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Pseudogap Formation in the Intermetallic Compounds $(\text{Fe}_{1-x}\text{V}_x)_3\text{Al}$

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Optical conductivity data of the intermetallic compounds $(\text{Fe}_{1-x}\text{V}_x)_3\text{Al}$ ($0 \leq x \leq 0.33$) reveal that their density of states around the Fermi energy (E_F) is strongly reduced as x is increased. In particular, Fe_2VAl ($x = 0.33$) has a deep, well-developed pseudogap of 0.1–0.2 eV at E_F and a small density ($\sim 5 \times 10^{20} \text{ cm}^{-3}$) of carriers, which is highly unusual for intermetallic compounds. It is shown that the pseudogap results from the band structure of Fe_2VAl , rather than from temperature-dependent correlation effects. Based on the present results, we propose a simple model that consistently explains both the semiconductorlike transport and the metallic photoemission results previously observed for Fe_2VAl .

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In the physics of metals and their alloys, it is commonly regarded that an intermetallic compound, consisting of metal elements only, is also likely to exhibit metallic characters. Recently, however, Nishino *et al.* [1] have reported that Fe_2VAl , a Heusler-type intermetallic compound, exhibits anomalous physical properties including semiconductorlike temperature dependence of electrical resistivity. Fe_2VAl belongs to a series of intermetallic compounds $(\text{Fe}_{1-x}\text{V}_x)_3\text{Al}$, which crystallize into the cubic, $D0_3$ structure in a wide range of V composition x . Fe_3Al ($x = 0$) is a ferromagnetic metal with the Curie temperature $T_c \sim 780$ K. With increasing x , T_c is lowered rapidly and the resistivity (ρ) becomes larger, with a negative temperature (T) dependence appearing above T_c . Fe_2VAl ($x = 0.33$) remains paramagnetic down to 2 K, and $\rho(T)$ shows a negative slope in the range $2 \leq T \leq 1200$ K, reaching $\sim 3 \times 10^3 \mu\Omega \text{ cm}$ at 2 K. This value is 2 to 3 orders of magnitude greater than those seen for usual metals and their alloys. $\rho(T)$ of Fe_2VAl above 400 K fits to a thermally activated form, suggesting an energy gap of 0.1 eV. In striking contrast to the semiconductorlike transport property, the photoemission spectrum of Fe_2VAl at 40 K has shown a clear Fermi edge [1], indicating metallic electronic structures around the Fermi energy (E_F). In addition, Fe_2VAl has shown an enhancement in the electronic specific heat at low temperatures, which is reminiscent of those observed for the f -electron heavy fermion compounds [1].

These anomalous properties of Fe_2VAl have attracted much interest. Band calculations [2–4] have predicted that Fe_2VAl should be a compensated semimetal having a strong pseudogap at E_F and a small density ($\sim 10^{20} \text{ cm}^{-3}$) of carriers. These works considered effects of spin fluctuations and electron correlations to account for the observed unusual properties. An NMR study [5] of Fe_2VAl has suggested the existence of an energy gap of ~ 0.2 eV

and a small density of states (DOS) at E_F . A Hall effect study [6] has found excess holes in Fe_2VAl , with a density of $\sim 5 \times 10^{20} \text{ cm}^{-3}$ at 300 K. More detailed photoemission experiments have been performed on Fe_2VAl and Fe_3Al [7].

The purpose of this work is to examine the electronic structures of $(\text{Fe}_{1-x}\text{V}_x)_3\text{Al}$ based on their optical conductivity spectra, $\sigma(\omega)$, obtained from their reflectivity spectra, $R(\omega)$, measured in the photon energy range $0.008 \leq \hbar\omega \leq 30$ eV at temperatures $9 \leq T \leq 295$ K. The $\sigma(\omega)$ spectra clearly show that Fe_2VAl indeed has a well-developed pseudogap of 0.1–0.2 eV throughout the measured temperature range. Although a (pseudo)gap in Fe_2VAl has been suggested by transport [1] and NMR [5] experiments and has been predicted by band calculations [2–4], this is the first apparent demonstration of a pseudogap as a function of energy. Based on the present results, we propose a simple model for the electronic structures of Fe_2VAl that accounts well for both the semiconducting transport and metallic photoemission data observed previously.

The $(\text{Fe}_{1-x}\text{V}_x)_3\text{Al}$ samples ($x = 0, 0.1, 0.2, 0.3, 0.33$) were produced by arc melting the constituent metals with appropriate molar ratio, followed by heat treatments for the $D0_3$ ordering [1]. Samples of approximately $5 \times 5 \times 1 \text{ mm}^3$ were cut from the ingots, and their surfaces were mechanically polished. Near-normal incidence reflectivity measurements were made using a Fourier interferometer and conventional sources for $\hbar\omega \leq 2.5$ eV, and using synchrotron radiation source at the beam line BL7B of the UVSOR Facility, Institute for Molecular Science, for $\hbar\omega \leq 30$ eV [8]. To complete $R(\omega)$, the Hagen-Rubens extrapolation was used for the lower-energy end, and the ω^{-4} extrapolation for the higher-energy end [9]. The $\sigma(\omega)$ spectra were obtained from the measured $R(\omega)$ spectra using the Kramers-Kronig relations [9].

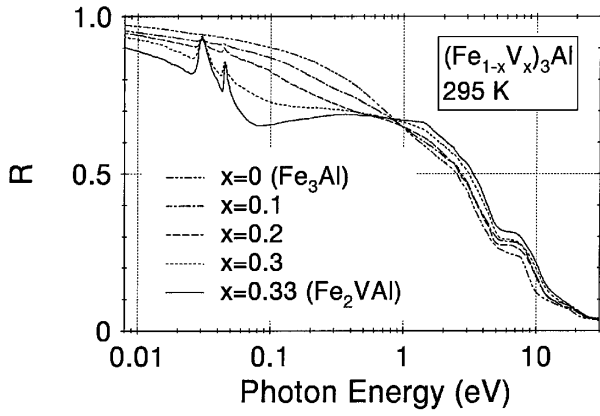


FIG. 1. Optical reflectivity (R) spectra of $(\text{Fe}_{1-x}\text{V}_x)_3\text{Al}$ at 295 K.

Figures 1 and 2 show $R(\omega)$ and $\sigma(\omega)$, respectively, of $(\text{Fe}_{1-x}\text{V}_x)_3\text{Al}$ at 295 K. The spectra for $x = 0$ (Fe_3Al) are metallic, with a high R in the infrared region that approaches 1 toward $\omega = 0$ and a sharp rise of $\sigma(\omega)$. These features are due to a large amount of free carriers in metallic Fe_3Al . With increasing x , $R(\omega)$ shows systematic decreases below 1 eV, and $\sigma(\omega)$ shows a rapid decrease of spectral weight below ~ 0.5 eV. For $x = 0.33$ (Fe_2VAl), $\sigma(\omega)$ is strongly depleted below 0.5 eV, with the onset of conductivity at ~ 0.1 eV as indicated by the arrow in Fig. 2(b). Below the onset energy, a weak, Drude-like continuum is observed together with two sharp peaks, which we attribute to optical phonons [10]. The continuum indicates the presence of a small amount of free carriers. These spectral features show that the carrier density and the DOS around E_F are strongly reduced as more V substitute for Fe, and that Fe_2VAl has a deep *pseudogap* of about 0.1–0.2 eV with a small density of carriers. Since $(\text{Fe}_{1-x}\text{V}_x)_3\text{Al}$ maintain the DO_3 structure in the measured range of x , the increasing intensity of the phonon peaks for larger x is likely to result from weaker screening caused by the decreasing density of carriers. In addition to the pseudogap, a broad absorption band, centered at ~ 1 eV, is formed as x becomes larger. This band corresponds to optical excitations across the pseudogap, or gap excitations. The $\sigma(\omega)$ spectra for $x = 0.3$ and 0.33 are qualitatively similar, and the pseudogap appears well developed also for $x = 0.3$, although it is slightly narrower than that for $x = 0.33$.

To roughly estimate the carrier density giving rise to the continuum, we fit the low-energy part of the $\sigma(\omega)$ spectrum for Fe_2VAl according to

$$\sigma(\omega) = \frac{\sigma_0}{1 + \omega^2/\Gamma^2} + \sum_{i=1,2} I_i \frac{\gamma_i \omega^2}{(\omega^2 - \omega_i^2)^2 + \gamma_i^2 \omega^2}, \quad (1)$$

where the first term is the Drude model for the free carrier continuum and the second term is the Lorentz oscillator model for the phonon peaks [9]. For simplicity, we assume

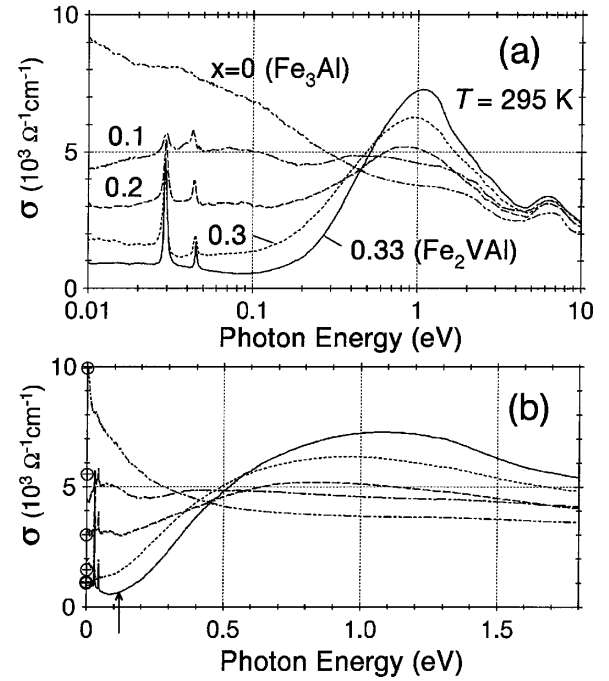


FIG. 2. (a) Optical conductivity (σ) spectra of $(\text{Fe}_{1-x}\text{V}_x)_3\text{Al}$ at 295 K. (b) σ of $(\text{Fe}_{1-x}\text{V}_x)_3\text{Al}$ at 295 K below 1.8 eV. The arrow indicates the onset of σ discussed in the text. The circles on the vertical axis show the measured dc conductivity for each x .

only one kind of free carrier. The fitted results are shown in Fig. 3(a). The effective carrier density N_{eff} contributing to the continuum can be expressed as [9]

$$N_{\text{eff}} = \frac{n}{m^*} = \frac{2m_0}{\pi e^2} \int \sigma_D(\omega) d\omega. \quad (2)$$

Here, n is the carrier density, m^* is the effective mass in units of the rest electron mass m_0 , and $\sigma_D(\omega)$ is the Drude term in (1). Using the fitted Drude function $\sigma_D(\omega)$ in (2), we obtain $N_{\text{eff}} = n/m^* = 3.7 \times 10^{20} \text{ cm}^{-3}$, or 0.018 per formula unit. Band calculations for Fe_2VAl have given effective masses of $m_e^* \sim 0.5$ and $m_h^* \sim 1.0$ [3,4]. Using these m^* values and the obtained N_{eff} , $n = (4-7) \times 10^{20} \text{ cm}^{-3}$ is obtained. This value agrees well with the carrier density measured by Hall effect experiment, $n_H = 4.8 \times 10^{20} \text{ cm}^{-3}$ at 300 K [6]. This simple fitting procedure is difficult for $x \leq 0.3$, since the free-carrier and the interband contributions have a large overlap.

In Fig. 3(b) we show the temperature dependence of $\sigma(\omega)$ for Fe_2VAl ($x = 0.33$) in the range $9 \leq T \leq 295$ K. With decreasing T , the free-carrier continuum becomes weaker, showing that N_{eff} is reduced at low T . Fitting procedures the same as above show that N_{eff} is reduced from $3.7 \times 10^{20} \text{ cm}^{-3}$ at 295 K to $1.8 \times 10^{20} \text{ cm}^{-3}$ at 9 K. Since m^* is unlikely to change substantially in this T range [11], the decrease in N_{eff} should be due to that in n . This decrease is much smaller than that expected for a semiconductor with an energy gap of 0.1 eV, which will be discussed later. The onset

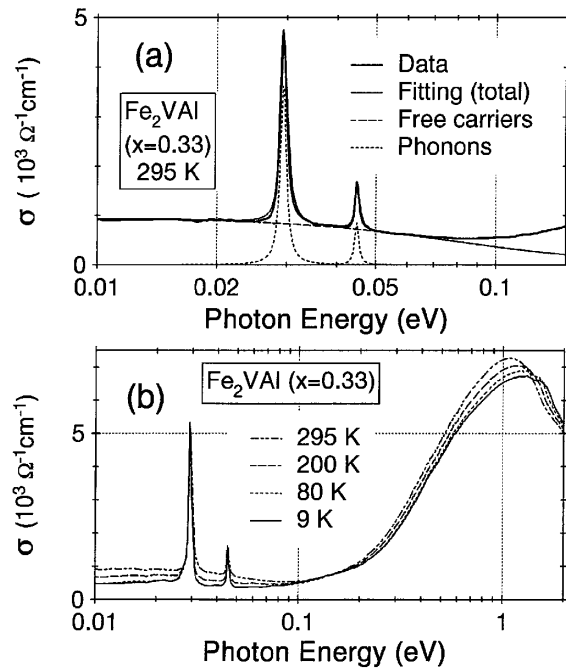


FIG. 3. (a) Low-energy part of the optical conductivity (σ) spectra of Fe₂VAI ($x = 0.33$) at 295 K, and the results of fitting discussed in the text. (b) σ of Fe₂VAI at several temperatures.

position, on the other hand, shows only minor shifts with decreasing T ; i.e., the magnitude of the pseudogap is basically unchanged throughout the measured temperature range. This result is in striking contrast to those of correlation-related energy gaps in, e.g., the Kondo semiconductors such as FeSi [12] and YbB₁₂ [13], where the energy gap in $\sigma(\omega)$ is strongly T dependent.

Band calculations [2–4] have predicted that Fe₂VAI is a compensated *semimetal* having a deep pseudogap in the DOS at E_F , with a minimum direct gap of 0.1–0.15 eV and a carrier density of $(1\text{--}5) \times 10^{20} \text{ cm}^{-3}$. The calculated band structures are schematically sketched in Fig. 4 (where E_F is marked as E_F^0). The DOS around E_F is very small, but it rises steeply at ~ 0.2 eV below E_F . Three hole pockets are located around Γ point and an electron pocket at the X point. Since optical excitations can occur between k -conserving states only in the dipole approximation [9], we cannot simply compare the observed $\sigma(\omega)$ with the calculated DOS, which has been summed over all k states. Nevertheless, it is apparent that the pseudogap and the gap excitation band observed in $\sigma(\omega)$, together with the n value estimated from $\sigma(\omega)$, are qualitatively very consistent with the results of band calculations in Fig. 4. The small T dependence of the pseudogap in $\sigma(\omega)$ strongly suggests that it is a hybridization (pseudo)gap in the band structure of Fe₂VAI, as predicted in the band calculations, rather than that induced by T -dependent correlation effects. Various aspects of a (pseudo)gap formation in the band structure of intermetallic Fe₂VAI have been analyzed theoretically [2–4].

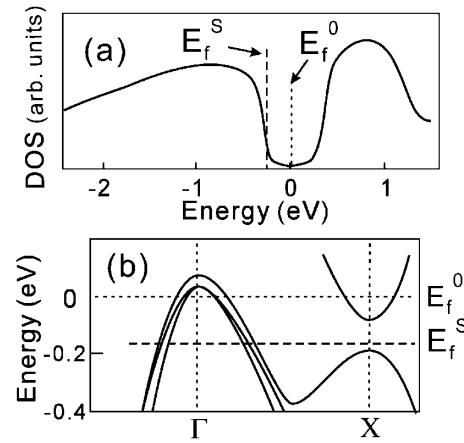


FIG. 4. Schematic illustrations of (a) the density of states (DOS) and (b) band structures near the Fermi energy based on the band calculations for Fe₂VAI in Refs. [2–4]. E_F^0 represents the Fermi energy given by the band calculations (where Fe₂VAI is a compensated semimetal), and E_F^S represents that proposed in this work. Sharp peaks of DOS in the original calculations are not shown here, since they are not relevant to the present discussions.

As mentioned before, $\rho(T)$ of Fe₂VAI above ~ 400 K shows a thermally activated form indicating an energy gap of $E_g = 0.1$ eV [1]. If Fe₂VAI is an intrinsic semiconductor with $E_g = 0.1$ eV, the onset in the photoemission spectrum (PES) would be observed at 50 meV below E_F . However, the measured PES of Fe₂VAI at 40 K does not show such a shift, showing instead a metallic, clear Fermi edge exactly at E_F [1]. A Hall effect study of Fe₂VAI [6], on the other hand, has found excess holes in Fe₂VAI, with a density of $n_H = 4.8 \times 10^{20}$ (2×10^{20}) cm^{-3} at 300 K (78 K). While n_H is very close to the total carrier density from the band calculations, the presence of excess holes is in contrast to the prediction of compensated carriers in the band calculations [2–4].

These contrasting results and the present optical data can be understood consistently if one assumes that E_F in Fe₂VAI is located at the sharply rising portion of the valence band DOS, rather than at the center of the pseudogap as in the band calculations. In Fig. 4, the proposed position of E_F is indicated by E_F^S , and that from the band calculations by E_F^0 . This lowering of E_F is consistent with the Hall effect observation of excess holes, and also with the metallic Fermi edge in PES since the DOS rises sharply at E_F^S . Since optical transitions give the energy difference between occupied and unoccupied states, the gap magnitude in $\sigma(\omega)$ is not sensitive to the lowering of E_F . Hence the situation in Fig. 4 with E_F^S is still consistent with the observed pseudogap in $\sigma(\omega)$. In addition, the hole density in the proposed situation (where $E_F = E_F^S$) can be close to the total carrier density in the band calculations (where $E_F = E_F^0$), since the lowering of E_F reduces the electron density while it increases the hole density. Indeed, the observed value of n_H agrees well

with the total density from the band calculations as mentioned before, and also with the estimated value in this work, $n \sim (3.5-7) \times 10^{20} \text{ cm}^{-3}$.

It has been pointed out by Weht and Pickett [4] that removing Al from Fe_2VAl is analogous to removing three valence electrons from the cell without removing bands. The estimated deviation from the ideal Fe_2VAl composition in our samples is less than 0.3% [1]. Assuming that an Al vacancy removes three valence electrons, a deficiency of $\leq 0.3\%$ from the ideal Al content will lead to a decrease of valence electrons by $\leq 1.9 \times 10^{20} \text{ cm}^{-3}$. This value is well comparable to the observed n_H mentioned above [6]. Recently, Nishigori *et al.* [14] have found that a deviation of a few percent in the Al content of Fe_2VAl varies ρ by a few orders of magnitude. Their results are likely to result from the predicted relation between the Al content and the valence electron density. Given the observed small DOS within the pseudogap, the position of E_F should be sensitive to even a small deviation in the density of valence electrons. Hence the presence of excess holes and the associated shift of E_F in Fe_2VAl are probably due to a small deviation from the ideal Al composition.

At low temperatures, although $\rho(T)$ of Fe_2VAl still has a negative slope, it is significantly smaller than that expected from a thermally activated form with $E_g = 0.1 \text{ eV}$ [1]. In addition, the carrier density estimated from $\sigma(\omega)$ has much smaller T dependence than a thermally activated one, as mentioned before. These results are explained as follows. At high T regime, $k_B T$ is comparable to E_g , so that a large number of carriers are thermally excited across the pseudogap. In this situation the small DOS within the pseudogap is unimportant and the T -dependent population of carriers determines $\rho(T)$. Hence, $\rho(T)$ behaves like that of a semiconductor with $E_g = 0.1 \text{ eV}$. At low T where $k_B T \ll E_g$, thermal excitations of carriers are inhibited, and the relaxation time of the carriers rather than their population determines $\rho(T)$. In this regime, spin-dependent scatterings probably give rise to the observed negative slope in $\rho(T)$, as discussed in Ref. [1].

We have reported an unusual pseudogap formation in $\sigma(\omega)$ spectra of the intermetallic compounds $(\text{Fe}_{1-x}\text{V}_x)_3\text{Al}$, in particular in Fe_2VAl . The magnitude of the pseudogap (0.1–0.2 eV) and the small density of carriers revealed in $\sigma(\omega)$ are consistent with the results of previous band calculations. We have proposed a model of electronic structures that accounts consistently for the semiconducting transport and the metallic photoemission data observed previously for Fe_2VAl . Although the energy

gap has been explained as a band gap based on our data, this does not mean that all the physical properties can be understood by simple Fermi liquid theory. The anomalous properties at lower temperatures reported in Ref. [1], which are not addressed in this Letter, are indeed likely to result from many-body electron correlation. In this respect, these compounds deserve further studies, including optical experiments at lower temperatures.

We thank S. Nishigori for showing us his results on Fe_2VAl prior to publication.

Note added.—After the submission of this work, we became aware of another band calculation study on Fe_2VAl [15] and the optical observation of a clear energy gap in intermetallic RuAl_2 [16].

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