NMR probe of pseudogap characteristics in $Fe_{2+x}V_{1-x}Al$

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We report the results of a ^{51}V nuclear magnetic resonance (NMR) study of $Fe_{2+x}V_{1-x}Al$, near the ordered composition with $x=0$, at temperatures between 4 and 500 K. All compositions are found to be metallic or semimetallic, though electrical resistivity has indicated a metal-insulator transition at $x=0$. The low-temperature NMR relaxation rates for stoichiometric ($x=0$) and nonstoichiometric ($x=0.10$ and -0.05) compounds follow a Korringa law, associated with a finite density of carriers at the Fermi level. High-temperature relaxation rates for $x\le0$ go over to a semiconductorlike activated form, providing information about the gap structure near the Fermi energy. The results are consistent with pseudogap features identified by recent band-structure calculations, although with smaller energy splittings. We analyze pseudogap changes vs composition, and compare the band-filling behavior to a recent coherent potential approximation calculation.

I. INTRODUCTION

The Heusler-type compound Fe_2VAl has been found to possess a pseudogap in the Fermi-level density of states $[g(E_f)]$.[1] An apparent metal-semiconductor transition was observed at $x=0$ in $Fe_{2+x}V_{1-x}Al$ alloys, accompanied by the disappearance of ferromagnetic order.[2] Substitution of V onto Fe sites, slightly off the stoichiometric composition Fe_2VAl, showed that the low-temperature resistivity grows dramatically, suggesting a narrow pseudogap or a real gap in $Fe_{2+x}V_{1-x}Al$ with $x<0$. Several recent theoretical calculations[3–7] have indicated the formation of a gap with no direct overlap between disconnected bands in Fe_2VAl, due to hybridization effects. With an indirect band overlap at the Fermi energy (E_f), band-structure calculations indicated Fe_2VAl to be semimetallic, and our recent nuclear magnetic resonance (NMR) study[1] has confirmed the intrinsic semimetallic behavior of this material. However, the apparent Fermi cutoff observed in photoemission studies[2] does not appear to be consistent with the band theory for this material, and the specific heat has been found to be considerably enhanced compared to the expectation for this semimetal.[2,8]

A pseudogap appearing at the Fermi level is a common occurrence in transition-metal–metalloid compounds.[6] There have been considerable advances in understanding how a gap may form in the region of the Fermi level, due to hybridization between d and s-p states.[9,10] Quasicrystalline materials, typically composed of transition-metal–metalloid constituents, also feature Fermi-level pseudogaps that dominate the electronic properties of the materials.[11] Recent attention has been focused upon Kondo lattice materials, in which semiconducting behavior can occur because of the Kondo interaction mechanism rather than band hybridization.[12] Electron correlations combined with a hybridization mechanism may be important in real materials[13] and it is interesting to examine whether some of the anomalies observed in Fe_2VAl may be due to correlation effects. Excitonic correlations have also been proposed to explain the resistivity behavior in Fe_2VAl.[5]

In this paper we examine the electronic states in the pseudogap region of $Fe_{2+x}V_{1-x}Al$ by means of NMR spectroscopy. We have investigated alloys with $x=-0.05,0,$ and 0.10 in order to understand how the pseudogap and the conduction-electron density behave under doping with excess Fe or V.

II. EXPERIMENT

Samples studied here were prepared from 99.97% Fe, 99.7% V, and 99.9% Al by mixing appropriate amounts of elemental metals. They were placed in a water-cooled copper crucible and then were melted several times in an Ar arc furnace. Typical sample mass is near 3 g. The loss of weight upon melting was about 0.1%. The resulting ingots were annealed in a vacuum-sealed (10^{-5} torr) quartz tube at 800–1000 °C for 2 days, and then annealed for DO_3 ordering at 400 °C for more than 12 h followed by furnace cooling. The compounds were identified by x-ray powder diffraction with Cu $K\alpha$ radiation.

The experiments were performed using a 9-T home-built pulse NMR spectrometer, described elsewhere.[14] ^{51}V NMR spectra were thus detected around 101 MHz. The powder samples mixed with granular quartz were placed in a plastic vial for 4 to 300 K measurements, while we put the specimens in a Teflon tube for high-temperature purposes.

Observed room-temperature powder patterns for all $Fe_{2+x}V_{1-x}Al$ alloys are demonstrated in Fig. 1, measured by spin-echo integration vs frequency. We found relatively narrow NMR line shapes in Fe_2VAl and $Fe_{1.95}V_{1.05}Al$, though the latter exhibits some structure, presumably due to different neighbor configurations in the mixed alloy. The NMR response was quite different for the case of $Fe_{2.1}V_{0.9}Al$, which showed a significantly broadened ^{51}V spectrum, which can be attributed to strong local magnetism, corresponding to the bulk magnetism as reported for $x>0$.[2]

The ^{51}V spin-lattice relaxation rate, denoted as $^{51}(1/T_1)$, was measured using the inversion recovery method in the T range of 4–500 K. We recorded the signal strength by integrating the spin echo fast fourier transform of the ^{51}V($I=7/2$) lines. We irradiated only the central portion of the ^{51}V NMR spectra, which also exhibited broad wings, attributed to a distribution of quadrupole satellites. The central peaks behaved as $-1/2\leftrightarrow+1/2$ transitions, which are well
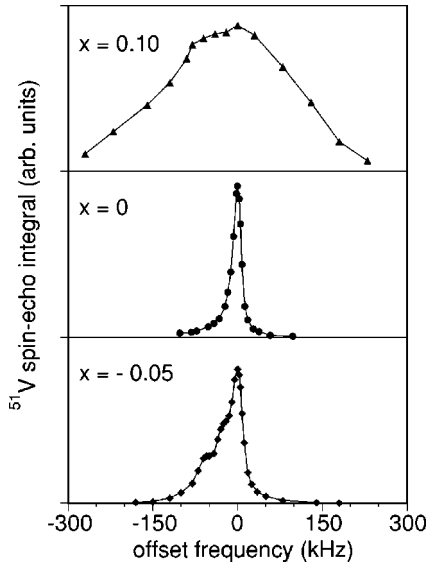
FIG. 1. ^{51}V room-temperature powder patterns of Fe$_{2+x}$V$_{1-x}$Al.

known to give a multiexponential recovery. The $^{51}T_1$'s were extracted by fitting to such recovery curves.[15]

The T-dependent $^{51}(1/T_1)$'s in Fe$_{2+x}$V$_{1-x}$Al are indicated by solid triangles, solid circles, and open diamonds for $x=0.10$, 0, and -0.05, respectively, in Fig. 2. There exists a T-independent background term over the entire temperature range, for all samples. A likely explanation for the constant relaxation term is the mutual interaction of local moments, which can give a T-independent contribution, as proposed by Moriya.[16]

For all studied compounds, the $^{51}(1/T_1)$'s exhibit a constant T_1T behavior, confirming a Korringa relaxation process at low temperatures. The resulting Korringa terms, from a least-squares linear fit, are 1.8×10^{-3}, 6.6×10^{-5}, and 3.7×10^{-4} s^{-1} K^{-1} for $x=0.10$, 0, and -0.05, respectively. These values can be used to evaluate $g(E_f)$, and we will discuss these results in the next section.

Above 250 K, $^{51}(1/T_1)$'s for $x=0$ and -0.05 rise rapidly and are inconsistent with a normal Korringa process. Instead, the relaxation behavior can be explained by conduction elec-
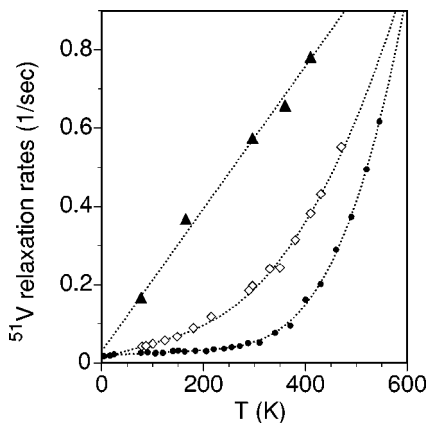

FIG. 2. Temperature dependence of relaxation rates for ^{51}V in Fe$_{2+x}$V$_{1-x}$Al, indicated by solid triangles, solid circles, and open diamonds for $x=0.10$, 0, and -0.05, respectively. Dotted curves: fits to the behavior described in the text.

TABLE I. V partial $g(E_f)$, in units states/eV atom, and energy splitting (ΔE) in meV.

x	0.10	0	-0.05
$g(\epsilon_f)$	0.120	0.023	0.053
ΔE		138	48

trons excited across a gap, as observed in semiconductors, as follows:[17]

$$\frac{1}{T_1} \propto \sqrt{T} n_e \propto T^2 e^{-\Delta E/k_B T}. \qquad (1)$$

In this relation, n_e is the number of carriers excited to a band edge separated by ΔE from the E_f, and assuming an effective-mass approximation for the band edge. For intrinsic semiconductors with symmetric valence and conduction bands, ΔE is equivalent to one-half the width of the gap, which was how the result was reported previously for Fe$_2$VAl.[1] Equation (1) combined with a Korringa term extracted from the low-temperature behavior, plus a constant background term, provided good agreement with the data for $x=0$ and -0.05, with least-squares fits plotted in Fig. 2. The values extracted from these fits are recorded in Table I. For $x=-0.05$ we find that the excitation energy is smaller relative to Fe$_2$VAl, while the increase in $^{51}(1/T_1T)$ indicates an increase in $g(E_f)$ for the $x=-0.05$ material. On the other hand, $^{51}(1/T_1)$ for $x=0.10$ follows a Korringa relation at all temperatures, with an increased value of $^{51}(1/T_1T)$, indicating that the Fermi level has moved out of the gap for that material.

III. DISCUSSION

The Korringa contributions to $^{51}(1/T_1)$ can be evaluated to provide a measure of $g(E_f)$ as reported previously for Fe$_2$VAl.[1] For d-spin relaxation, the Korringa process is given as

$$(T_1 T)^{-1} = 2h k_B [\gamma_n H_{hf}^d g(E_f)]^2 q, \qquad (2)$$

where $g(E_f)$ is the partial d-spin contribution for a given site, q is a reduction factor equal to the reciprocal of the degeneracy,[18] and H_{hf}^d is the d core polarization hyperfine field. We assume that the relaxation is dominated by electron pockets at position X in the zone, having e_g orbital symmetry, as indicated by band-structure calculations for Fe$_2$VAl,[3–5] so that the degeneracy is 2. We have used $H_{hf}^d = -86$ kG, consistent with recent calculations for V metal.[14,19] (An older value, $H_{hf}^d = -117$ kG, was used in our previous paper,[1] but this does not affect the conclusions.) In this way, we obtain 0.023 states/eV atom for the partial $g(E_f)$ based in V d states, in stoichiometric Fe$_2$VAl. This result is comparable to, though smaller than by approximately one-half, a band-structure calculation including gradient corrections and spin-orbit effects.[5]

There is general agreement[3–5] from band theoretical calculations that outside of the electron and hole pockets at X and Γ, further band edges appear in the conduction and valence bands within 0.4 eV of E_f in Fe$_2$VAl. A conduction-band edge having little dispersion between X and Γ is pre-

dicted 0.3 or 0.4 eV above E_f, while a valence-band maximum appears at X, approximately -0.2 eV below E_f. While the upturn in $^{51}(1/T_1)$ could be attributed to either of these band features, it is plausible that the conduction-band feature, having low dispersion and hence a large state density, would dominate the relaxation processes. On the other hand, the lower-mass valence-band maximum could dominate the electrical transport, and be responsible for the observed activated behavior for the electrical resistivity.[2] Indeed, the exponent extracted from the resistivity data[1,2] corresponds to an energy splitting of approximately 45 meV, significantly smaller than the splitting extracted from NMR (Table I). The NMR and resistivity data are thus consistent with excitations to two different band edges, which may correspond to those predicted from band theory, although the measured splitting is considerably less than predicted.

For $Fe_{1.95}V_{1.05}Al$, with reduced Fe content, $^{51}(1/T_1T) = 3.7 \times 10^{-4} s^{-1} K^{-1}$ yields a V d-based $g(E_f) = 0.053$ states/eV atom, using the method described above. On the opposite side, substituting Fe onto V sites with $x = 0.10$ also increases the Korringa term, giving $g(E_f) = 0.12$ states/eV atom for V d states, as summarized in Table I. Although a mean-free-path reduction in mixed alloys can also have the effect of increasing $1/T_1$,[20] when combined with the observed change in ΔE, the results provide support for the picture in which E_f is located at the pseudogap minimum for Fe_2VAl, moving away from the minimum for either sign of transition-metal doping.

In a simple rigid-band model, each additional Fe should contribute three additional band electrons in the mixed alloys. Using the approximate effective masses given by Weht and Pickett[5] for the electron and hole pockets, one finds that electron removal corresponding to the composition $x = -0.05$ will empty the hole pockets, moving E_f well outside the pseudogap, giving a significantly larger $g(E_f)$ change than observed. Our observations indicate a reduced splitting energy for this composition, but with E_f still within the pseudogap. For the composition $x = 0.10$, we do not know the effective mass of the split-off electron band,[5] but it is clear that the simple rigid-band model gives a much larger change in $g(E_f)$ than observed from the Korringa term. [Note that disorder effects,[20] cited above, will only go in the opposite direction, with a relaxation rate enhancement overstating the apparent $g(E_f)$.]

A more realistic approach is provided by a recent Korringa-Kohn-Rostoker–coherent potential approximation-(CPA) calculation for these and other alloys.[7] Rather than filling states near E_f, the effect of Fe additions to Fe_2VAl is to enhance low-lying Fe-dominated states. As a result, E_f moves down relative to the pseudogap with the addition of Fe, rather than up as in the simple rigid-band picture. Assigning ΔE observed here to an electron excitation into the conduction band, described above, the reduction in ΔE for $x = -0.05$ corresponds to E_f moving up relative to the pseudogap with the removal of Fe, the same trend as indicated by the CPA calculation. The more steeply diverging $\rho(T)$ for this composition[2] would correspond to E_f moving away from the valence-band edge that dominates the high-transport processes, again supporting the model in which the resistivity and NMR relaxation behavior are associated with excitations to two different band features. For $x = 0.10$ in this model, E_f has moved to the low-energy side of the pseudogap, although the disappearance of the activated term in $1/T_1$ indicates that the sharp conduction-band density of states feature has disappeared with this level of disorder.

Therefore, the NMR results are reasonably consistent with the results of band theory for these alloys. We find all compositions studied to be metallic or semimetallic, with pseudogap features evident in the relaxation behavior for $x \leq 0$. This is in contrast to the resistivity,[2] which indicates a metal-insulator transition at $x = 0$. Clearly strong disorder scattering, or possibly correlation effects, reduce the conductivity due to low-density carriers in the $x = 0$ and -0.05 compositions. The Fermi cutoff observed in photoemission[2] also remains unexplained.

It is worthwhile mentioning that another Heusler-type compound, Ni_2ZrSn, also attracted considerable interest due to indications of possible gapped states at the Fermi level.[21] This material is nonmagnetic and band-structure calculations as well as the x-ray photoemission analysis show a small but finite $g(E_f)$ (0.46 states/eV atom). Accordingly, the magnetic and electronic characteristics of this compound are very similar to the present case of $Fe_{2+x}V_{1-x}Al$, which allows us to classify both systems to the common group of intermetallics with a pseudogap at the Fermi surface.

IV. CONCLUSIONS

In summary, a study of $Fe_{2+x}V_{1-x}Al$ alloys indicates that band features above and below E_f are responsible for the semiconductorlike resistivity and NMR behavior of this system. These features are consistent with band signatures identified in band-structure calculations, but only if the splitting is considerably smaller than that predicted. Changes of the band-edge features of the pseudogap evidenced by NMR relaxation measurements cannot be explained by a simple rigid-band picture, but are reasonably consistent with results of CPA calculations.

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