, $\sigma_{2u} \approx \sigma$, where σ_{2u} is the current carried by the t_{2u} electrons, and σ the bulk conductivity. A 3-band model for t_{2u} , t_{2g} , and e_g electrons gives⁹

$$R_H = \frac{[-\sigma_{2u}^2/\nu_e(t_{2u}) + \sigma_{2g}^2/\nu_h(t_{2g}) - \sigma_g^2/\nu_e(e_g)]/\sigma^2 N e}{[-\mu_{2u}^2 \nu_e(t_{2u}) + \mu_{2g}^2 \nu_h(t_{2g}) - \mu_g^2 \nu_e(e_g)] e N / \sigma^2} \quad (1)$$

(μ = mobility, ν_e = number of electrons, ν_h = number of holes per atom). The first term in Eq. (1): $\sigma_{2u}^2/\sigma^2 \nu_e(t_{2u}) N e$ is, with $\nu_e(t_{2u})$ of the order of one for chromium [Goodenough suggests that $\nu_e(t_{2u}) = 3$] approximately 10^{-12} V-cm/A-G. It is usually assumed that d electrons have a much lower mobility than s and p electrons therefore $\mu_{2u} \gg \mu_{2g}$, $\mu_{2u} \gg \mu_g$. Further, the t_{2g} band is practically filled near chromium and the e_g band just begins, therefore $\nu_h(t_{2g}) \lesssim 1$ and $\nu_e(e_g) \lesssim 1$. This shows [see Eq. (1)] that the contributions to R_H from e_g and t_{2g} electrons are small compared with the contribution from t_{2u} electrons. In other words, a simple system with 3 parabolic energy bands cannot explain the experimental data.

Magnetic interaction (polarization) between electrons may influence the Hall effect. Pugh⁸ suggested that this magnetic interaction could be taken care of by assuming that each electron band has to be subdivided in sub-bands with parallel and antiparallel spin. This approach has been used successfully by Dreesen and Pugh¹² to explain the Hall coefficient of ferromagnetic alloys. Resistance measurements by Rajan *et al.*¹⁰ on Cr and Cr-Fe alloys indicated that the conduction process is markedly influenced by the anti-ferromagnetic properties of the alloys. There is also a change in slope of R_H (pure chromium) at the Néel temperature.⁹ Irkin¹³ predicted that an antiferromagnetic ordering could split the conduction band into sub-bands with opposite spins where one subband is

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¹² J. A. Dreesen and E. M. Pugh, Phys. Rev. **120**, 1218 (1960).

nearly filled. This would produce a resistance maximum, as observed on Cr and Cr-Fe alloys.¹⁰ A nearly filled *s*-electron subband would also explain the large positive R_H value near chromium in the antiferromagnetic alloys. The first term in Eq. (1) would change to $\sigma_{2u}^2/\sigma^2\nu_h(t_{2u'})Ne$, where $\sigma_{2u'}$ would be the conductivity of the sub-band $t_{2u'}$ and $\nu_h(t_{2u'})$, the number of holes in the $t_{2u'}$ sub-band, would decrease to zero, giving a large R_H contribution.

On the other hand, Goodenough (private communication) suggests that the t_{2u} and t_{2g} electrons have orbitals of similar symmetry, so that they tend to mix. They form essentially a single band, where the electronic

density of state is given by the sum of t_{2u} and t_{2g} states. This band can be approximated by a single parabolic band left of the minimum in the density of state curve of chromium. The effective number of holes in this parabolic band can become very small near chromium, giving a large R_H value.

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Anisotropic hfs Interactions in Ferromagnets from Mössbauer Effect Studies

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The anisotropy of the magnetic hyperfine interaction in ferromagnetic $ZrFe_2$ has been demonstrated with the Mössbauer effect. It is suggested that such anisotropy is responsible for the failure to observe domain-wall enhanced NMR in similar materials. It may also account for the failure to detect the NMR of iron atoms with impurity neighbors in dilute ferromagnetic alloys. These atoms are easily seen in Mössbauer effect studies.

INTRODUCTION

RECENT Mössbauer effect (ME) studies of dilute iron alloys have shown that the hyperfine structures of iron atoms with impurity atoms in the near- and next-near-neighbor shells are readily resolved.¹ These configurations have not been detected in nuclear magnetic resonance (NMR) experiments on similar alloys. Attempts to observe the NMR of Fe^{57} in certain intermetallic compounds have been similarly unsuccessful² despite the fact that the hfs fields were accurately known from ME studies.

We suggest that the difficulties encountered in domain-wall-enhanced NMR are a direct result of the effects of an anisotropic magnetic hfs interaction which is allowed when the Fe occupies a site of noncubic point symmetry. From a ME study in the particular ferromagnet $ZrFe_2$ we will show that the anisotropy exceeds 7%, an amount that would make the observation of NMR difficult at best. The implications that this has for NMR and ME observation in Fe alloys will be considered.

To see the effects that anisotropy produces on domain-wall-enhanced NMR in a ferromagnet, let us consider a simple example, that of uniaxial anisotropy. We choose a uniaxial crystal in which the easy axis of

magnetization coincides with the c axis, and let this axis be the z axis of our coordinate system. If we consider a domain wall in which the spins lie in the xz plane, Fig. 1, then the local fields at the nuclei will vary as a function of the y coordinate in the wall provided the hfs interaction is anisotropic. If $H_{hfs} = \mathbf{I} \cdot \mathbf{A} \cdot \mathbf{S}$ with $A_z \neq A_x = A_y$, then the fractional variation of the hyperfine field $\Delta H/H$ is equal to $C(A_z - A_x)/A_z$, where C is a number of order unity. (Detailed NMR lineshape analyses have been made for anisotropic hfs interactions in magnetite, where the resonances are enhanced by domain rotation.³)

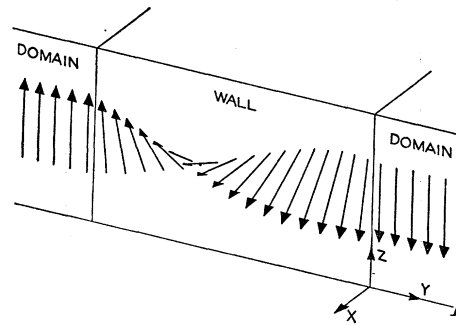


FIG. 1. Change in the direction of magnetization within a domain wall lying in the xz plane of a uniaxial crystal.

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