

High pressure and itinerant antiferromagnetism in chromium and Cr-alloys

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Alloying and pressure studies have revealed the richness and variety of effects associated with the spin density wave state ordering in chromium. A brief account of the important aspects of the subject is presented in this article.

At ambient pressure pure chromium exhibits a unique type of antiferromagnetic ordering, when cooled below 311 K (ref. 1). Neutron diffraction studies² have characterized the ordering as a sinusoidal modulation of magnetic moment associated with the conduction electrons. Since there is no local moment on the Cr, the ordered state has been called the spin density wave state (SDW) ordering. In pure chromium the periodicity of the SDW is incommensurate (IC) with that of the lattice and its polarization is longitudinal in the range 311 K to 50 K and transverse below 50 K. Under alloying the ordering can become commensurate (C).

From the theoretical point of view it is a recondite many-body-problem in condensed matter physics. The so-called band model, first proposed by Lomer³ and Overhauser⁴, ascribes the effect to Coulomb interaction between certain parts of the hole and electron Fermi surfaces of Cr, which have approximately the same size, shape (Figure 1). The term 'nesting' has been coined to describe this. The band model, further elaborated by Fedders and Martin⁵, has shown that a part of the Fermi surface is wiped out at the transition, due to excitonic pairing (due to Coulomb interaction) resulting in a depletion of the conduction electrons. This gives rise to a well marked resistance anomaly (Figure 2) which is very convenient to track the transition. It is worth pointing out here that the triplet spin state assumed by the pairs leads to the antiferromagnetic state.

Extensive alloying studies with nonmagnetic transition metal additions to Cr and high pressure experiments have lent support to the band model. A group of us at Bell Labs were very much involved in studying this phenomenon many years ago⁶. Since then a lot more publications on the subject have come out. Further, two excellent and comprehensive reviews on the subject by Fawcett⁷ and by Fawcett *et al.*⁸ have appeared. To quote

Fawcett, 'The beauty and mystery of Cr do not derive from the fact that it is an antiferromagnet, of which there are many, but from the fact that it is a spin density wave antiferromagnet, "Par excellence"'. This paper will briefly revisit this field, to bring out some of the subtle and beautiful features of the SDW state of chromium. The latter appears to be the only elemental metal that undergoes this transition, and this is attributed to its being a 3-d transition element with the right band structure and pairing interaction.

This seemed to me as an appropriate topic for the present issue devoted to the birth centenary of K. S. Krishnan. After his collaboration with C. V. Raman on the discovery of the Raman effect, Krishnan moved into the field of magnetism and made seminal contributions to the subject of diamagnetism and structure. I had the privilege of meeting him on several occasions. He was a great scientist, a scholar extraordinary, and a philosopher as well. His erudition and manner of speech left a deep impression on any one who met him. It is a pleasure and honor for me to contribute to this issue, devoted to the memory of one of the great Indian scientists.

Effect of alloying and high pressure on the AF state of Cr

Néel was the first to point out that Cr might be an antiferromagnet. Interestingly, it was Bridgman, the father of high pressure physics, who provided the first experimental evidence for the transition, by observing the resistivity anomaly associated with it, and even determined the pressure dependence of the transition. Only later, neutron diffraction studies proved the precise nature of the ordering.

Chromium possesses 6 valence electrons and therefore has an electron to atom ratio (e/a) of 6. When it is alloyed with a transition metal with e/a greater than 6, the Néel temperature T_N increases sharply with concentration, and the ordering changes to the commensurate type (Figure 3a). For e/a less than 6, as for vanadium addition shown in the figure, the T_N decreases, and the magnetic state remains incommensurate, as in pure Cr. Within the framework of the band model, this can be accounted for nicely, and the argument is as follows:

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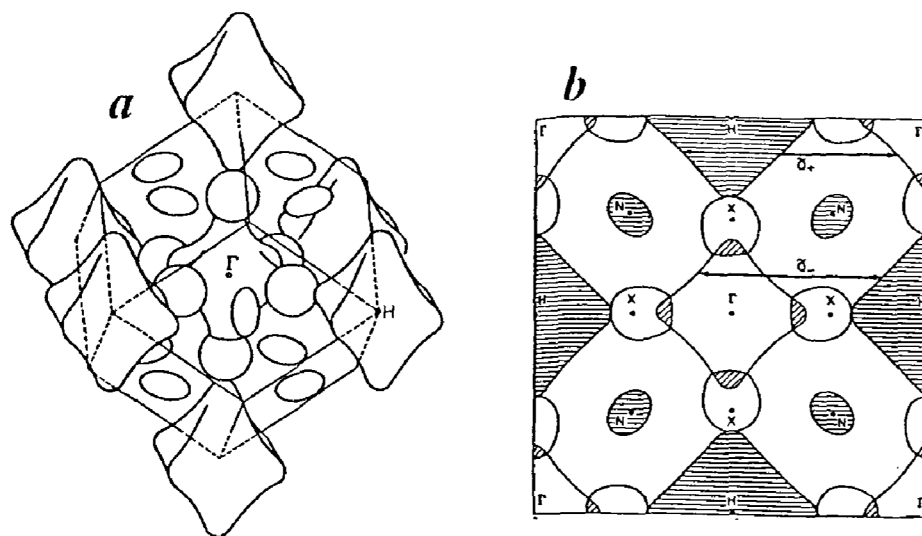


Figure 1. *a*, Fermi surface sketch for Cr of Mattheiss (see ref. 8). The electron pocket at the Γ point and the hole octahedron at the H point are involved in the antiferromagnetic ordering. *b*, Fermi surface cross-section (100 plane) showing the nesting vectors $Q \pm = (0, 0, 1 \pm \delta)$ connecting the electron and hole surface at Γ and H points respectively. Alloying additions to Cr and pressure affect the size of the electron surface principally, and increase or decrease the nesting area (see text).

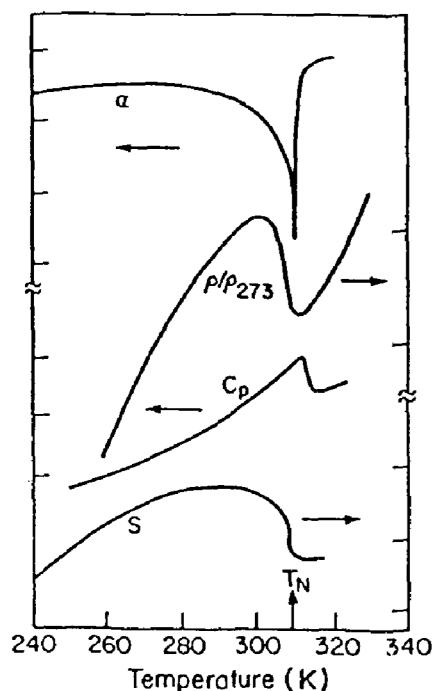


Figure 2. Anomaly in linear thermal expansivity α , the resistivity R relative to its value at 273 K, the specific heat C_p , and the thermoelectric power S at the Néel transition. The units are (10^{-6} K^{-1}) for α (10^{-6} V K^{-1}) for S . Of these, the resistivity anomaly is the easiest to measure and track the transition, especially in pressure experiments.

the addition of electron to the d-band of Cr enlarges the electron Fermi surface and brings about a better matching with the hole surface. Consequently the 'nested area' becomes larger, the T_N increases, and the ordering

becomes commensurate type. For e/a less than 6, the electron Fermi surface shrinks, the matching worsens, causing T_N to drop dramatically.

The effect of Fe and Co additions on the SDW state of Cr is shown in Figure 3 *b*. In both the cases T_N drops initially, as opposed to Mn, but the commensurate phase appears for concentrations greater than 2 at.% as expected from the e/a argument. The anomalous suppression of T_N is believed to be due to strong local moment scattering.

High pressure

Because of the sensitivity of the phenomenon to the detailed nature of the Fermi surface, application of pressure has a striking effect on the T_N . The results of high pressure experiments show (Figures 4 and 5) that T_N of both the commensurate and the incommensurate phases decrease with pressure, the former dramatically so. This effect combined with the alloying studies strongly suggests that application of high pressure acts in the direction of decreasing e/a on the system. This means that pressure causes the electron Fermi surface to shrink in relation to the hole surface, making the matching worse. Triple points at which the C-IC-P meet have been located in many systems, using pressure as the variable. However, resistivity as a tool to probe the transitions becomes less effective, as pressure increases. The strong anomalies seen at low pressure become progressively weak and finally, it becomes impossible to precisely locate the transition. The C-IC

boundary for instance could not be determined at all with resistivity measurements.

Recently, Ramesh and Shuba⁹ have used the thermoelectric power (TEP) technique to study the SDW transitions under pressure and have demonstrated that TEP is a far superior probe to locate transitions, including the C-IC. With TEP, the anomalies are clearcut even at high pressures, and this has enabled them to delineate the phase boundaries in the Cr-Fe alloy system unambiguously.

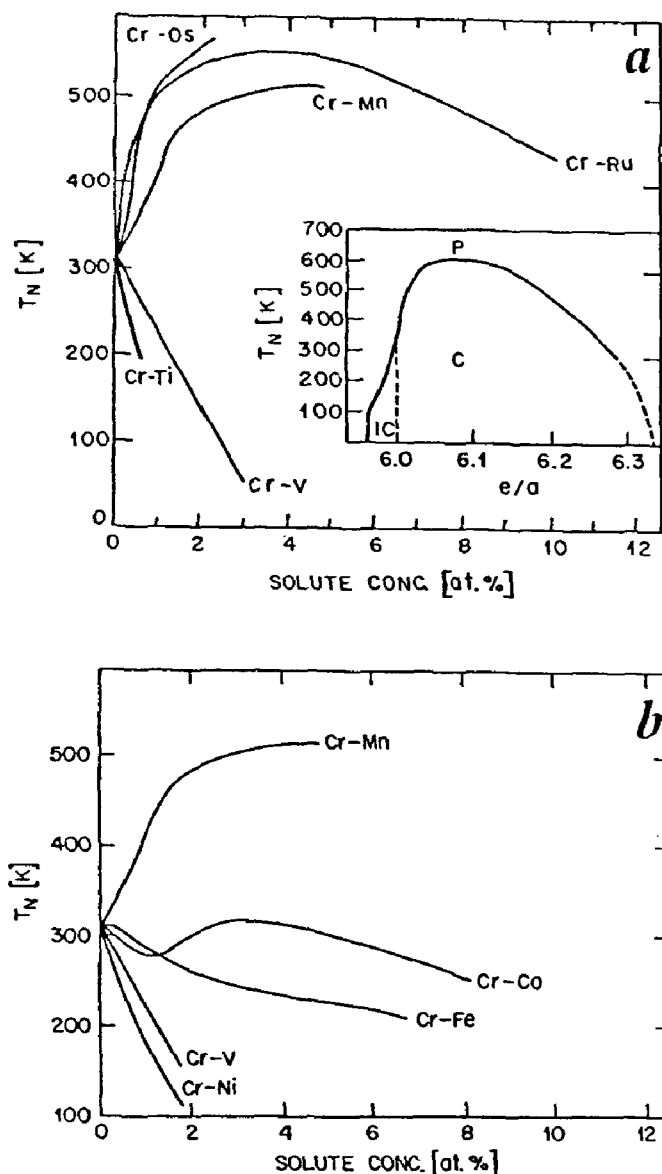


Figure 3. *a*, Effect of nonmagnetic transition metal additions to Cr on the Néel temperature T_N . Metals with $e/a > 6$ raise the T_N steeply and at some point the ordering switches to commensurate (C) type, the Q-vector becomes equal to the lattice vector. Note the lowering of T_N with metals having $e/a < 6$. The inset shows T_N vs e/a obtained from alloying studies. The dashed line marks the switchover from incommensurate to commensurate type ordering. *b*, Effect of Co, Fe, and Ni addition on the T_N of Cr. Data for Mn, V, and Ni are shown for comparison (see text for the explanation of the anomalous behavior of Co and Fe).

PT diagrams published for a number of Cr alloy systems (see ref. 8) show that nonmagnetic transition metal additions to Cr can simulate the effect of positive or negative pressure. For instance, the equivalent of high negative pressure, an impossibility in practice, can be induced by doping Cr with Ru or Mn. This is shown in Figure 5 *b* for the Cr-3% Fe, by doping the latter with Ru. Compare the diagram in the inset with the one presented in the main Figure 5 *b*. In this case, doping with 0.6% Ru is equivalent to applying about 10 kbar negative pressure. The results discussed above drive home the point that transition metal additions and high pressure act consistently.

Nontransition metal additions

The effect of a wide variety of nontransition metal additions has been investigated⁸. In Figure 6 *a*, the effect

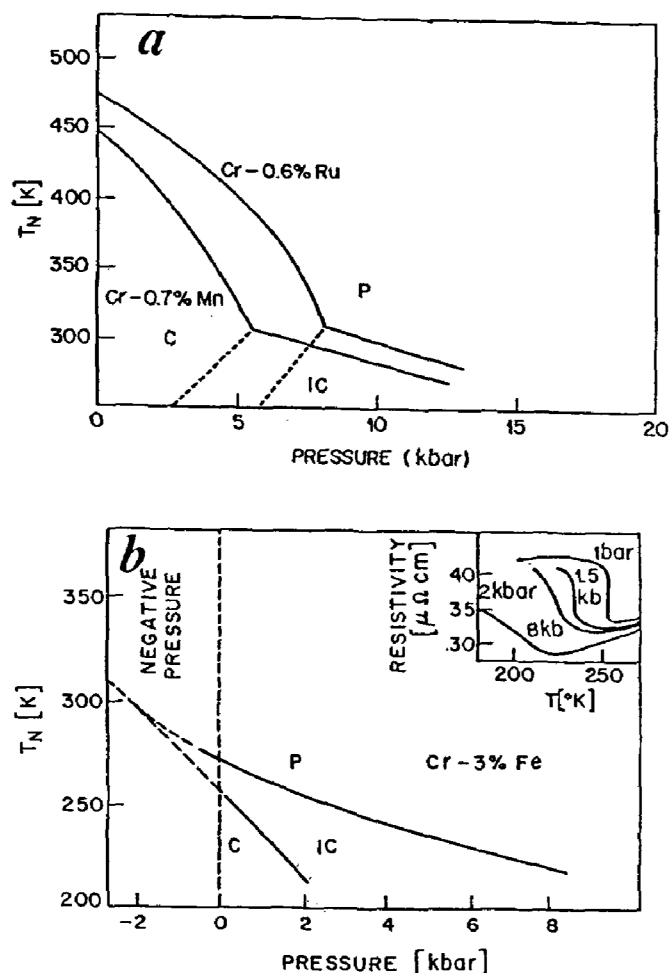


Figure 4. *a*, P-T diagram for Cr-0.6 at.% Ru and Cr-0.7 at.% Mn. Experimentally determined triple points among C, IC, and P phases are shown. *b*, P-T diagram for Cr-3 at.% Fe. Note the reverse ordering of P and C compared to Mn or Ru addition. This is attributed to a greater depression of T_N for the commensurate phase compared to the incommensurate phase. The inset shows the resistivity anomaly at different pressures.

of Be, Al, Ga, Si, Ge, and Sn additions to Cr are shown. Except in the case of Be, all the above additions result in the stabilization of the CSDW phase, at concentrations between 1 and 1.5 at. %.

In the case of Cr-Si and Cr-Ge, both neutron diffraction work and pressure studies⁸ have established that the CSDW phase is stabilized. Their P-T diagrams are shown in Figure 6b. The inset shows the resistance anomalies at different pressures and they are comparable to that of Cr-Fe.

The stabilization of the CSDW phase requires electron transfer to the d-band of Cr, in the framework of the rigid band model. But it is hard to understand how Al, Ga, Si, Ge, and Sn can do this, for their e/a ratio is less than 6.

There have been attempts^{10,11} to explain the behavior of Cr-Si and Cr-Ga alloys on the basis of Nakanishi-Kasuya theory¹², which is based on the nesting model. Teraoka and Kanamori¹³ in their model, regard a non magnetic impurity as a magnetic vacancy in the Cr lattice. The latter is assumed to decrease the Cr-Cr bonds, which in turn increases the density of states and the AF susceptibility at the center of the d-band, through a decrease of the band width. Arajis *et al.*¹⁴ have invoked the presence of virtual impurity levels above the Fermi level of Cr. According to them, alloying with Ge and Si alters the host density of states, which shifts the Fermi level giving rise to an 'apparent' e/a ratio, different from the 'bare' rigid band result. A quantitative theory which will consistently explain the results of nontransition metal additions is yet to be developed.

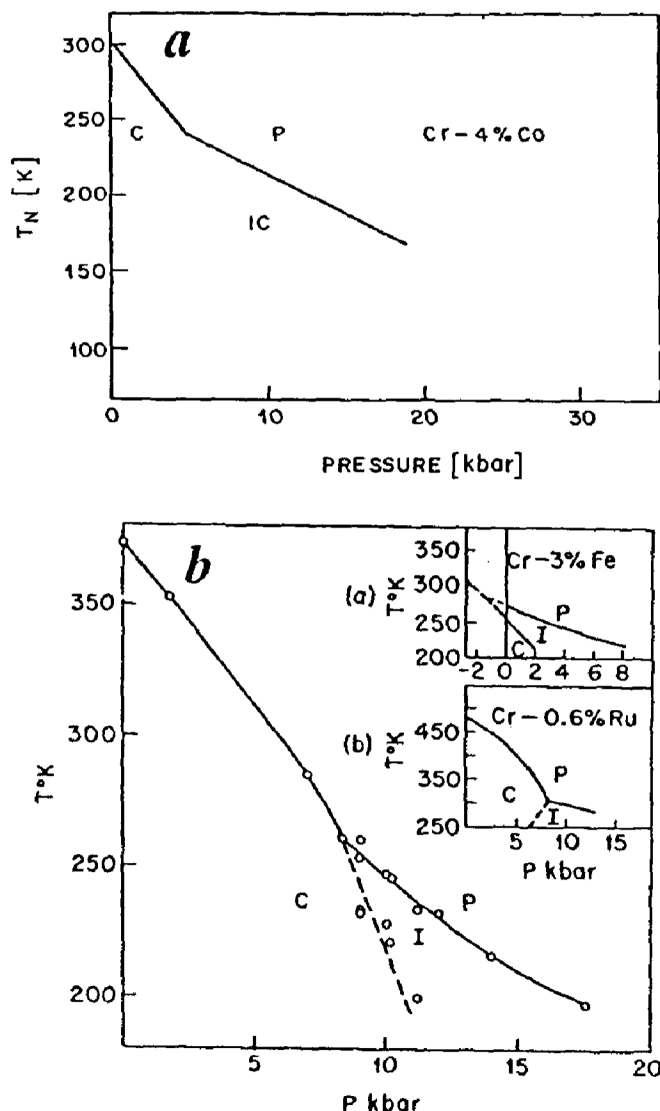


Figure 5. a, P-T diagram for the Cr-4% Co alloy. The commensurate-incommensurate boundary is not shown. b, P-T diagram of Cr-3 at. % Fe alloy, with 0.6 at. % Ru. The effect of Ru simulates negative pressure and this is shown in the two insets (a) and (b).

Impurity scattering and the SDW state

The transition metal additions irrespective of their e/a ratio are indeed impurities in pure Cr and all of them depress the T_N (see ref. 8 for full details). The effect is remarkably like that of magnetic impurities in a superconductor. In the latter, magnetic impurities depress T_C by scattering and consequent depairing of Cooper pairs. In Cr the impurity scattering has a similar effect on the T_N . This is shown in Figure 7. The T_N values were obtained by extrapolating back to zero pressure the P-IC transition boundaries (see Figure 4a). These are the temperatures at which the P-IC transition would have occurred, if the P-C transition had not come first. The values of the T_N thus obtained are plotted against e/a in Figure 7. In this, the dashed line represents the T_N without impurity scattering, scaled to e/a only. The drop in T_N from this line for any actual alloy is due to ordinary impurity scattering. This seems to be stronger the farther away the added element is from Cr. When the added element carries a local moment, the depression in T_N is even stronger. Impurity scattering is believed to affect the sharpness of the electron Fermi surface, making it fuzzy; the latter in turn degenerates the 'nesting'.

Magnetic impurities, Kondo-like behavior and SDW state

Magnetic susceptibility measurements on Cr-Fe and Cr-Co show that both Fe and Co have a local moment in Cr alloys. In the case of Cr-Fe, a Curie-Weiss behavior is observed down to very low temperatures, whereas the susceptibility behavior of Cr-Co alloys does not follow the above law, and appears to be independent of temperature at low temperatures. From this it is concluded that while the Co local moment is strongly

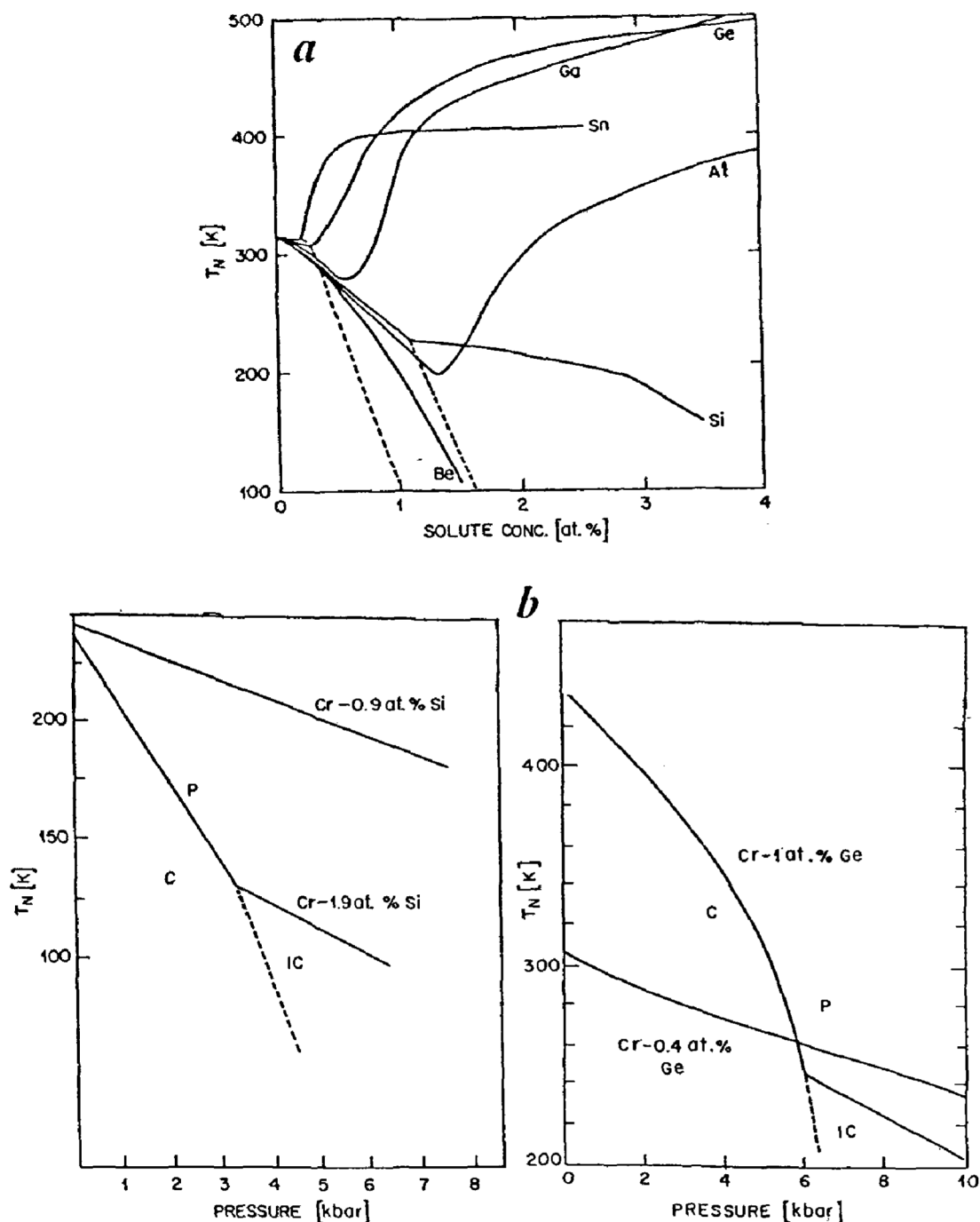


Figure 6. Effect of some nontransition metal additions to Cr on the Néel transition. Si, Ge, Al, Ga, and Sn additions result in the stabilization of the C-phase. The lower two are P-T diagrams for Cr-1.9 at.% Si, Cr-1 at.% Ge, and Cr-0.4 at.% Ge. The phase boundaries are labeled and the behavior is similar to others shown for Cr-Mn, Cr-Ru, etc. For Cr-0.9 at.% Si and for Cr-0.4 at.% Ge, there is no C-phase, only a transition from P to IC phase is observed.

coupled to the SDW, the Fe local moment is only weakly coupled.

The presence of a local moment in a metallic host is a situation favorable for Kondo effect, but in a magnetically ordered system, the exchange field usually suppresses the Kondo state. What is remarkable is that both Cr-Fe and Cr-Co alloys in their ordered state exhibit a Kondo-like resistance minimum at low tem-

peratures. These minima occur below 30 K, and shift with concentration and pressure. Figure 8 shows the resistance minimum observed in Cr-Fe and Cr-Co alloys. The minimum is seen only in the ISDW (IC) and paramagnetic phases of Cr-Fe alloys, and only in the paramagnetic and CSDW (C) phases of Cr-Co alloys.

The effect of pressure on the low temperature resistivity minimum T_{\min} has also been extensively investigated.

This is shown for Cr-0.6 at.% Fe and Cr-4 at.% Co in Figure 9. The shift in the T_{\min} and the variation of the depth of the minimum with pressure are shown in Figure 10 for the two alloys.

The interesting point about the resistivity behavior at low temperatures is that the data are consistent with Kondo-like behavior. But this view has been questioned (see Fawcett *et al.*⁸) on the basis that pronounced R_{\min} in Cr alloys are seen in situations where no local

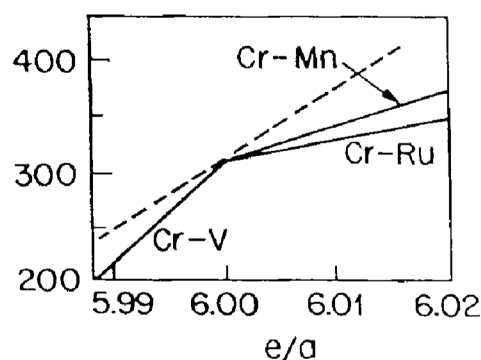


Figure 7. A plot of T_N vs e/a obtained from several transition metal additions, to demonstrate the depression in T_N by ordinary impurity scattering. In the case of Cr-Mn and Cr-Ru, the P to IC transitions were obtained by extrapolation of the P to IC phase boundary to ambient pressure. The dotted line represents the variation of T_N only based on e/a , and was drawn by assuming that the depression due to V and Mn would be symmetrical around pure Cr.

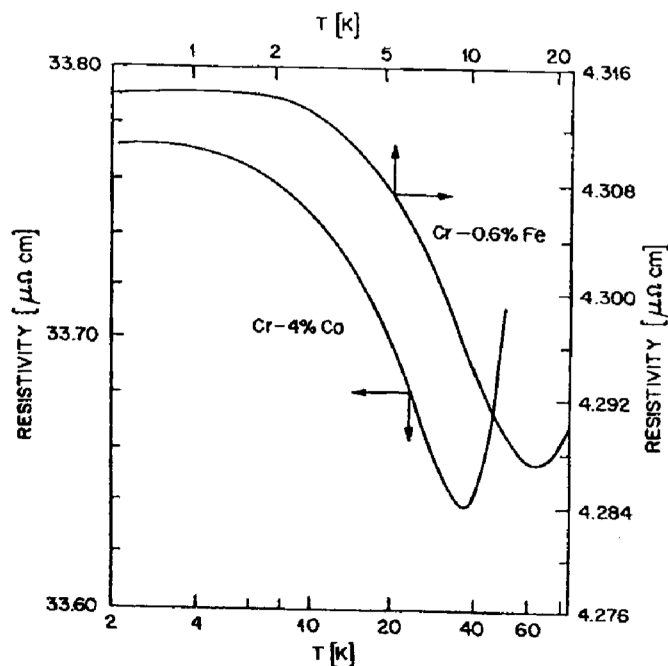


Figure 8. The resistivity minimum observed with magnetic transition metal additions, viz. Fe and Co for two compositions. The respective scales are shown in the figure by the arrows. The minima are reminiscent of Kondo-like minima observed in metallic systems with localized magnetic impurities.

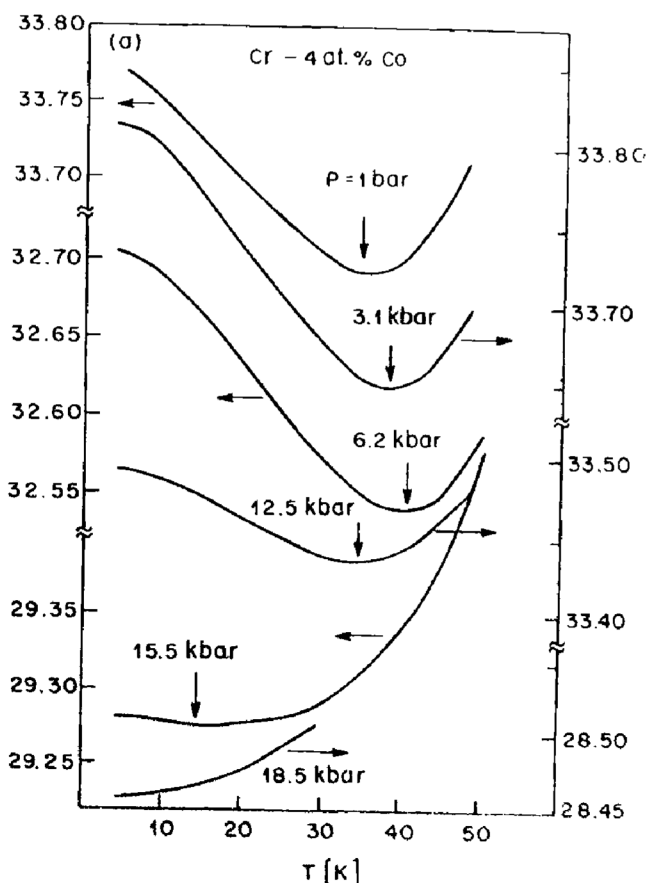
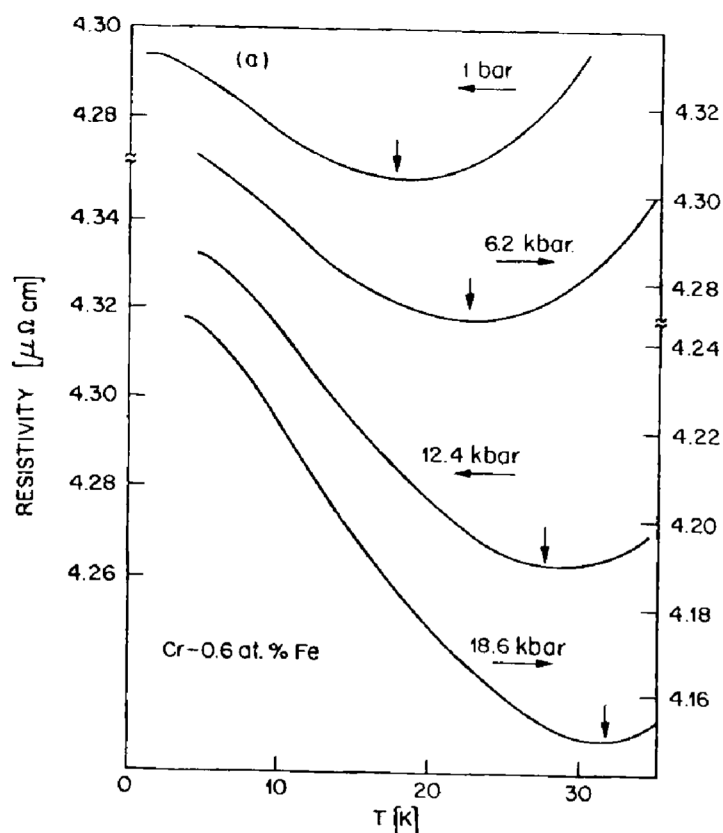


Figure 9. Effect of pressure on the resistivity minimum for the Cr-0.6 at.% Fe and Cr-4 at.% Co alloys.

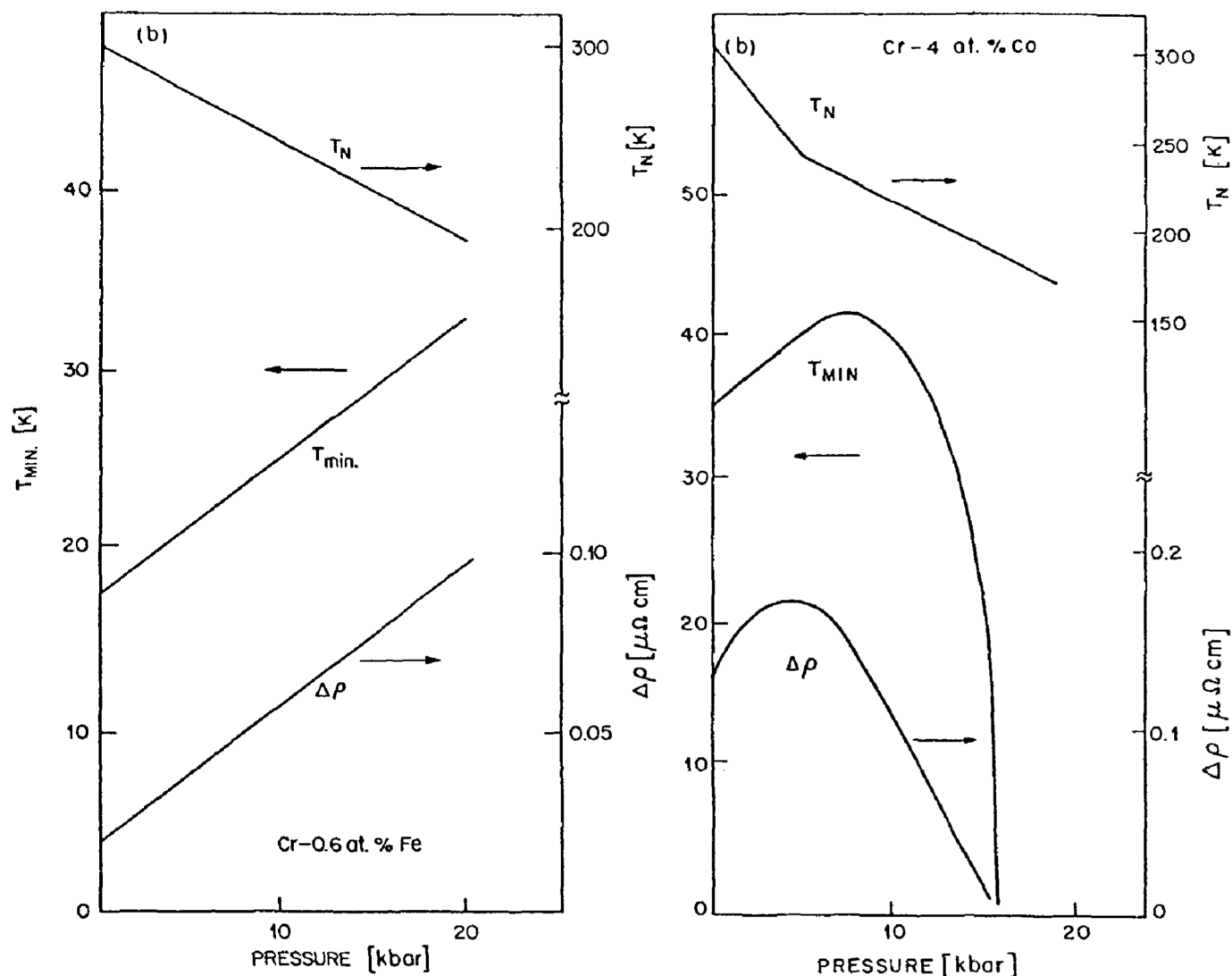


Figure 10. Effect of pressure on the resistivity minimum R_{\min} , T_N , and the depth of the resistivity minimum R_{\min} for the Cr-0.6 at.% Fe and Cr-4 at.% Co alloy.

moment on the impurity exists, viz. Cr-Mo, Cr-V. Further, the behavior of Cr-Si is found to be analogous to Cr-Fe, and Si is clearly nonmagnetic. Also, the low temperature resistivity behavior of Cr-Fe at high Fe concentrations, Fe > 2 at.%, is not at all expected out of a Kondo alloy. These considerations have thrown doubts on the interpretation of the resistivity minimum as Kondo effect.

An alternative explanation in terms of a resonant interaction between the Fermi level and the impurity level has been suggested, which can make both positive and negative contributions to the resistivity at low temperatures, depending upon the position of E_f with respect to the impurity level.

A remarkable feature of the low temperature resistivity minimum in Cr alloy systems is the similarity between the effect of pressure and that of tuning the Fermi level by alloying with vanadium, for example. For a full

discussion of these effects see Fawcett *et al.*⁸. It should however be noted that the interpretation of the resistivity behavior of the Cr-Fe and Cr-Co alloys in terms of Kondo-like behavior cannot be ruled out. The origin of the R_{\min} is by no means a closed subject, and is complicated by several effects simultaneously contributing to resistivity.

Concluding remarks

There are other aspects connected with the SDW ordering in Cr and Cr alloys, viz. the behavior of thermopower, optical and magnetoelastic properties. There exists a large body of experimental results of diverse nature. The review articles by Fawcett⁷ and Fawcett *et al.*⁸ have covered these in great detail. The interested reader should go to the above two reviews for a complete coverage of the subject. In this brief account, I have highlighted

some of the aspects in which I have played a role, and have projected the usefulness of high pressure as a tool in elucidating the spin density wave state of Cr and Cr-alloys.

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Modern magnetism and the pioneering experiments of K. S. Krishnan

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In this article we relook at the pioneering experimental contributions of K. S. Krishnan in the area of magnetism. In the early days of quantum mechanics when it was applied to understand magnetism, the precise experiments of his on magnetic anisotropy of diamagnetic as well as paramagnetic crystals provided the much needed experimental foundation for our understanding of an important component of modern magnetism. Classic was his experiment on the Landau diamagnetism of graphite which was shown for the first time as a model of 2-d free electron gas. He was current and much ahead of his peers. He combined most recent physical concepts with precise experiments.

THOSE were the days in twenties when the physics of solids was getting its foundations built on the newly discovered wave mechanics. From atoms and molecules to solids—the basic concepts were developed and many unanswered questions were settled. For the pioneers, magnetism in solids was the frontier that needed to be explored.

Theoretical work of Bethe¹, Van Vleck² and others had set the frame work in which one could understand magnetism in solids. The period 1925–1935 saw some of the basic concepts developed. New experiments were done to give support to these theories. It is in this period K. S. Krishnan and his colleagues did some of the most precision experiments in magnetism that

gave the much required quantitative base to the new theories. The experiments started when K. S. Krishnan joined C. V. Raman as a research scholar in 1922 at the Indian Association for the Cultivation of Science (IACS) at Bowbazar, Calcutta. He followed it up as a Reader in Physics at Dacca University (1929–1933) and then again as a Professor (occupant of the prestigious Mahendra Lal Sircar Chair) at IACS till he left for Allahabad. During his stay in IACS between 1933 and 1942, Krishnan made two pioneering contributions. (C. V. Raman who occupied the M. L. Sircar chair prior to Krishnan left for IISc, Bangalore in 1933.) Through a series of magnetic susceptibility measurements down to liquid air temperature he established experimentally the role of crystalline electric field on the energy levels of transition metal ions in a solid and particularly the role of crystal symmetry. The second was even more fascinating. From a measurement of magnetic susceptibility of crystalline graphite from 1250 K to 90 K he showed how the theory of Landau diamagnetism of free electron gas can be used to explain the results. He bravely made the suggestion that the electrons in the basal planes of graphite form a 2-d free electron gas. Needless to say the work on graphite received instant recognition from the international scientific body. The Royal Society had to invite yet another Professor from Bowbazar to London. The experiment on graphite was so advanced both in techniques and physical analysis of the data that it was nearly a decade after this that experimenters in other parts of the world started achieving this level of sophisti-

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