very efficiently equalized. In summarizing the foregoing discussion, we may state that for experiments with a sample orientation $\Theta = 26°$ the assumption of the theory may not fully apply; that, however, the results of the theory are not very sensitive.

For a more conclusive check of the theory and a more accurate determination of the intervalley rate constant, we propose measurements of the anisotropy near $\Theta = 90°$, where in a specified region of the electric field all our assumptions apply and where, furthermore, as is shown by Figs. 11 and 12, the anisotropy is very sensitive to the intervalley rate constant.

APPENDIX I

The relation (30) between γ^* and the intervalley rate constant w_2 can be derived if

$$\left[\frac{\partial f_0^{(i)}}{\partial t}\right]_{\text{int}} = A \sum_{l \neq i} \left\{ \left(\frac{\epsilon}{\hbar\omega_0} + 1\right)^{\frac{1}{2}} \left[(n_i+1)f_0^{(l)}(\epsilon+\hbar\omega_i) - n_i f_0^{(i)}(\epsilon)\right] \right.$$

$$\left. + \left(\frac{\epsilon}{\hbar\omega_0} - 1\right)^{\frac{1}{2}} \left[n_i f_0^{(l)}(\epsilon-\hbar\omega_i) - (n_i+1)f_0^{(i)}(\epsilon)\right] \right\}, \quad (A1)$$

where $[\partial f_0^{(i)}/\partial t]_{\text{int}}$ is the rate of change of the distribution function due to intervalley scattering, and

$$A = \frac{\sqrt{2}4\pi^2 D_i^2 m_0^{\frac{3}{2}}(\hbar\omega_i)^{\frac{1}{2}}}{\rho \hbar^3 \omega_i [\det\bar{\alpha}]^{\frac{1}{2}}} \quad (A2)$$

are applied to the experiment of Weinreich et al. In this experiment, electrons in the two different pairs of valleys behave like particles with positive and negative acoustical charges q in an acoustical potential Φ. The rate of transfer of positive acoustical particles into negative acoustical particles can be obtained if the four-equation (A1) is collected in pairs and the Boltzmann average is performed. Taking the asymptotic behavior of the modified Hankel function $K_1(\hbar\omega_i/kT)$ for $\hbar\omega_i/2kT \ll 1$ properly into account, the rate of transfer

$$d\delta n_+/dt = d\delta n_-/dt = -8A \exp(-\hbar\omega_i/kT)\delta n_+ \quad (A3)$$

is found, where δn_+ is the deviation of the population of the positive pair of valleys from their equilibrium population,

$$n_{+0} = n_0(1 - q\Phi/kT).$$

Comparison of (A3) with Eqs. (3.6) and (8.4) of Weinreich, Sanders, and White shows that

$$w_2 = 3A. \quad (A4)$$

Insertion of (A2) and (18) gives (30).

Low-Temperature Specific Heat of Ti Alloys with CsCl-Type Ordered Structure

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A continuous solid-solution field extends at 1100°C in the Ti-Fe-Co ternary system between the CsCl-type binary phases TiFe and TiCo. In the Ti-Co-Ni ternary system a similar solid-solution field extends at 1175°C from TiCo at least to Ti$_4$Co$_3$Ni.

The electronic specific heat coefficient of TiFe-TiCo alloys and of Ti$_4$Co$_3$Ni was found to have a large peak at the same average electron concentration where the γ peak for the bcc Cr-Fe alloys occurs.

INTRODUCTION

A STUDY of the electronic specific heat at low temperatures of bcc alloys of first long-period transition elements[1] indicated that in different alloy systems the variation of the electronic specific heat with the average electron concentration (the average number of electrons outside the closed shells of the various component atoms) is very similar. This similarity suggests that, at least in a first approximation, these alloys may be described in terms of a nearly rigid 3d-band model.

[1] C. H. Cheng, C. T. Wei, and Paul A. Beck, Phys. Rev. **120**, 426 (1960).

(However, any changes that may take place in the 4s band would hardly make recognizable contributions to the electronic specific heat vs electron concentration curves. Therefore, no conclusion may be drawn from these results as to the degree of "rigidity" of the 4s band.) Recent results by Schröder and Cheng[2] show that TiFe, an alloy with ordered CsCl-type structure, has a very low electronic specific heat. Since this alloy has an average electron concentration equal to that of Cr, an element which also has a low electronic specific heat, these results may again be interpreted in terms of a nearly rigid d band, assuming that the CsCl-type ordering does not affect the band structure appreciably.

In order to extend the data for CsCl-type ordered structures over a range of electron concentrations where the large maximum of the electronic specific heat occurs in the Cr-Fe system, the present investigation was undertaken with TiFe-TiCo and TiCo-TiNi alloys.

EXPERIMENTAL PROCEDURE

Alloys were prepared by arc-melting in argon atmosphere from electrolytic iron, cobalt, and nickel, and iodide titanium. No chemical analyses were available,

FIG. 1. Lattice parameter at room temperature in Å vs composition in TiFe-TiCo solid solutions.
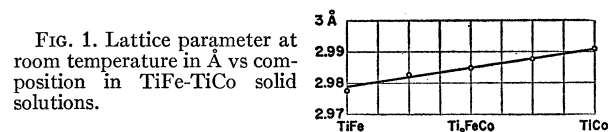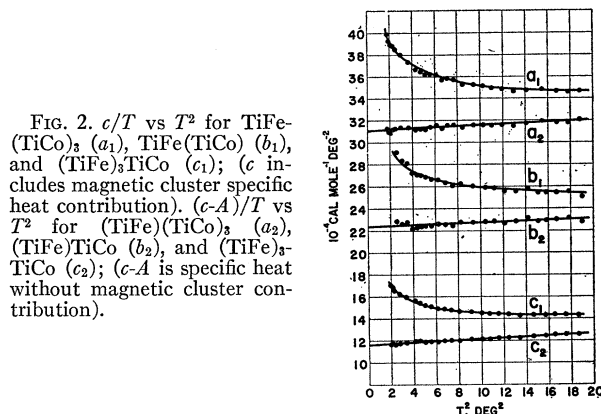
but the weight losses on melting were usually less than 0.2%. The buttons were wrapped in a molybdenum sheet and annealed in vacuum for 24 hr at 900°C, followed by 72 hr at 1100°C. The Ti-Co-Ni alloy was given an additional anneal of 72 hr at 1175°C. Metallographic examination of the annealed specimens showed slight coring in the Ti_4Fe_3Co and Ti_2FeCo alloys. Phase identification and lattice parameter measurements were made by x-ray diffraction, using FeK radiation. The low-temperature specific heat measurements were carried out as described previously.[1]
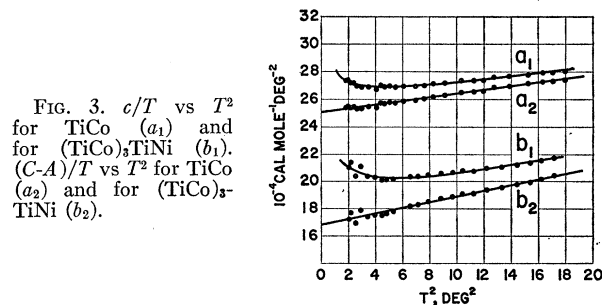
RESULTS

It was found that a continous solid-solution field extends at 1100°C in the Ti-Fe-Co ternary system between the CsCl-type binary phases TiFe and TiCo. The lattice parameter vs composition is shown in Fig. 1. In the Ti-Co-Ni ternary system, a similar solid-solution field was found to extend at 1175°C from TiCo at least to Ti_4Co_3Ni. The lattice parameter of the latter was 2.998 Å. All ternary alloys, as quenched from 1100°C to 1175°C showed CsCl-type ordering. The (100), (111), and (210) superlattice lines have been detected in the x-ray diffractometer traces, using FeK_α radiation, with a Mn filter and a scintillation counter-pulse height

FIG. 2. c/T vs T^2 for TiFe-$(TiCo)_3$ (a_1), TiFe(TiCo) (b_1), and $(TiFe)_3TiCo$ (c_1); (c includes magnetic cluster specific heat contribution). $(c-A)/T$ vs T^2 for $(TiFe)(TiCo)_3$ (a_2), $(TiFe)TiCo$ (b_2), and $(TiFe)_3$-TiCo (c_2); ($c-A$ is specific heat without magnetic cluster contribution).

analyzer arrangement. The existence of these solid-solution fields made it possible to study the electronic specific heat vs electron concentration, as intended.

The c/T vs T^2 data for the TiFe-TiCo ternary alloys are given in Fig. 2. These show anomalies similar to that found previously[2] in the case of TiFe. For the latter alloy, the specific heat anomaly could be accounted for on the basis of some simple assumptions with regard to magnetic clusters, consistent with the magnetization data obtained by Nevitt[3] for the same alloy specimen. It was, therefore, assumed that the anomalies observed in ternary TiFe-TiCo alloys are of a similar nature, and that here, too, the magnetic cluster specific heat A may be considered as independent of the temperature in the range of 1.5° to 4.2°K.[4,5] On this basis, the experimental data were fitted to the equation $c = A + \gamma T + \beta T^3$ by a least-squares method, using the Illiac digital computer. The $(c-A)/T$ vs T^2 lines, given in Fig. 2, show a rather satisfactory degree of fit of the data with the above formula. A similar analysis was carried out with the data for TiCo and Ti_4Co_3Ni, as shown in Fig. 3. The θ_D and A values for all alloys are given in Table I, which lists also the standard deviation of the data from the equation, with the parameter values listed. The γ vs electron concentration curve for the CsCl-type ordered alloys, Fig. 4, has a large peak at the same electron

FIG. 3. c/T vs T^2 for TiCo (a_1) and for $(TiCo)_3TiNi$ (b_1). $(C-A)/T$ vs T^2 for TiCo (a_2) and for $(TiCo)_3$-TiNi (b_2).

[2] K. Schröder and C. H. Cheng, J. Appl. Phys. 31, 2154 (1960).

[3] M. V. Nevitt, J. Appl. Phys. 31, 155 (1960).
[4] K. Schröder, J. Appl. Phys. 32, 880 (1961).
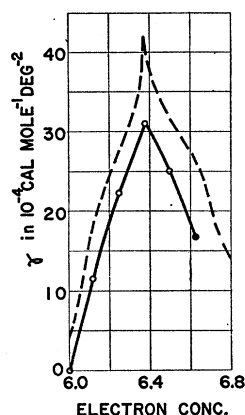[5] J. D. Livingston and C. P. Bean, J. Appl. Phys. 32, 1964 (1961).

FIG. 4. Electronic specific heat coefficient γ vs average electron concentration of alloys with CsCl-type ordered structure. Empty circles represent TiFe-TiCo alloys. Filled circle stands for alloy (TiCo)$_3$TiNi. Dashed curve gives γ values for bcc Cr-Fe alloys[1].

TABLE I. Parameters derived from specific heat data by least-squares fitting to the equation, $C = A + \gamma T + \beta T^3$.

Alloy	γ (10⁻⁴ cal mole⁻¹ deg⁻²)	β (10⁻⁴ cal mole⁻¹ deg⁻⁴)	θ_D (°K)	A (10⁻⁴ cal mole⁻¹ deg⁻¹)	Standard deviation (10⁻⁴ cal mole⁻¹ deg⁻¹)
TiFe	−0.2	0.038	495	21.9	0.036
Ti$_4$Fe$_3$Co	11.6	0.053	444	7.5	0.015
Ti$_2$FeCo	22.3	0.037	502	10.0	0.067
Ti$_4$FeCo$_3$	31.0	0.048	459	11.4	0.045
TiCo	25.0	0.135	325	2.7	0.025
Ti$_4$Co$_3$Ni	16.8	0.207	282	5.5	0.047

concentration where the γ peak for the bcc Cr-Fe binary alloys occurs. It should be emphasized that these variations in γ are very much larger than the uncertainty arising from the assumptions used in the interpretation of the magnetic cluster specific heat. This uncertainty in γ is estimated to be less than $\pm 2 \times 10^{-4}$ cal mole⁻¹ deg⁻².

The θ_D values obtained for the Ti-Fe-Co alloys (Table I) appear quite reasonable. The differences between them may not have real physical significance, since estimated limits of error here are not better than about $\pm 40°$K. However, the θ_D values for TiCo and for the Ti-Co-Ni alloy are definitely low, suggesting that the T^3 term of the specific heat may comprise a contribution other than the true lattice specific heat, as it appears to be the case also with bcc Cr-Fe alloys.[6]

As seen in Table I, the magnetic cluster specific heat values, A for the alloys tested vary in an irregular manner. Neutron diffraction work[7] shows that any atomic moments present in TiFe must be very small. The same is undoubtedly true for the Ti-Fe-Co and Ti-Co-Ni alloys studied in the present work. It is probable that these atomic moments vary sensitively with the nearest neighbor surroundings of each Fe, Co, and Ni atom. Very likely the magnetic clusters encountered in these alloys are connected with local irregularities in atomic ordering and, thus, they may be affected by slight nonreproduceable variations in heat treatment.

DISCUSSION

The high peak of the electronic specific heat at electron concentration values near 6.4 has now been observed in the following four alloy systems: Cr-Fe, Cr-Mn, V-Fe, and TiFe-TiCo. At concentrations near the peak the Cr-Fe alloys are ferromagnetic, with T_c

approximately 50°K. The peak in the electronic specific heat of these alloys was observed not only at low temperatures,[1] but also at room temperature[8] and up to 350°C,[6] i.e., far above T_c. The Cr-Mn alloys are antiferromagnetic, with T_N above 500°K. In the V-Fe alloy system the concentration where the maximum of γ occurs lies probably near the borderline of ferromagnetism. The TiFe-TiCo alloys here studied are essentially paramagnetic, with some weak unaligned permanent moments, probably associated with local irregularities in atomic ordering. Thus, the present data further strengthen the conclusion[1] that these high specific heat values are not of magnetic origin, but may be ascribed to the high density of states in the $3d$ band at an electron concentration near 6.4. It is rather striking that the average electron concentration for the three atomic species in these ternary alloys can be used as successfully as suggested by Fig. 4 to characterize the level to which the d band is filled.

The present data indicate that the CsCl-type ordering does not introduce any important change in the structure of the d band, as revealed by the density of states. The same conclusion was reached by Rayne[9] on the basis of electronic specific heat measurements with ordered and disordered AuCu$_3$. This result is reasonable if one considers that the additional x-ray reflections resulting from ordering are quite weak and that, thus, the Brillouin zones of the ordered alloy are essentially identical with those of the corresponding disordered one.

ACKNOWLEDGMENTS

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[8] K. Schröder, Phys. Rev. 117, 1500 (1960).
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